

**GREENHOUSE GAS EMISSION FROM A PRAIRIE POTHOLE LANDSCAPE
IN WESTERN CANADA**

BY

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ABSTRACT

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Knowing the control of landscape position in greenhouse gas (GHG) emission from the Prairie pothole region is necessary to provide reliable emission estimates needed to formulate strategies for reducing emission from the region. Presented here are results of a study investigating the control of landscape position on the flux of nitrous oxide (N_2O) and methane (CH_4) from an agricultural soil. Field flux of N_2O and CH_4 and associated soil parameters from the Upper, Middle, Lower and Riparian slope positions were monitored from spring to fall of 2005, and spring of 2006, at the Manitoba Zero-Tillage Research Association (MTRZA) farm, 17.6km North of Brandon, MB. The field site consisted of a transect of 128 chambers segmented into the four landscape positions, with either all chambers or a subset of the chambers (32) sampled on select days. Spring thaw is an important period for annual inventory of N_2O emission, thus, soil samples were also collected from the four slope positions in fall 2005, and treated in the laboratory to examine how antecedent moisture and landscape position affect the freeze-thaw emission of N_2O from soil.

Daily emissions of N_2O and CH_4 for 2005 were generally higher than for 2006, the former being a wetter year. There was high temporal variability in N_2O and CH_4 emission, with high fluxes associated with events like spring thaw and

fertilizer application in the case of N_2O , and rapid changes in soil moisture and temperature in the case of CH_4 . There was a high occurrence of hotspots for N_2O emission at the Lower slope, associated with its high soil water-filled porosity (WFP) and carbon (C) availability. The Riparian zone was not a source of N_2O emission, despite its soil WFP and organic C being comparable with the Lower slope. The hotspot for CH_4 emission was located at the Riparian zone, associated with its high soil WFP and C availability. The Upper and Middle slope positions gave low emission or consumed CH_4 , associated with having low soil WFP and available C. This pattern in N_2O and CH_4 emission over the landscape was consistent with examination of entire 128 chambers on the transect or the 32 subset chambers.

Significantly lowering the antecedent moisture content of soil by drying eliminated the freeze-thaw emission of N_2O , despite the addition of nitrate to the soil. This was linked to drying slightly reducing the denitrifying enzyme activity (DEA) of soil. The highest and earliest freeze-thaw emission of N_2O was from the Riparian zone, associated with its high antecedent moisture content, DEA and total organic C content. The addition of nitrate to soil before freezing failed to enhance freeze-thaw emission of N_2O from the Upper, Middle and Lower slope positions, but increased emission three-fold for the Riparian zone. Despite the greater potential of the Riparian zone to produce N_2O at thaw compared to the Upland slopes, there was no spring-thaw emission of N_2O from the zone on the field. This was because this zone did not freeze over the winter, due to insulation by high and persistent snow cover, vegetation and saturated condition. The

denitrifying potential and freeze-thaw N₂O emission increased in going from the Upper to the Lower slope position, similar to the pattern of N₂O emission observed on the field.

The localization of hotspots for N₂O and CH₄ emission within the landscape was therefore found to be driven by soil moisture and C availability. When estimating GHG emission from soil, higher emission index for N₂O and CH₄ should be given to poorly-drained cropped and vegetated areas of the landscape, respectively. The high potential of the Riparian zone for spring-thaw emission of N₂O should not be discountenanced when conducting annual inventory of N₂O emission at the landscape scale. When fall soil moisture is high, snow cover is low, and winter temperature is very cold, freeze-thaw emission of N₂O at the Riparian zones of the Prairie pothole region may be very high.

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FOREWORD

This thesis has been prepared in the manuscript format in adherence with the guidelines established by the Department of Soil Science at The University of Manitoba. The Canadian Journal of Soil Science was the reference style used in this document. Chapters 2 and 3 may be submitted to a peer-reviewed journal to be decided in the future. For all papers, I will be the lead author and co-authorship will be designated accordingly. A list of all abbreviations used throughout this thesis is provided in the appendix section.

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1. INTRODUCTION

1.1 The Climate Change Challenge

There possibly exists only a few other issues that attract so much national and global attention as that of the imminent potential for climate change. This is because a scenario whereby the climatic pattern as we have it now continues to change unabated can pose a serious threat to human existence and survival. This is justifiable as it has been reported that a change in global mean temperature of 1.4 – 5.8 ° C, in combination with changes in precipitation and increased frequency of extreme weather events, is likely to continue till 2100 (IPCC, 2001). Starting from a change in the weather pattern, to the possible melting of the polar ice, and the resulting rise in ocean levels, the “prospects” of climate change seem too scary. A change in weather pattern for instance will affect the length of the growing season, the water and sunlight energy resources available for crop maturity, and subsequently restrict the choice of crops that can be successfully grown in a given area. An alteration in the weather pattern could also trigger the incidence of new pests and diseases of crops, animals and humans. The occurrence in recent times of such “natural disasters” like Tsunami, Hurricane Katrina, Tornadoes and mudslides have been linked directly or remotely to climate change and some geologic phenomena. All these and other possible threats to the fragile “mother nature” humans depend upon for survival have continued to sound a wake-up call regarding the enormity of the challenges associated with climate change.

1.2 The Role of Greenhouse Gases in Climate Change

The increasingly warm trend in the earth's surface temperature over the past 50 years is likely caused by human activities (IPCC, 2001). Directly responsible for this climate change is the sustained increase in the atmospheric concentrations of greenhouse gases (CO_2 , CH_4 and N_2O) from their pre-industrial baseline concentrations. The atmospheric concentrations of CO_2 , CH_4 and N_2O have been reported to be increasing at 0.4, 0.6 and 0.25% per annum, respectively (IPCC, 1996). These greenhouse gases alter the energy budget of the earth by influencing the amount of heat exchange between the earth surface and the atmosphere. N_2O for instance, absorbs infra-red radiation (Wang et al., 1976) and causes the destruction of the stratospheric ozone (Crutzen, 1981) that shields the harmful ultra-violet radiation of the sun from reaching the earth. Human industrial, agricultural and environmental activities have been implicated for the phenomenal increase in the atmospheric concentrations of these greenhouse gases.

1.3 The Contribution of the Agricultural Sector to Total Greenhouse Gas Emission

The agricultural sector constitutes a major source of CH_4 and N_2O emission in Canada, with over one-third of total CH_4 , and almost four-fifths of total N_2O emissions from agriculture, either directly or indirectly (Kulshreshtha et.al., 2000). These two major greenhouse gases from agriculture are of great importance to the anthropogenic greenhouse effect, as N_2O and CH_4 have about

310 and 21 times the global warming potential¹ of CO₂, respectively (Environment Canada, 1997). N₂O emission from the agricultural sector comes from crop production (Robertson et al., 2000) and animal manure management practices (Desjardins and Riznek, 2000), while CH₄ emission is associated with animal production and highly anaerobic soils (Gregorich et al., 2005). The spring-thaw period has been recognized as an important temporal window for annual emission of N₂O from agricultural soils in Canada (Lemke et al., 1998).

The reduction of greenhouse gas emission from the agricultural sector in Canada becomes important in order to reduce total emissions from all sectors of the economy. One of recommendations under the government of Canada's "National Implementation Strategy" for mitigating greenhouse gases from agriculture is the "development of emission estimates from agricultural production...." (Kulshreshtha et.al., 2000). The approach for the estimation of greenhouse gas' emission from agricultural soils is the up-scaling of point measurements (such as from chamber or tower) to regional "emission coefficients" that are incorporated into models designed for estimating each region's contribution to total national estimates. The reliability of the current models used in the estimation of greenhouse gases from agricultural soils is however undermined by the high spatial and temporal variability associated with field measurements of greenhouse gas emission. This variability presents itself in

¹ *Global warming potential (GWP) is the capacity of a greenhouse gas to cause radiative forcing, relative to the strength of carbon dioxide, which is responsible for climate change. Carbon dioxide, being the reference greenhouse gas, is assigned a GWP of 1.*

the form of data from field measurements of greenhouse gas emission with highly skewed frequency distributions, and coefficient of variation (CV) as high as 150% and sometimes greater (Grant and Pattey, 2002).

1.4 The Significance of the Prairie Pothole Region to Upscaling for Greenhouse Gas Emission

The Prairie pothole region (PPH) is an area extending over part of the North-Central United States of America and South-Central Canada (Kantrud et al., 1989). It covers an area of 775,000 km², and is made up of short-grass, tall-grass and mixed-grass Prairies (Brenton, et al., 1999). The PPH encompasses the states of North and South Dakota, Montana, Iowa and Minnesota in the United States of America, and the Canadian provinces of Alberta, Saskatchewan and Manitoba. The region is characterized by topographically complex landscapes, varying from the top knolls to the depressions, and interspersed with wetlands. The wetlands are found at the hillslopes of the poorly-drained landscape depressions or “potholes” that were formed as a result of receding glaciers during the most recent glaciation (Brenton et al., 1999). While the top knolls are relatively well-drained and usually cropped, the wetlands have standing water either all the time (permanent) or occasionally (ephemeral), serving as habitats for perennial grasses and birds. The Riparian zone serves as the transitional zone between the cultivated uplands and the permanently vegetated wetlands, supporting perennial grasses.

The agricultural sector in Canada contributes about 8% of total anthropogenic greenhouse gas emissions (Environment Canada, 2002), with agricultural soils being a major source and sink for these gases (Jansen et al., 1998). The accuracy of current models used in estimating greenhouse gas emission from the agricultural soil of the PPH is affected by the complex nature of the topographies of the region. This is because the topographic complexity of this region determines the distribution of soil factors and patterns of soil processes that drive the emission of greenhouse gases. The kind and severity of soil processes is known to be influenced by landscape, as topography controls the movement of water and the consequent redistribution of dissolved or transported material (Pennock, 1994).

A high spatial variation in soil N and C cycling processes has been reported (Schimel et al., 1985; Groffman et al., 1993). The “hotspot” for denitrification and N₂O emission was observed to be concentrated at the Lower slopes of a Prairie landscape (Elliot and de Jong, 1992). Higher soil N₂O fluxes were observed at the foot slope and depressions of the cultivated area of a PPH landscape, while the vegetated depressions gave low or negative fluxes (Yates et al., 2006). The production of CH₄ was observed to be high in organic-C rich and poorly-drained parts of the landscape, while the well-drained areas serve as sink for CH₄ (Reiners et al., 1998).

Also, the seasonal variation in N₂O emission from agricultural soils has been studied. The temporal significance of the spring-thaw period to total annual inventory of N₂O emission from agricultural soils has been reported by several

researchers (Lemke et al., 1998; Wagner-Riddle and Thurtell, 1998). The emission of N₂O from thawing soil at spring is very vigorous but brief, with peak emission usually lasting for only a few days (Christensen and Tiedje, 1990). However, the potential of different landscape positions of an agricultural soil for spring-thaw emission of N₂O has not been studied.

Therefore, the reliability of the models used to estimate greenhouse gas emission from the PPH would be improved if the estimates are landscape-based and not field-based. Knowledge of the role of landscape position in N₂O and CH₄ emission from the PPH is necessary to provide reliable estimates of the contribution of agricultural soils in the region to total anthropogenic emissions. The estimates are important, as they serve as the basis for alteration of old, and formulation of new strategies for reducing greenhouse gas emission from human sources. Detailed information on the landscape pattern of field emission of both N₂O and CH₄ within a year, and between years differing in weather conditions, is lacking. There is also no previous knowledge of how soils from different landscape positions differ in their potential for spring-thaw emission of N₂O. Therefore, the objectives of this thesis were:

- (a) To determine the pattern of N₂O and CH₄ emission from the Upper, Middle, Lower and Riparian slope positions of a typical PPH landscape, and the periods and soil factors that are critical for N₂O and CH₄ emission at these landscape positions (Chapter 2),

- (b) To examine if increasing the number of replicate chambers sampled per landscape position will improve the resolution of assessing the spatial variation in N₂O and CH₄ fluxes from a PPH landscape (Chapter 2),
- (c) To examine how lowering the soil moisture before freezing will affect the freeze-thaw emission of N₂O from soil (Chapter 3), and
- (d) To determine the variation in the potential of soils from different landscape positions for freeze-thaw emission of N₂O, and the soil factors important for this variation (Chapter 3).

Field and laboratory experiments were conducted to achieve the above objectives. The field flux of N₂O and CH₄, and associated soil parameters from the Upper, Middle, Lower and Riparian slope positions of a PPH agricultural soil were monitored over spring-thaw to fall of 2005, and spring-thaw to post-fertilizer application periods of 2006. Soil samples were obtained in fall of 2005 from the landscape positions monitored on the field, and assayed in the laboratory to understand how the antecedent moisture and landscape position affect the freeze-thaw emission of N₂O from soil.

Chapter 2 of this thesis details the results of the field investigation of how landscape position affects the emission of N₂O and CH₄ from the PPH soil. It highlights the critical areas within the landscape and the periods that are important for N₂O and CH₄ emission, as well as the soil factors associated with this spatial and temporal variation in emission. Chapter 3 deals with the

laboratory investigation of how soil moisture prior to freezing affects the emission of N₂O from soil. It also reports how the potential of different landscape positions for freeze-thaw emission of N₂O differs, and the soil factors responsible for these differences in potential. Chapter 4 is an overall synthesis of the findings of the field and laboratory investigations. This thesis as a whole is an effort towards having a better understanding of the importance of spatial and temporal variation in the soil processes and factors that affect N₂O and CH₄ emission from the PPH. This understanding will help to improve the current estimates of the contribution of the region's agricultural soils to total national emissions.

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CHAPTER 2

FIELD INVESTIGATION OF THE PATTERN OF GREENHOUSE GAS EMISSION FROM A PRAIRIE POTHOLE AGRICULTURAL LANDSCAPE

2.1 Abstract

In order to effectively manage the complex topographies of the Prairie pothole region to achieve reduced N_2O and CH_4 emissions, the knowledge of the areas within the landscape that are critical to emission, and the soil factors driving emission are important. Presented here are the results of a field study investigating the temporal and spatial variation in the emission of N_2O and CH_4 , the critical areas of high N_2O and CH_4 emission within the landscape, and the soil factors associated with this variation.

The field flux of CH_4 and N_2O and associated soil parameters were monitored from spring to fall of 2005 and spring-thaw to post-fertilizer application periods of 2006 using static-vented chambers located at the Upper, Middle, Lower and Riparian slopes of a 128-chamber transect. There was high temporal variability in N_2O and CH_4 emission, with high fluxes being event-based. The daily emission of N_2O was higher in magnitude in 2005 compared to 2006, the former year being wetter. The spring-thaw and post-fertilizer application periods were the most important for N_2O emission, while CH_4 emission occurred briefly several weeks post thaw, occurring when the soil water-filled porosity was decreasing and soil temperature was increasing in the Riparian zones.

While there was no difference in N₂O emission from the Upper, Middle and Lower slopes, there was high occurrence of hotspots for N₂O emission at the Lower slope, resulting from its comparatively higher soil moisture and carbon (C) availability. A hotspot for N₂O emission was from a replicate chamber at the Lower slope, which had 1.2 times the average total organic content of the Lower slope, contributing about 65% of total cumulative N₂O from the Lower slope position. The Riparian zone was not a source of N₂O emission, despite its soil water-filled porosity being comparable to that of the Lower slope.

The emission of CH₄ was highest in the Riparian zone, with some emission from the Lower slope. There was either no emission or CH₄ was consumed at the Upper and Middle slopes. The hotspot for CH₄ emission in the Riparian zone accounted for up to 98% of total cumulative emission from the zone. The select chamber associated with this hotspot had 117 times less the average soil sulphate content for the Riparian zone, indicating the inhibitory effect of sulphate on methanogens. The high salinity of the Riparian zone was due to sulphate. The observed landscape pattern in N₂O and CH₄ emission did not change with increased number of chambers sampled for each landscape position.

Therefore, it was observed from this study that there is localization of hotspots for N₂O and CH₄ emission within the landscape, being driven by high soil moisture and C availability. Thus, higher N₂O emission index should be given to cropped areas within the landscape having poor drainage, while uncropped areas with poor drainage should be given higher CH₄ emission index when estimating greenhouse gas emission from the Prairie pothole region.

2.2 Introduction

The Prairie pothole region (PPH) is the area that extends over part of the North-Central United States of America and South-Central Canada (Kantrud et al., 1989), encompassing an area of 775,000 km² and comprised of short-grass, tall-grass and mixed-grass Prairies (Brenton et al., 1999). The region encompasses the states of North and South Dakota, Montana, Iowa and Minnesota in the United States of America and the Canadian provinces of Alberta, Saskatchewan and Manitoba. The region is characterized by a complex undulating topography of uplands and wetlands. The wetlands are found at the hillslopes of poorly-drained landscape depressions (Niemoth and Solberg, 2003). These landscape depressions or “potholes” were formed as a result of receding glaciers during the most recent glaciation (Brenton et al., 1999). They form an important hydrologic feature of the region by holding water as permanent or ephemeral wetlands. While the uplands are relatively well drained and usually put to agricultural use, the wetlands have standing water either all the time (permanent) or occasionally (ephemeral), and serve as habitats for perennial grasses and birds. The Riparian zone serves as the transitional zone between the cultivated uplands and the grassy wetlands, usually supporting perennial grasses or forages.

Nitrous oxide and methane are two of the three important greenhouse gases that cause the radiative forcing of the atmosphere, the third being carbon dioxide. The agricultural sector in Canada contributes about 8% of the total

anthropogenic emissions of greenhouse gases (Environment Canada, 2002), with agricultural soils being a major source and / or sink for greenhouse gases (Jansen et al., 1998). In order to formulate effective strategies to reduce the contribution of agricultural soils to total anthropogenic greenhouse gas emission, there is need for the accurate estimation of emissions from soil.

The complex nature of the PPH landscapes may affect the accuracy of current models used in estimating greenhouse gas emission from the region. This is due to high variability in soil factors and processes that directly affect emissions from complex agricultural landscapes, such as those in the PPH. Soil factors like available carbon, N source, moisture availability, soil aeration and soil temperature that directly affect soil processes producing greenhouse gases from soil are highly variable along these landscapes. Izaurre et al. (2004) reported that landscape position influences soil N dynamics, with higher pre-thaw nitrate content at the footslope and depressions compared to the shoulder and back slope positions. Corre et al. (1996) also observed the total nitrogen and total organic carbon on the footslope of a PPH soil to be higher compared to the shoulder. Nitrous oxide emission, for instance, was observed to be closely tied to the landscape pattern of moisture redistribution, with lower emission from the well-drained Upper slope position of the landscape compared to the poorly-drained Lower slope (Corre et al., 1996). Such processes like nitrification and denitrification for N₂O production, and methanogenesis for CH₄ production, are therefore expected to be variable along the landscape, as dictated by the distribution pattern of the soil factors driving these processes.

Biological denitrification and nitrification are the two processes leading to N₂O emission from agricultural soils (Blackmer and Bremner, 1978; Smith and Arah, 1990). While nitrification is the microbial oxidation of NH₄⁺ to NO₃⁻ in soil, denitrification is the microbial reduction of soil NO₃⁻ to N₂. N₂O is one of the many intermediates of these two processes. The dominant of these two processes is determined by soil conditions, especially the aeration status of the soil and available N source. Whereas nitrification requires the ample supply of oxygen to proceed in the soil, denitrification requires limiting amount of oxygen to occur, as oxygen and nitrate are the terminal electron acceptors for nitrifier and denitrifier micro-organisms, respectively. Biological denitrification is widely believed to be the major source of N₂O in soils above 60% soil water-filled porosity (Dobbie, et al., 1999; Abbasi and Adams, 2000; Skiba and Ball, 2002). Methane on the other hand is produced in soil by anaerobic methanogenic microbes (Le Mer and Roger, 2001), while consumption is as a result of the activities of methanotrophic bacteria that utilize the methane as a source of cellular carbon and energy (Topp and Pattey, 1997). Therefore, the highly variable soil conditions along the landscapes of the PPH region may have serious implications for nitrification, biological denitrification and methanogenesis, and consequently N₂O and CH₄ production.

There has been past research efforts directed at investigating the seasonal pattern of N₂O emission from agricultural soils (Lemke et al. 1998; Wagner-Riddle & Thurtell 1998) and the variation at the landscape-scale in denitrification and N₂O emission (Yates et al., 2006; Izaurrealde et al., 2004; Corre

et al., 1996; Pennock et al., 1992). The emission of N_2O is seasonally variable, with generally high emission at spring thaw as a result of high soil moisture, carbon and N availability, as well as high early-summer emission associated with fertilizer application and frequent rainfall events (Corre et al., 1996). There is also inter-annual variation in N_2O emission, with higher emission for years having high soil moisture availability, either from snow melt during spring or high rainfall during the growing season. Izaurre et al. (2004) reported that the highest N_2O emission was from the back slope in summer of 1995, but at spring thaw of 1996, the highest emission was from the depression. While the highest N_2O emission was also from the back slope in summer of 1996, emission was order of magnitude larger than that of summer of 1995.

There is also a high spatial variation in N and C cycling processes in soil (Schimel et al., 1985; Groffman et al., 1993). The production of CH_4 is high in organic C-rich and poorly-drained parts of the landscape, where organic matter is decomposed, and CO_2 is reduced by micro-organisms under highly anaerobic conditions (Reiners et al., 1998). In contrast, the well-drained portions of the landscape serve as a sink for CH_4 . The “hotspots” for denitrification and N_2O emission was observed to be concentrated at the Lower slopes in the landscape compared to the Upper slope positions (Elliot and de Jong, 1992; Corre et al., 1996). Higher soil N_2O fluxes were observed at the foot slope and depressions of the cultivated area of a PPH landscape, while the vegetated depressions (Riparian) gave low or negative fluxes (Yates et al., 2006). This landscape-scale pattern in N and C cycling is as a result of disparity in the intensities of soil

processes (denitrification, nitrification and methanogenesis) in each landscape element, with these processes controlled by hydrologic and pedologic processes as dictated by landscape (Pennock et al., 1992).

The regional estimates of greenhouse gas emission will only become reliable if the predictive models used for these estimates are landscape-scale based and not field-scale based. Knowing the role of landscape position in the emission of greenhouse gases from soil is important for the accurate estimation of the PPH agricultural sector's contribution to total anthropogenic greenhouse gas emission. The accuracy of these estimates is important to provide the basis for the alteration of old, and formulation of new strategies for reducing greenhouse gas emission from human sources. This reduction in emissions is necessary to reverse the current trend of increasing concentrations of greenhouse gases in the atmosphere (IPCC, 2001) which can potentially cause climate change.

Detailed information on the landscape pattern of the field emission of both N₂O and CH₄ within a year and between years is lacking. This information is vital especially for such a complex topography as that of the Prairie pothole region where huge variability in soil conditions and factors within the landscape can potentially have serious implications for greenhouse gas emission. This is because topography, which is a critical factor modifying both the microclimatic and hydrological conditions of a landscape (Rowe, 1984), influences the

movement of water, with consequent redistribution of dissolved / transported materials, and can influence the kind and severity of soil processes within a landscape (Pennock et al., 1994).

This study was carried out to investigate how landscape position affects the field emission of CH₄ and N₂O over the course of a growing season for two consecutive years. The first year of study (2005) was dedicated to identifying the critical periods over the growing season when GHG emission is important, and the pattern of emission over the landscape. The second year of study (2006) was designed to closely monitor how landscape position affects GHG emission over the identified critical periods of spring thaw and post-fertilizer application, and the soil factors that are driving this landscape pattern of N₂O and CH₄ emission. The objectives of this study was to determine: (a) what is the pattern of N₂O and CH₄ emission over the Upper, Middle, Lower and Riparian landscape positions and (b) the critical periods and soil factors that are of importance to N₂O and CH₄ emission at different positions over the landscape.

2.3 Materials and Methods

2.3.1 Site Location and Description

The experimental site was located at the Manitoba Zero Tillage Research Association (MZTRA) farm, latitude 49°55'N, longitude 99°57'W, and 17.6km North of the city of Brandon, Manitoba. It is situated within the Aspen Parkland of the Prairies Ecoregion of South-West Manitoba, and part of the Prairie pothole

region of the province. It has an undulating to hummocky landscape with gently sloping (2-5%) topography (Podolsky and Schindler, 1993). The mean annual temperature at the site is 1.9°C, while total annual precipitation and mean annual rainfall are 472 and 373.1mm, respectively, for the period between 1971 and 2000 (Environment Canada, 2006a). The soil at the site was mapped as predominantly being a Newdale Clay Loam series belonging to the Black Chernozems formed over calcareous glacial tills (Podolsky and Schindler, 1993).

The MZTRA farm was intensively tilled over decades before it was put under zero-till crop production starting in 1993. It was planted to Canadian Prairie Spring (CPS) wheat (variety 5701) in the growing season of 2005, shortly after the commencement of this study, and fertilized with 74 kg ha⁻¹ total N (as 67 kg ha⁻¹ of 28-0-0 UAN and 7 kg ha⁻¹ of 11-52-0 MAP). In 2006, the field was planted to flax (variety Bethune), with the application of 67 kg ha⁻¹ total N as 28-0-0 UAN solution. Mono-ammonium Phosphate (MAP) fertilizer was applied with the seeds, while the Urea Ammonium Nitrate (UAN) solution was side-dribbled on the soil surface beside the seed row.

2.3.2 Field Establishment of Transect, Sections and Subset Collars for Gas Sampling

A 444.5m-long transect having 128 collars, spaced at 3m interval, was set up at the field site in fall 2004, the transect being oriented to a West, Northwest direction (Figure 2.1). The transect intersects a representative sample

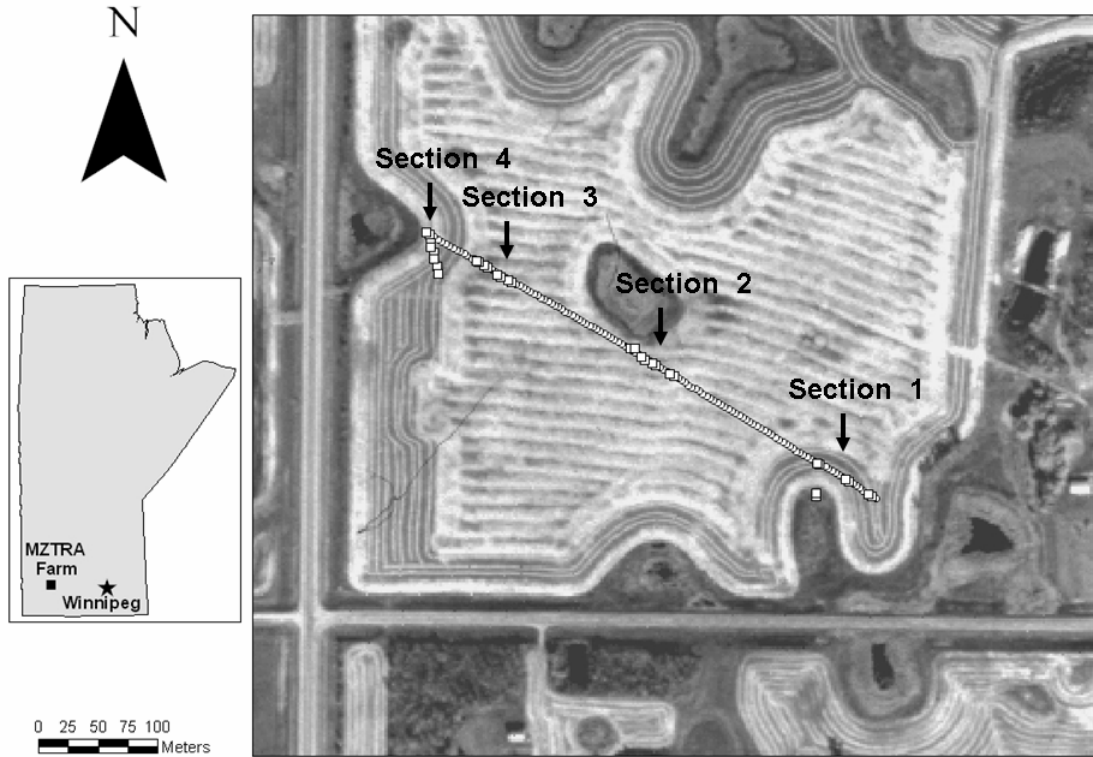


Figure 2.1 Map of the field site showing the location and direction of the transect, sections of the transect, positions of the 128 collars on the transect and the subset chambers that were off the transect. The collars are shown as white squares. The distinct squares are the subset chamber locations at the Upper, Middle, Lower and Riparian slope positions of the replicate sections 1 to 4.

of landforms, with the 128 collars installed at an angle of 300.7 degrees true bearing from Southeast to Northwest (Figure 2.1). The approximate co-ordinates and distances of the transect determined by Ozyexplorer and waypoint files were 433141, E5544815N for the Northwest end, and 433517, 5544582N for the Southeast end. The collars were made of reflective PVC, with an internal diameter of 14.7cm, and a total length of 7.5cm, with 3cm of this length driven into the soil through a beveled edge. The collars were held firmly into the soil by means of 7/16"-diameter eye bolts driven into the soil through three 3/8" anchor bolts attached to the sides of the collars. The collars were installed horizontal to the soil surface, irrespective of the aspect of the slope.

The transect was segmented into the landscape elements (Upper, Middle, Lower and Riparian) by analysis of digital elevation data measured with Light Detection And Ranging (LIDAR Aerostan International Inc.) and LandMapR software (MacMillan, 2003). Each collar on the transect was then classified by comparing the collar location waypoints with the landform polygons in Oxyexplorer software (Newman, 2004).

The entire transect was divided into four catenas (sections) serving as replicates (Figure 2.2), with each section having 8 subset collars, which were either part of the entire transect or among the extra collars that were off the transect. There were six of these extra collars installed at the Northwest end of the transect in section 4, at about Northwest45°South to the transect, while another extra 2 collars each were installed at the Riparian zones of sections 1 and 2. The Riparian zones of sections 1 and 2 were between 1 to 4 meters away

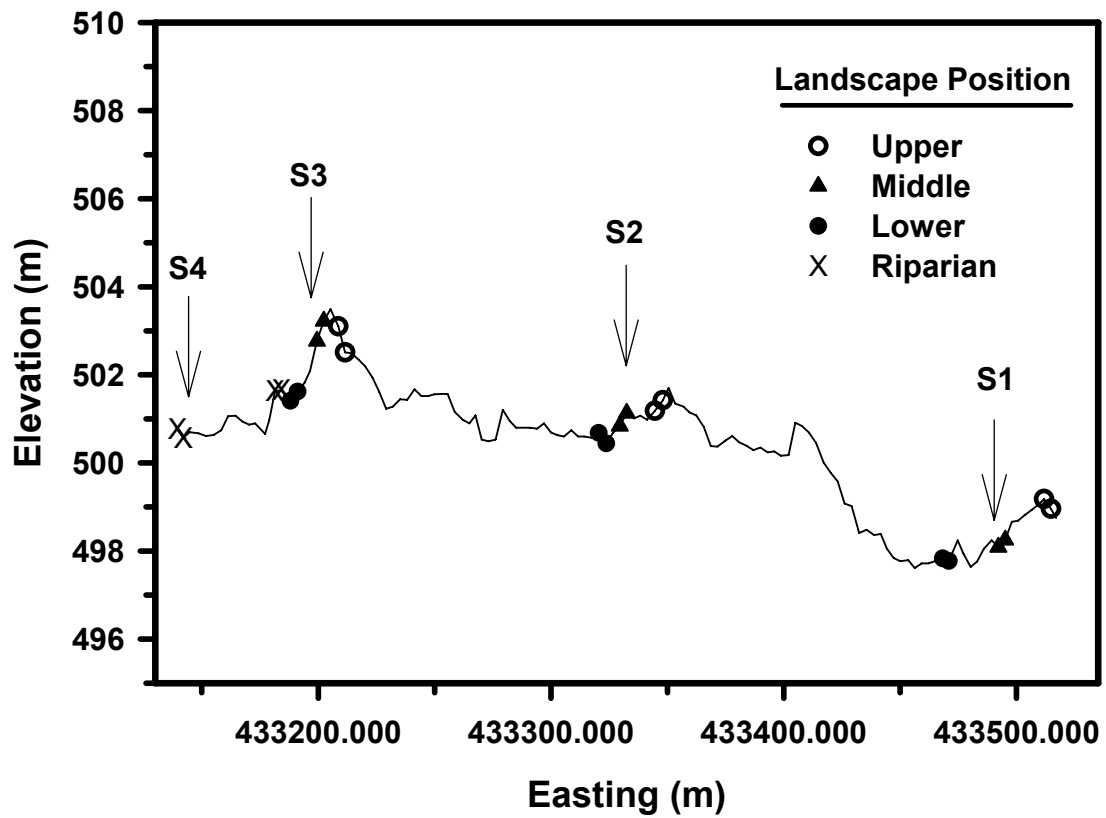


Figure 2.2 Cross-section of the 128-chamber transect showing the positions of the subset chambers located on the transect at the Upper, Middle, Lower and Riparian slope positions. The transect is shown divided into four catenas of section 1 (S1), section 2 (S2), section 3 (S3) and section 4 (S4).

from the transect. Two each of the extra six collars at the Northwest end of transect were located at the Upper, Middle and Lower slope positions. The extra collars were installed in order to have a complete set of subset chambers for each landscape element, as the transect neither passed through the Riparian zones of sections 1 and 2, nor cut through a complete catena in section 4. Therefore, there were 22 of the subset chambers directly on the transect and 10 off it. There were 2 collars in each section for each landscape position, making a total of 8 collars for each of Upper, Middle, Lower and Riparian slope positions. One of the 2 collars was sampled in 2005, while both were sampled in 2006, making a total of 4 and 8 subset collars sampled for each landscape position in 2005 and 2006, respectively. The number of replicate chambers sampled for each landscape position had been doubled in 2006 in order to improve the gas flux values determined for each landscape position.

The 128 collars on the transect were segmented into the four landscape positions by using a combination of the landform (as earlier described) and the agricultural use to which each landscape element was put. This was done to evaluate the spatial pattern of greenhouse gas emission over the landscape on select days with greater power and detail by increasing the number of chambers monitored per landscape position. Though the entire 128-chamber transect was sampled less frequently, it afforded the detailing of the pattern of greenhouse gas emission with landscape position on days it was sampled. The 32 subset chambers located at the Upper, Middle, Lower and Riparian slope positions of

sections 1 to 4 of transect were however sampled more often to capture the temporal pattern in greenhouse gas flux with landscape position.

The installed collars were removed during major field operations (seeding and fertilizer application, herbicide application and harvesting) and re-installed after each operation. The collars were finally removed early summer, 2006, when the study was completed and the transect was taken down. Soil properties varied with the landscape positions at the field site, with higher soil salinity and total organic carbon contents at the Riparian and Lower slope positions, compared to the Upper and Middle slopes (Table 2.1).

2.3.3 Weather Monitoring; Precipitation and Air Temperature Data

Daily precipitation and air temperature data from AAFC Phillips Farm, 3.5km Southeast of the field site was used for the year 2005. In 2006 however, precipitation and air temperature were monitored at the field site. Any missing precipitation or air temperature data due to faulty weather monitoring equipment was substituted for with corresponding data from Brandon Airport, which was about 15km South of the field site. The 30-year average weather data for the Airport was also used as a baseline for comparison of the field weather data to determine if the temperature and precipitation pattern during the study period deviated from average for the period between 1971 and 2000.

The total rainfall received on the site from April 1 to September 30, 2005 was 340.6mm (Figure 2.3a), which is the same as the average of 339.5mm for

Table 2.1 Soil properties at 0-10cm depth of different landscape positions determined for the field site (MZTRA farm) in fall, 2005

Position	pH (H ₂ O)	EC (m S m ⁻¹)	Sulphate (g S kg ⁻¹)	Tot. Org. C (%)	Textural Class
Upper	7.43 (0.13)	26.3 (6.3)	0.03 (0.01)	4.81 (0.09)	clay loam
Middle	7.58 (0.19)	18.8 (1.8)	0.03 (0.01)	4.95 (0.13)	clay loam
Lower	7.40 (0.09)	165.0 (53.6)	2.08 (0.81)	5.21 (0.38)	clay loam
Riparian	7.30 (0.07)	445.0 (142.2)	7.02 (2.34)	7.01 (1.37)	clay loam

Values are means for soil pH (determined in H₂O), electrical conductivity (EC), sulphate content, total organic carbon and textural class of 4 independent replicates for each landscape position. Values in parentheses are 1 standard error of the mean.

Brandon Airport for the period (Environment Canada, 2006a). About 79% of this total rainfall was received between May 20 (day 140) and July 19 (day 200) in 2005. The total rainfall for April 1 to June 2, 2006 was 152.16mm (Figure 2.3b), being greater than the 30-year average of 70.2mm for the same period. The rainfall events for 2006 were more evenly distributed over the sampling period (Figure 2.3b). Even though the total rainfall recorded in 2005 for a period equivalent to the 2006 sampling period was 92.3mm, the total snow from January to May of 2005 was almost 1.5 times the total snow for the same period in 2006 (Environment Canada, 2006b). Therefore, snow melt was a major source of soil moisture in 2005 compared to 2006. Also, the total rainfall received over the fall of 2004 was more than twice that received in fall of 2005. A combination of the moisture from snow melt and preceding fall rainfall made the spring of 2005 wetter than the spring of 2006, especially in the Lower and Riparian slope positions. In 2005, the months of April, June and July were warmer than the 30-year average for the same period, while May and August were colder than average. In 2006, April was warmer and May was colder than average (Environment Canada, 2006b).

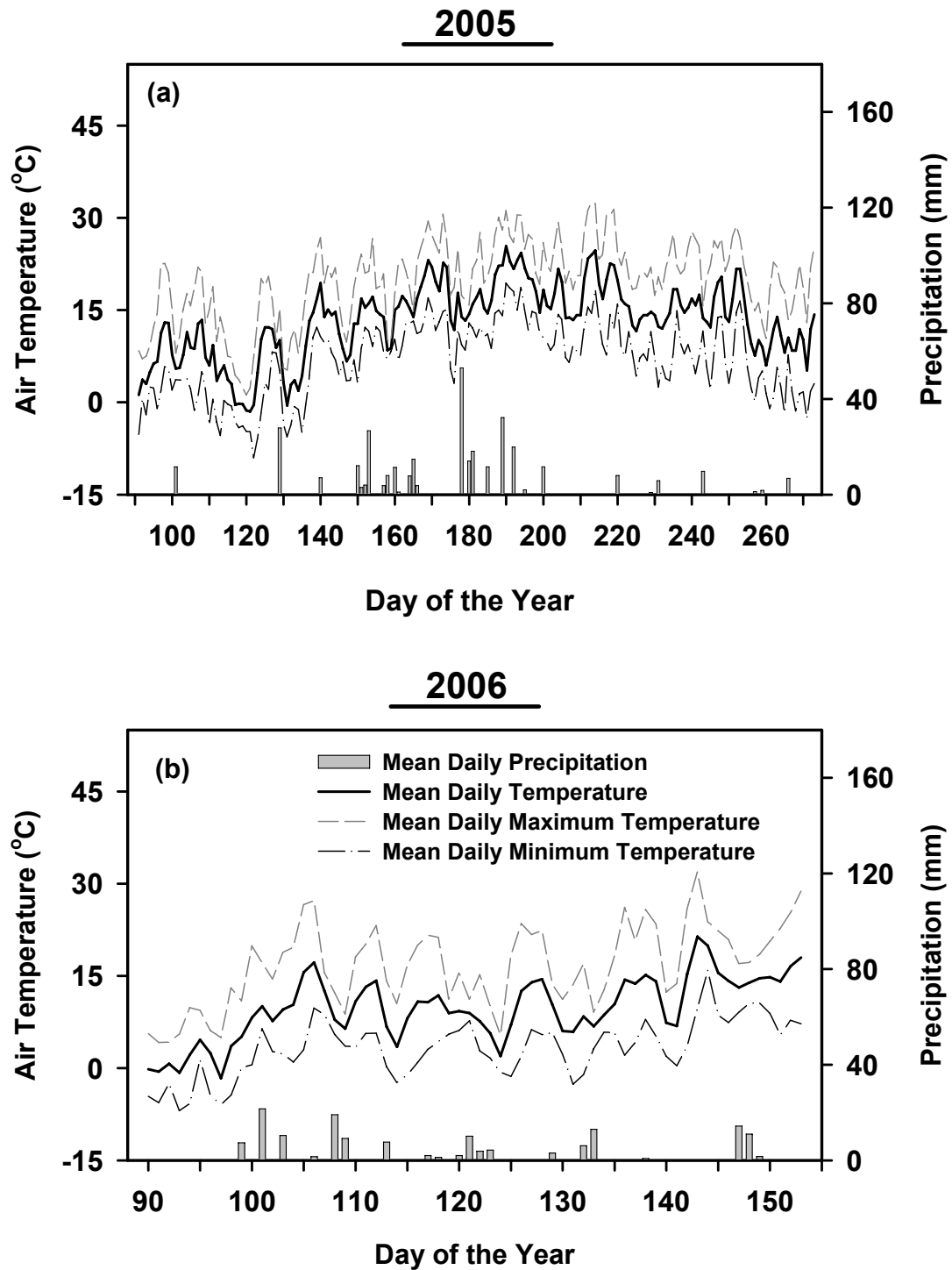


Figure 2.3 Mean daily, maximum and minimum air temperatures, and mean daily precipitation for the experimental site for the period between; (a) April 1 to September 31, 2005 and (b) April 1 to June 2, 2006.

2.3.4 Measurement and Analysis of Greenhouse Gas Emission from Soil

Greenhouse gas flux was measured from the spring thaw, through post-fertilizer application and summer, until the fall of 2005, and spring thaw to post-fertilizer application of 2006. The spring thaw was the period (usually few weeks) in spring, when snow cover from winter started to disappear, and the frozen soil started to melt. The post-fertilizer application period was the period following seeding and fertilizer application until early summer. The flux of N₂O, CH₄ and dark-chamber CO₂ from the Upper, Middle, Lower and Riparian slope positions was measured using a modified static-vented chamber technique of Hutchinson and Livingston (2002). The static-vented chamber consisted of a PVC collar (base) pre-installed in the soil and lids carrying a rubber-septum sampling port, with a vent to ensure that the pressure inside the chamber is in equilibrium with the atmospheric pressure. The lids were made of reflective PVC having an internal diameter of 16.2 cm and a height of 11 cm, with metallic handle for placing the lids on the installed collars. The lids were placed on the pre-installed collars at the start of gas sampling, and removed after sampling was finished. The total volume of the chamber after placing the lid was 3.81 L, and a smear of grease at the collar-lid interface ensured the chamber was air-tight.

Headspace gas of chambers (20mL) was removed at 0, 9, 18 and 27 minutes, using a PrecisionGlide[®] needle (25G, 5/8") mounted on Becton-Dickenson syringe (Fisher Scientific, Nepean, ON), and injected into 12ml Labco Exetainer[®] gas vials (Labco Limited, Buckinghamshire, UK). The gas vials had been evacuated and flushed thrice with Helium gas to a pressure of 500millitorrs,

with the top of the vials sealed with Mastercraft silicone and left to dry prior to gas sampling. The silicone seal was to ensure the vial septa were air-tight. The samples were transported to the laboratory and stored at room temperature in the dark until they were analyzed. The integrity of the gas samples during storage was ensured by means of low and high standard gas samples (Welders Supplies, Winnipeg, MB) prepared, taken to the field, and returned to the laboratory for analysis along with the gas samples. The low standard gas sample composed of 193ppm CO₂; 4.25ppm CH₄ and 0.46ppm N₂O, while the high standard gas composed of 897ppm CO₂; 15.8ppm CH₄ and 0.84ppm N₂O (concentrations determined by the soil ecology laboratory). The gas samples were then analyzed for N₂O, CH₄ and CO₂ using a gas chromatograph (Varian 3800, Mississauga, ON) fitted with ECD, FID and TCD detectors, with the detectors operated at 300, 250 and 130°C, respectively. The gas chromatograph was equipped with a Combi-PAL autosampler (CTC Analytics, Switzerland) that injected 2.5mL volume of sample to the GC to deliver the sample into the three detectors. The volume of each sample loop for the gas chromatograph was 500 microlitres. The flux was calculated from the gas concentration, molecular mass of N or C in gas of interest, chamber area and volume, air temperature at sampling and atmospheric pressure using the Ideal Gas Law ($PV=nRT$). The flux from each chamber was determined by fitting a linear regression line of best fit through at least three of the four sampling points, removing any outlier to achieve a minimum r^2 of 0.85.

2.3.5 Determination of Environmental Conditions Associated with Greenhouse Gas Emission from Soil

Soil environmental factors such as temperature, moisture regime and nutrient status are known to be of great importance for greenhouse gas production and emission (Smith et al., 2003), and are therefore critical for the interpretation of gas flux results. For both 2005 and 2006, the air temperature ($Temp_{air}$) and soil temperature at 15cm depth ($Temp_{15}$) were measured using soil Traceable[®] thermometers (Fisher Scientific Company, Nepean, ON) with 2.5cm- and 15cm-length probes, respectively. The soil temperature at 2.5cm depth was also measured in 2006, using the 2.5cm length soil thermometer. The soil temperature at 2.5cm and 15cm depths was measured to determine how greenhouse gas production is associated with soil temperature at these depths.

The soil volumetric moisture content at 0-10cm depth was measured using a Hydrosense[®] water content sensor (Campbell Scientific Corp., Edmonton, AB) and Delta-T WET Sensor connected to a HH2 moisture meter (Delta-T Devices Limited, Cambridge, UK) in 2005 and 2006, respectively. The 2 sensors used were calibrated using soil gravimetric moisture content values determined from intact soil cores. The soil volumetric moisture content was required to calculate the soil water-filled porosity (WFP) using the dry bulk density of soil samples determined from intact soil cores. The soil WFP was to serve as an index of the oxygen status and redox condition of the soil. In 2006, the soil electrical conductivity (EC) and snow depth were also determined using the Delta-T WET Sensor and a 1 meter ruler, respectively. The EC was measured to determine

how variation in soil salinity within the landscape would affect the emission of greenhouse gases, while the snow was monitored to see the pattern of snow distribution and progression of disappearance over the landscape. All the previously mentioned soil environmental parameters were determined immediately following gas sampling.

The dark-chamber CO₂ emission from chambers was measured in both years, using the gas samples taken for the determination of N₂O and CH₄ emission on the field. The dark-chamber CO₂ emission was determined by gas chromatography as previously described for N₂O and CH₄, and was used as an indication of substrate (carbon) availability for microbial activities. Soil samples for N species (NO₃⁻ and NH₄⁺) analysis were taken once a month in 2005, and once a week in 2006, to determine substrate availability for denitrification and nitrification, respectively. The samples used for the analysis were taken from each landscape position by using a garden trowel to obtain four sub-samples from four spots, about 0.5m radius around each collar, bulking the sub-samples and taking a homogenous sub-sample from the mixture. The samples were kept frozen at -20°C until they were analyzed for nitrate and ammonium.

2.3.6 Soil Samples' Extraction, N species, Total N, Total Organic C and Soil Sulphate Analyses

A K₂SO₄ extraction for ammonium and nitrate was carried out for soil samples taken from the field in 2005 and 2006, respectively. A sample (5g) of air-dried and pulverized soil was placed inside a conical 50mL Fisherbrand®

centrifuge tube (Fisher Scientific Canada, Edmonton, AB), followed by the addition of 25mL 0.5M K_2SO_4 solution. The mixture was then placed on a reciprocating shaker at 110epm for 30 minutes, followed by centrifuging at 3000 rpm (1,560 X *g*) for 1.5 minutes. Using an autopipetter, 10mL of the clear supernatant was transferred into a labeled scintillation vial, while rinsing the tip of the autopipetter with distilled water between transfers. Gravimetric moisture contents of the samples were also determined at the time of extraction. The extracts were kept at -20°C, if not analyzed within a week after extraction. The nitrate and ammonium concentrations of the extracts were determined by the automated Cadmium reduction (Method No. 4500-NO3 (F)) and Phenate (Method No. 4500-NH3 (G)) methods, respectively, using Technicon™ Autoanalyzer II system (Pulse Instrumentation Ltd, Saskatoon, SK).

Total organic carbon (TOC) contents of soil samples collected in fall of 2005 were determined once by using a Truspec Carbon / Nitrogen Determinator (LECO Instruments Limited, Mississauga, ON). Pulverized air-dried 0.25g of soil samples were placed inside small tin capsules that were then loaded into the instrument for total organic C and total N analysis. The instrument comprised of combustion and secondary furnaces, maintained at 950°C and 850°C, used for combustion and oxidation of samples, respectively. The oxidized samples were then passed through a CO₂ infrared detector and a thermal conductivity cell to determine total organic C and total N, respectively, the values in % being read from a personal computer connected to the instrument. The samples were not

pre-treated for carbonate removal as the field, being highly eroded, had a neutral pH (Table 2.1).

Also, a one-time determination of the sulphate content of soil samples collected in fall of 2005 was done using a ICS 1000-Ion Chromatography System (Dionex Corporation, Oakville, ON) consisting of pump heads, auto-regenerant suppressor and a DS6 heated conductivity cell maintained at a temperature of at least 7°C above the ambient temperature. A 1:2 water extraction of pulverized air-dried samples (25g of soil in 50mL distilled water) was placed on a shaker at 110rpm for 30minutes and then filtered with 0.45µm nylon membrane filter (Whatman No. 7404-002) to obtain the extract. A 5mL sample of the extract was injected into the ion chromatograph by means of an attached AS40 Automated Sampler (Dionex Corporation, Oakville, ON), while the pump heads pumped the mobile phase (28.7mM sodium hydroxide) that carried the analyte to the conductivity cell that detected the conductivity of the analyte. The concentration of sulphate contained in the analyte was then determined by calibration with certified standards (Lot no. SC6214488; SCP Science, Baie D'urfe, QC) of known concentrations and conductivity, while the values were read off on an external personal computer unit attached to the ion chromatograph.

2.3.7 Data Analyses

Statistical analyses of all data were done using the SAS statistical package version 9.1 (SAS Institute Inc., Cary, NC, USA).

2.3.7.1 Field Flux Data. A generalized linear model (GLM) analysis of variance (ANOVA) was carried out on the cumulative flux data for N₂O and CH₄ to determine treatment (landscape position) and block (section) effects. The cumulative data was calculated by adding up the daily flux values for a chamber for the entire period (such as spring thaw and post-fertilizer application) being considered. The flux values for days when there was no gas sampling were calculated by linear interpolation of flux values for days that were sampled prior to, and after those days. Flux data for 2005 and 2006 were analyzed separately due to the different number of replicate chambers in each landscape position*section combination. The section and section*position interaction were specified as random factors while position was specified as a fixed factor. A $\alpha = 0.05$ level of significance was adopted for the statistical analyses, allowing for the high degree of variability usually associated with uncontrolled field-based experiments (Corre et al., 1996, Mosier and Hutchinson, 1981, Goodroad and Keeney, 1984). The cumulative flux data was either log (base 10) or power-transformed after the addition of a common coefficient of 2 (to avoid negative fluxes) in order to improve both the normality and homogeneity of the distribution of the error variances. Shapiro-Wilk and Levene tests were carried out in order to test for the normality and homogeneity of variance of the transformed flux data respectively. In cases where the error variances were not homogeneous, a “Mixed” procedure was used for the analysis of variance. Scheffe’s test or Least Squared Difference (LSD) was carried out to determine treatment (landscape position) mean groupings based on minimum significant

difference at $\alpha = 0.05$. The effect of landscape position on N_2O and CH_4 emission for flux data of the segmented 128-chamber transect was tested using unbalanced ANOVA, as the landform segmentation resulted in unequal number of collars for the four landscape positions. The association of N_2O and CH_4 fluxes to soil parameters was tested using Spearman rank correlation coefficient at $P < 0.05$ level of significance.

2.4 Results

2.4.1 Greenhouse Gas Emission

The daily emissions of N_2O and CH_4 in 2005 and 2006 showed high temporal and spatial variability. The coefficient of variation (CV) for N_2O in 2005 and 2006 ranged between 47 – 307 % and 63 – 157 %, respectively. The CV for CH_4 however increased from between 113 – 343 % in 2005 to between 80 – 497 % in 2006. The block (section) effect was not significant for N_2O and CH_4 emissions for both years, indicating that sections (catenas) were not different in the emission of the gases.

2.4.1.1 Landscape Position and Nitrous Oxide Emission using Subset

Chambers. There was high variability in N_2O emission in 2005, with the number of replicate chambers for each landscape position being four. There were two conspicuous periods of N_2O emission; spring thaw and post-fertilizer application periods (Figure 2.4a). There was either no emission or there was consumption of

N₂O at other times. In spring of 2005, N₂O emission increased briefly especially for the Middle and Lower positions, then decreased and remained low until after seeding and fertilizer application (Figure 2.4a). The emission of N₂O increased shortly after seeding and fertilizer application for the cropped area (Upper, Middle and Lower positions). The emission of N₂O from the uncropped Riparian zone remained low during the spring-thaw and post-fertilizer application periods (Figure 2.4a). There was a burst in N₂O emission at the Riparian zone on day 220. Emission of N₂O from the Upper, Middle and Lower slope positions gradually tailed off towards the end of summer, with crop maturity and eventual harvesting of the wheat crop, and emission thereafter remained low through the fall (Figure 2.4a).

There was no difference in cumulative N₂O emission from all landscape positions for spring thaw and post-fertilizer application periods (Table 2.2) in 2005. However, numerically, the highest cumulative emission was from the Middle and Lower slopes for spring thaw and post-fertilizer application periods, respectively. The high cumulative N₂O emission from the Middle slope position during spring thaw was as a result of one subset chamber in section 4 of the transect emitting most (62%) of the total cumulative N₂O from all subset chambers located at the Middle slope position. The fall soil nitrate content of this particular chamber (18 mg N kg⁻¹) was the highest, being 1.3 times the average fall soil nitrate content of all replicate subset chambers at the Middle slope positions (13.8 mg N kg⁻¹). One subset chamber in section 4 of the transect was also responsible for 42% of the total cumulative N₂O emission from all the subset

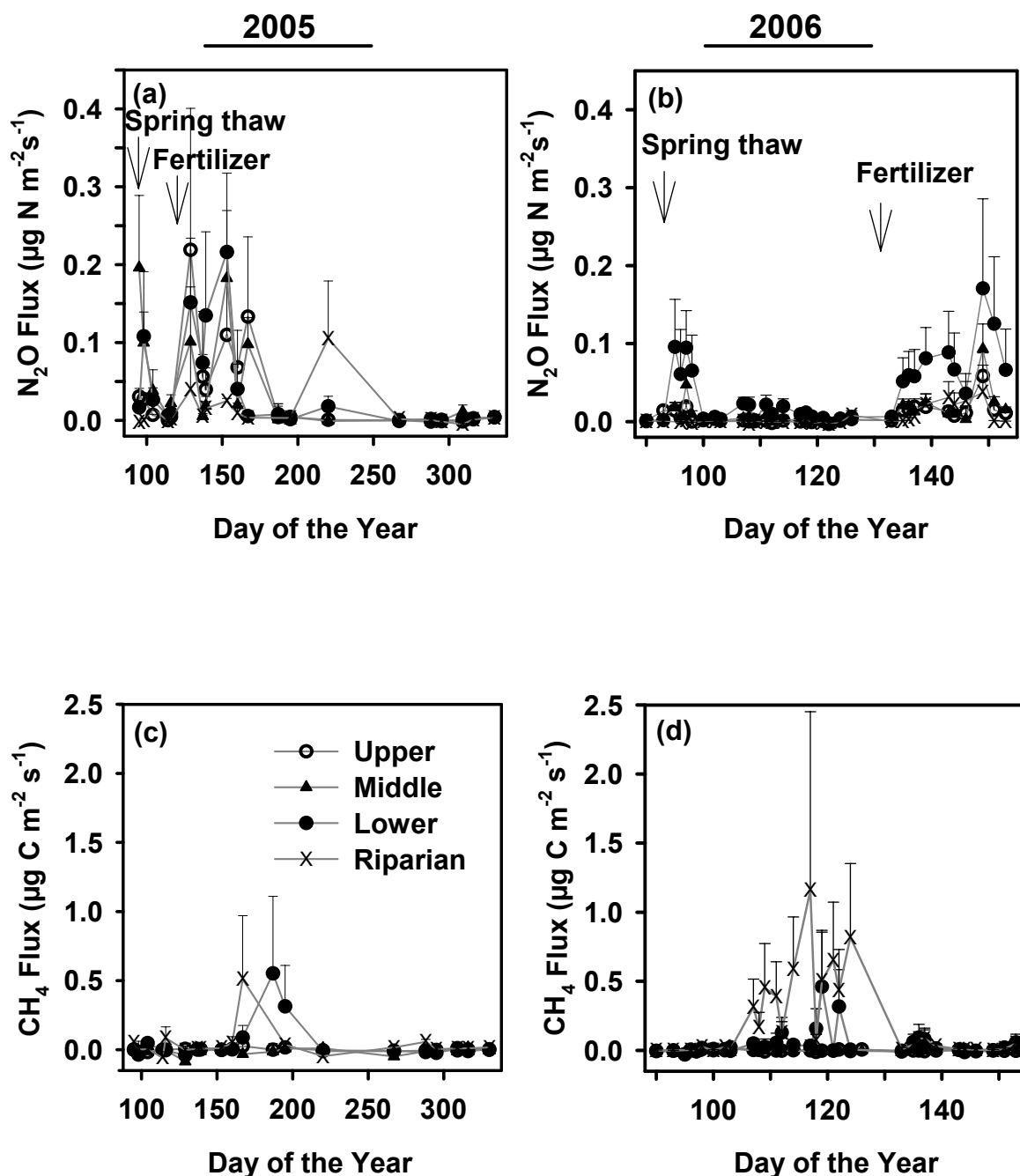


Figure 2.4 Nitrous oxide (N_2O) and methane (CH_4) emission from four landscape positions in the years 2005 and 2006; (a) N_2O in 2005, (b) N_2O in 2006, (c) CH_4 in 2005, and (d) CH_4 in 2006. Values shown are the mean plus 1 standard error of the mean for 4 replicate chambers in 2005 and 8 replicate chambers in 2006. Arrows indicate spring thaw and time of fertilizer application ($67.26 \text{ kg N ha}^{-1}$ as 28-0-0 UAN + $6.72 \text{ kg N ha}^{-1}$ as 11-52-0 MAP in 2005, and $67.25 \text{ kg N ha}^{-1}$ as 28-0-0 UAN in 2006).

Table 2.2 Cumulative nitrous oxide and methane emission from the four landscape positions for spring-thaw and post-fertilizer application periods in the years 2005 and 2006.

Spring-thaw	Year 2005		Year 2006	
	N ₂ O	CH ₄	N ₂ O	CH ₄
Position	(g N m ⁻²)	(g C m ⁻²)	(g N m ⁻²)	(g C m ⁻²)
Upper	0.16 (0.12)*	-0.02 (0.02)	0.011 (0.003) a	0.001 (0.011) b
Middle	0.26 (0.13)	-0.07 (0.04)	0.016 (0.003) a	-0.006 (0.003) b
Lower	0.15 (0.04)	-0.01 (0.01)	0.052 (0.027) a	0.501 (0.416) ab
Riparian	0.03 (0.04)	0.04 (0.03)	0.001 (0.001) b	0.748 (0.509) a
Post-fertilizer				
Upper	0.35 (0.23)	0.02 (0.02)	0.034 (0.018)	-0.011 (0.006) a
Middle	0.29 (0.07)	-0.05 (0.03)	0.044 (0.012)	-0.005 (0.004) a
Lower	0.40 (0.11)	0.04 (0.08)	0.145 (0.090)	0.157 (0.122) ab
Riparian	0.06 (0.04)	0.95 (0.90)	0.031 (0.018)	0.034 (0.015) b

*Mean of 4 replicate chambers in 2005 and 8 replicate chambers in 2006 for each landscape position. Values in parentheses are 1 standard error of the mean. Cumulative N₂O and CH₄ emission were calculated over 35 days in spring 2005, 42 days post-fertilizer application in 2005, 40 days in spring 2006 and 24 days post-fertilizer application in 2006. Mean values followed by the same letter (within columns) are not significantly different using Scheffe's test or LSD groupings of means at $P < 0.05$. The Scheffe's or LSD groupings are associated with significant treatment effects using ANOVA at $P < 0.05$. The ANOVA was done on log -transformed data for N₂O and power-transformed flux data for CH₄.

chambers at the Lower slope position during the post-fertilizer application period. The fall soil nitrate content of this subset chamber was the highest (25 mg N kg⁻¹) of all Lower slope subset chambers, and was 1.7 times the average fall soil nitrate content of all replicate subset chambers at the Lower slope position (15 mg N kg⁻¹).

The magnitude of N₂O emission on sampling days was slightly lower in 2006 compared to that in 2005 (Figures 2.4a and b). With the number of replicate subset chambers for each landscape position doubled to 8 in 2006, the variability in cumulative N₂O emission was lower compared to 2005, with CV being between 63 – 157%. There were also two periods of activity (spring thaw and post-fertilizer application) in terms of N₂O emission for the period monitored in 2006 (Figure 2.4b). There was a brief burst in N₂O emission at the Lower slope during spring thaw, with variability in emission. N₂O emission resumed at the Lower slope shortly after fertilizer application, also characterized by high variability. Emission of N₂O at the Upper, Middle and Riparian slope positions remained low for the spring-thaw and post-fertilizer application periods.

The highest cumulative N₂O emission in 2006 was from the Lower slope position during the spring-thaw event (Table 2.2). There was no difference in cumulative N₂O emission from all landscape positions during post-fertilizer application, but numerically, the highest cumulative N₂O emission was also from the Lower slope position. The high cumulative N₂O emission from the Lower slope was mostly from a replicate subset chamber in section 2 of the transect. This chamber contributed 56 and 65% of total cumulative N₂O from all subset

chambers located at the Lower slope position during spring thaw and post-fertilizer application periods, respectively. The 2005 fall soil total organic carbon content of this chamber (6.02%) was the highest of all subset chambers at the Lower slope, and 1.2 times the average total organic carbon content of all replicate subset chambers at the Lower slope (5.21%).

2.4.1.2 Landscape Position and Methane Emission using Subset Chambers.

The variability in cumulative CH₄ emission in 2005 was high, with a CV ranging from 113% to 343%. There was no CH₄ emission during the spring thaw of 2005 (Figure 2.4c). There was a late-spring to mid-summer (days 150 to 220) burst in CH₄ emission; day 167 for the Riparian zone and days 187 and 195 for the Lower slope position (Figure 2.4c). This burst in emission was still highly variable, with CV for daily emissions being between 179% and 201%. There was either no emission, or there was consumption of CH₄ at the Upper and Middle slope positions for the entire sampling period of 2005.

There was no difference in CH₄ emission from the four landscape positions during spring-thaw and post-fertilization periods in 2005 (Table 2.2). The Riparian zone however gave the numerically highest CH₄ emission for both periods. This high emission from the Riparian zone was mostly contributed by a replicate subset chamber in section 3 emitting 98% of total cumulative CH₄ emission from all replicate subset chambers at the Riparian zone. This chamber had the lowest fall soil sulphate content (0.06 g S kg⁻¹) that was 117 times less

than the average fall soil sulphate content (7.02 g S kg^{-1}) of all replicate subset chambers in the Riparian zone (Table 2.1).

The total cumulative emission of CH_4 from post-thaw through post-fertilizer application period was slightly lower in 2006 compared to 2005, especially at the Riparian zone (Table 2.2). The variability in CH_4 emission was increased in 2006 (CV of between 80 and 497%) despite the number of replicate subset chambers being increased two-fold from that of 2005. There was no emission of CH_4 in all four landscape positions during the spring-thaw event of 2006 (Figure 2.4d). There was variable emission about 2 weeks post thaw at the Riparian zone, which persisted for about three weeks (days 107 to 124). The Lower slope also gave some emission during this period (days 119 and 121). Again, there was either no emission, or there was CH_4 consumption at the Upper and Middle slope positions for the entire period of field monitoring in 2006.

Landscape positions differed in cumulative CH_4 emission during the post-thaw and post-fertilizer application periods in 2006. The Riparian zone and Lower slope gave the highest cumulative emission during post-thaw and post-fertilizer application periods, respectively (Table 2.2). The cumulative CH_4 emission from the Riparian zone was not different from the cumulative emission from Lower slope position for both periods (Table 2.2). Most (66%) of the high cumulative CH_4 emission from the Riparian zone for both periods was contributed by one replicate subset chamber in section 3 of the transect. This was the chamber with the lowest 2005 fall soil sulphate content. The high cumulative CH_4 emission from the Lower slope at post-fertilizer application period was due to a

replicate chamber in section 4 of transect contributing 76% of total cumulative emission for the period. This chamber had the highest 2005 fall soil sulphate content of 3.74 g S kg^{-1} , which was 1.8 times the average of 2.08 g S kg^{-1} for the Lower slope position.

2.4.1.3 Landscape Position's Control on Nitrous Oxide and Methane Emission using Entire 128 Chambers. The entire 128 chambers on the transect was segmented into the Upper, Middle, Lower and Riparian slope positions and used to assess landscape position's effect on N_2O and CH_4 emission in 2006. This was done to increase the number of replicate chambers for each landscape position and thereby increase the power with which the effect of landscape position on N_2O and CH_4 emission was determined. While 8 replicate chambers for each landscape position were used for the subset approach, 22, 70, 31 and 5 replicate chambers for Upper, Middle, Lower and Riparian slope positions, respectively, were identified for the 128-chamber approach.

The highest cumulative N_2O emission over a 36-day period in spring of 2006 was from the Lower slope position when the 128 chambers were used, similar to when the subset chambers were used (Table 2.3). The range of CV (109 – 308%) for cumulative N_2O emission using 128 chambers in 2006 was similar to that (CV of 70 – 371%) for cumulative N_2O emission over an equivalent period (36 days) using the subset chambers for same year (Table 2.3). Also, the numerically highest cumulative CH_4 emission was from the Riparian zone when

Table 2.3 Comparison of using subset chambers or entire 128 chambers to evaluate the effect of landscape position on cumulative greenhouse gas emission in 2006.

Position	Subset Chambers				128 Chambers			
	Cumulative N ₂ O (g N m ⁻²)				Cumulative N ₂ O (g N m ⁻²)			
	n	Mean	SD	%CV	n	Mean	SD	%CV
Upper	8	0.005 b	0.003	70	22	0.005 bc	0.005	109
Middle	8	0.010 ab	0.007	63	70	0.030 ab	0.070	234
Lower	8	0.037 a	0.037	100	31	0.071 a	0.148	210
Riparian	8	0.001 bc	0.005	371	5	0.002 bc	0.008	308
Position	Cumulative CH ₄ (g C m ⁻²)				Cumulative CH ₄ (g C m ⁻²)			
	n	Mean	SD	%CV	n	Mean	SD	%CV
	Upper	8	0.002	0.002	87	22	0.038	0.084
Middle	8	-0.004	0.008	180	70	0.023	0.077	329
Lower	8	0.580	1.399	241	31	0.197	1.009	512
Riparian	8	0.738	1.402	189	5	0.243	0.427	175

Values shown are the number of replicate chambers in each landscape position (n), mean, standard deviation (SD) and coefficient of variation (CV) of cumulative N₂O and CH₄. Cumulative N₂O and CH₄ calculated over 36 days by linear interpolation for the subset and 128 chambers. Mean values followed by the same letter (within columns) are not significantly different ($P < 0.05$) according to Scheffe's test of mean groupings. The significance of landscape position on cumulative emission tested using GLM ANOVA on log-transformed data.

the 128 chambers were used, just as for the subset chambers. The CV for the cumulative CH₄ emission was however increased (175 – 512%) when the 128 chambers were used, compared to when the subset chambers were used (87 – 241%).

2.4.2 Pattern of Soil Parameters over the Landscape

In 2005, the soil temperature at 15cm depth (Temp₁₅) increased steadily from spring, reached a peak in summer and decreased rapidly till late fall (Figure 2.5a). The Lower and Riparian slope positions were slightly warmer than Upper and Middle slopes, especially from early summer to early fall. The peak soil temperature for the Riparian zone was on day 220, when there was a burst in N₂O emission at the zone (Figure 2.4a). The water-filled porosity (WFP) at the Riparian and Lower slopes was comparably high, and greater than the WFP for the Upper and Middle slope positions (Figure 2.5b). The WFP at the Riparian zone over the entire sampling period in 2005 was lowest on day 220, coinciding with the isolated burst in N₂O emission on the same day (Figure 2.4a). Soil nitrate content for the Upper, Middle and Lower slopes were high, but low for the Riparian zone, except for days 129 and 220 (Figure 2.5c). The peak in soil nitrate content for the Riparian zone on day 220 coincided with peak in soil temperature (Figure 2.5a), lowest WFP (Figure 2.5b), and peaks in soil ammonium content (Figure 2.5d), dark-chamber CO₂ emission (Figure 2.5e) and N₂O emission from the zone (Figure 2.4a). This peak in soil nitrate content was highly variable as one replicate subset chamber in section 3 of transect had highest nitrate content

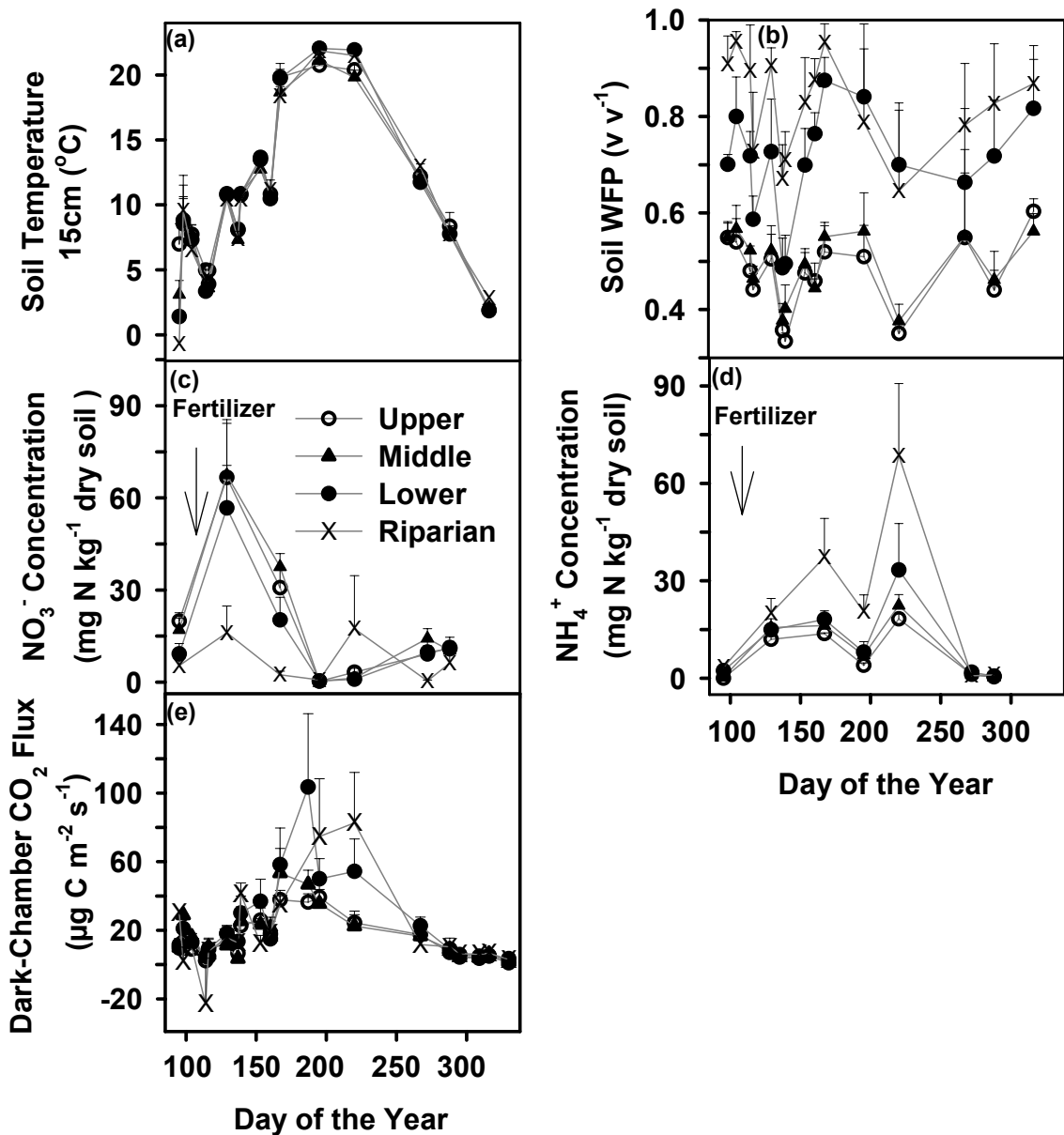


Figure 2.5 Soil parameters from four landscape positions in 2005; (a) soil temperature at 15cm depth, (b) soil water-filled porosity, (c) soil nitrate content, (d) soil ammonium content and (e) dark-chamber CO₂ emission. Values shown are the mean plus 1 standard error of the mean of 4 replicate subset chambers for each landscape position. Arrows indicate time of fertilizer application (67.26 kg N ha⁻¹ as 28-0-0 UAN solution + 6.72 kg N ha⁻¹ as 11-52-0 MAP).

of $345.9 \text{ mg N kg}^{-1}$, which was 4 times the average soil nitrate content ($87.0 \text{ mg N kg}^{-1}$) for all replicate subset chambers at the Riparian zone. The dark-chamber CO_2 emission was similar in pattern to the soil temperature at 15cm, with the Riparian and Lower slopes having higher CO_2 emission than the Upper and Middle slopes (Figure 2.5e).

The snow cover at the Riparian zone in 2006 was higher and persisted longer compared to the Upper, Middle and Lower slope positions (Figure 2.6a). The soil temperature at the 2.5cm depth in 2006 was generally more variable compared to the soil temperature at 15cm depth (Figures 2.6b and c), with the Lower and Riparian slopes being slightly warmer than the Upper and Middle slopes, especially at the 2.5cm depth. Soil temperature at the 15cm depth in 2006 (Figure 2.6c) was lower than the soil temperature at 15cm depth during an equivalent period in 2005 (Figures 2.5a). The soil WFP in 2006 (Figure 2.6d) was generally lower than in 2005 (Figures 2.5b), with the Lower and Riparian slope positions having higher WFP compared to the Upper and Middle slope positions (Figure 2.6d). The warmer and wetter soil conditions in 2005 compared to 2006 coincided with the magnitude of daily emission of N_2O being higher in 2005 compared to 2006 (Figure 2.4). The soil WFP for the Riparian zone remained high between days 107 and 124, coinciding with when CH_4 emission for the zone was very high (Figure 2.4d). The peak soil nitrate content for the Lower slope on day 146 (Figure 2.6e) was variable. This was from one replicate subset chamber in section 4 of transect which had the highest soil nitrate ($690.95 \text{ mg N kg}^{-1}$), and contributed 1.4 times the average N_2O emission of $0.036 \mu\text{g N m}^{-2} \text{ s}^{-1}$ from all

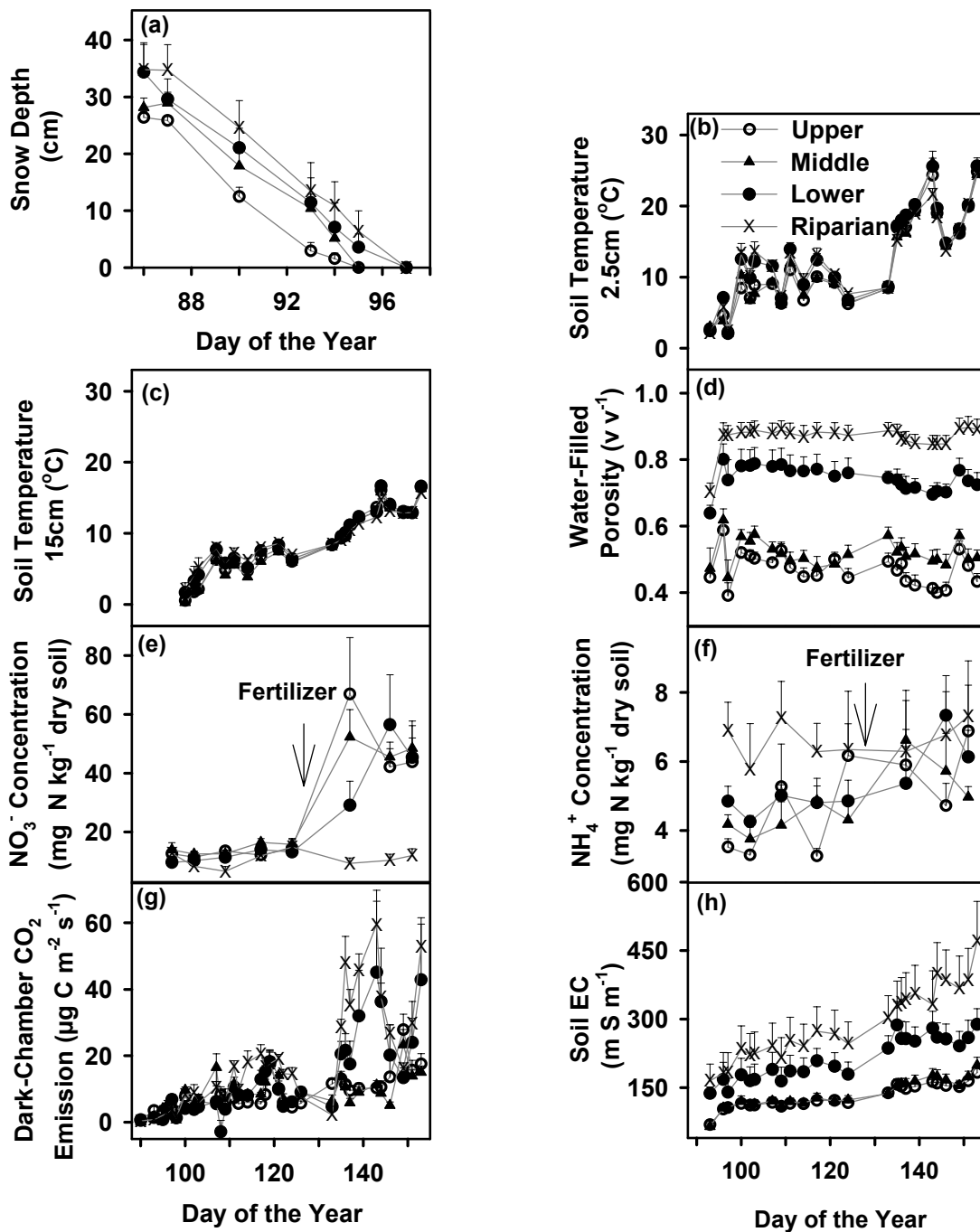


Figure 2.6 Soil parameters from four landscape positions in 2006; (a) snow depth, (b) soil temperature at 2.5cm depth, (c) soil temperature at 15cm depth, (d) soil water-filled porosity, (e) soil nitrate content, (f) soil ammonium content, (g) dark-chamber CO₂ emission, and (h) soil electrical conductivity. Values shown are the mean plus 1 standard error of the mean of 8 replicate subset chambers. Arrows indicate time of fertilizer application (67.25 kg N ha⁻¹ as 28-0-0 UAN).

replicate subset chambers at the Lower slope for this day. The soil nitrate content of this subset chamber was 2.4 times the average soil nitrate content of 282.35 mg N kg⁻¹ for all replicate subset chambers in the Lower slope for day 146. The soil ammonium content in 2006 was substantially lower for all slope positions (Figure 2.6f) compared to 2005 (Figure 2.5d). The dark-chamber CO₂ emission (Figure 2.6g) and N₂O emission were more similar in pattern to soil temperature at 2.5cm depth (Figure 2.6b) than to soil temperature at 15cm depth (Figure 2.6c). There was an increasing trend for soil electrical conductivity (EC) values in all slope positions, with the Riparian zone being consistently the most saline (Figure 2.6h).

2.4.3 Soil Factors Associated with Greenhouse Gas Emission over the Landscape

The soil factors that were significantly associated with N₂O and CH₄ emission varied, depending on the location within the landscape. This is expected as the limitation or abundance of different soil factors that are important to the processes leading to the emission of these greenhouse gases will vary from one landscape position to the other. The limitation (or abundance) of these soil factors will determine the extent of production and emission of N₂O and CH₄ in the different landscape positions.

2.4.3.1 Landscape Trend in Soil Factors Associated with N₂O Emission.

The dark-chamber CO₂ emission (CO₂), soil nitrate content (NO₃⁻), air temperature (Temp_{air}), soil temperature at 2.5cm depth (Temp_{2.5}) and the soil electrical conductivity (EC) were all positively associated with N₂O emission for the Upper, Middle and Lower slope positions (Table 2.4). The soil temperature at 15cm depth (Temp₁₅) was only positively associated with N₂O emission for the Upper and Middle slope positions, but not for the Lower slope position. The soil water-filled porosity (WFP) was strongly but negatively associated with N₂O emission only at the Lower slope. For the Riparian zone, there was no association of N₂O emission to any of the soil parameters, except its weak positive correlation to methane (CH₄) emission. When all the slope positions were considered, N₂O emission was associated with the dark-chamber CO₂ emission, water-filled porosity, soil temperature at 2.5cm and 15cm depths, air temperature, soil electrical conductivity and soil nitrate content (Table 2.4).

The regression of N₂O emission on some of the soil factors that were associated with it showed that emission was enhanced at the Lower slope by an increase in the soil temperature at 2.5cm depth than at the Upper and Middle slope positions (Figure 2.7a). Emission was almost non-responsive to a change in soil temperature at the 2.5cm depth for the Riparian zone. N₂O emission was also negatively related to the soil water-filled porosity at the Lower slope, but almost non-related to soil water-filled porosity at the Upper, Middle and Riparian slope positions (Figure 2.7b). The emission of N₂O was positively related to the soil electrical conductivity (EC) at the Upper, Middle and Lower slope positions,

Table 2.4 Spearman rank correlation coefficients for N₂O and CH₄ with measured soil parameters of different landscape positions from spring-thaw to post-fertilizer application periods in 2006.

Parameter	Landscape Position									
	Upper		Middle		Lower		Riparian		All Positions	
	N ₂ O	CH ₄	N ₂ O	CH ₄	N ₂ O	CH ₄	N ₂ O	CH ₄	N ₂ O	CH ₄
CH ₄	-0.15		0.24		-0.07		0.28 *		-0.06	
CO ₂	0.57 ***	-0.16	0.38 **	-0.02	0.34 **	0.10	0.03	-0.03	0.17 **	0.15 *
WFP	0.04	0.02	0.15	0.14	-0.57 ***	0.31 *	0.02	0.18	-0.28 ***	0.37 ***
Temp _{2.5}	0.59 ***	0.06	0.64 ***	0.35 **	0.44 ***	0.08	0.08	0.09	0.38 ***	0.14 *
Temp ₁₅	0.35 **	-0.01	0.38 **	0.20	0.26	0.07	0.11	0.09	0.24 **	0.11
Temp _{air}	0.55 ***	0.09	0.71 ***	0.25	0.44 ***	0.15	0.13	-0.10	0.41 ***	0.07
EC	0.49 ***	0.10	0.51 ***	0.28 *	0.57 ***	-0.15	-0.07	-0.49 ***	0.15 *	0.01
NO ₃ ⁻	0.47 ***	-0.04	0.54 ***	0.17	0.60 ***	-0.11	-0.09	-0.06	0.46 ***	-0.18 **
NH ₄ ⁺	0.20	-0.11	0.18	-0.003	0.03	0.22	0.12	0.02	0.05	0.12

*, ** and *** indicate the correlation is significant at $P < 0.05$, 0.01 and 0.001 level of significance respectively. Values with no symbol beside them are pairs of parameters that are not significantly correlated. Values in bold indicate pairs of parameters with significant correlation. There were 8 replicates for each landscape position.

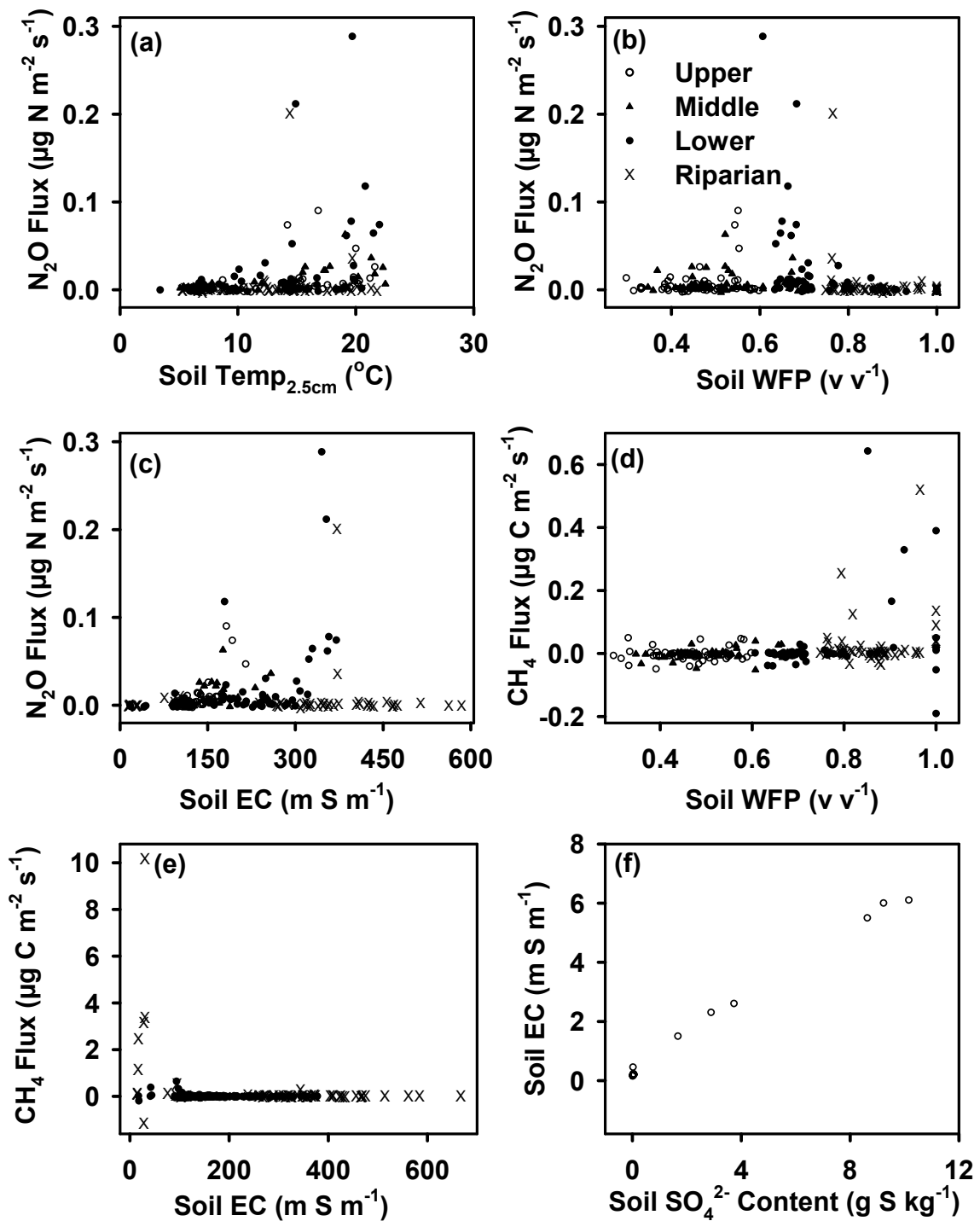


Figure 2.7 Regression of N₂O and CH₄ fluxes on some associated soil parameters; (a) N₂O and soil temperature at 2.5cm depth, (b) N₂O and soil water-filled porosity (c) N₂O and soil electrical conductivity, (d) CH₄ and soil water-filled porosity, (e) CH₄ and soil electrical conductivity for Upper, Middle, Lower and Riparian slope positions and (f) soil electrical conductivity and soil sulphate content for 16 of subset chambers with four replicates each at the Upper, Middle, Lower and Riparian slope positions for 2006 .

but N₂O emission was non-responsive to increasing soil EC at the Riparian zone (Figure 2.7c).

2.4.3.2 Landscape Trend in Soil Factors Associated with CH₄ Emission.

The dark-chamber CO₂ emission was not associated with methane emission at all the slope positions (Table 2.4). The soil water-filled porosity was positively associated with methane emission only at the Lower slope but not at the Riparian zone. The soil temperature at the 2.5cm depth was not associated with CH₄ emission at all slope positions, except for the Middle slope. When all slope positions were considered (Table 2.4), CH₄ emission was associated with the dark-chamber CO₂ emission, soil WFP, soil temperature at 2.5cm depth and the soil nitrate content. Regression of CH₄ emission on the soil WFP showed that CH₄ emission was positively related to soil WFP only at the Lower slope, while emission was non-responsive to changes in soil WFP at the Upper and Middle slope positions (Figure 2.7d). High CH₄ emission was however shown to be possible at almost the same soil WFP for the Riparian zone. The soil electrical conductivity was strongly negatively associated with CH₄ emission at the Riparian zone (Figure 2.7e). The emission of CH₄ was however not associated with soil nitrate content at the Riparian zone, indicating that anion(s) other than nitrate might be the source of salinity for the zone. The high soil sulphate content of the zone (Table 2.1) and the direct association of soil electrical conductivity with soil sulphate content (Figure 2.7f) suggest that sulphate was the source of the salinity in the zone.

2.5 Discussion

The accuracy of the current regional estimates for greenhouse gas inventory in the Prairie pothole region will continue to be undermined by the huge variability in emission observed at the field-scale. In the current study for instance, a CV as high as 371% for N₂O and 512% for CH₄ was recorded, even within the same field (Table 2.2). This high variability in field flux of greenhouse gas is characteristic of uncontrolled, field-based experiments (Corre et al., 1996; Smith et al., 2003). Therefore, only landscape-scale assessment of soil factors and greenhouse gas emission holds the key to establishing distinct patterns and relationships needed for accurate modeling (Pennock et al., 1992). The knowledge of where in the landscape is critical for the emission of N₂O and CH₄ and the soil factors driving these emissions is important not only for upscaling point measurements for inventory purposes, but also for managing the complex topographies found in the Prairie pot-hole region. These reliable inventories will form the basis for the formulation of strategies to reduce greenhouse gas emission from this region. This study was intended to provide information about the temporal variation in landscape-scale emission of N₂O and CH₄, the critical locations of high N₂O and CH₄ emission potentials within the landscape and what soil factors are associated with the capacity of these areas for high emission.

2.5.1 Temporal Variation in Nitrous Oxide and Methane Emission

The emission of N₂O and CH₄ was temporally variable throughout the entire period of this field experiment. The fluxes of N₂O and CH₄ is known to be event-based (Brumme et al., 1999), with high fluxes observed during events like rainfall, spring thaw and fertilizer application in the case of N₂O, and rainfall in the case of CH₄. High temporal variability was observed in this study as bursts of N₂O and CH₄ were associated with events like spring thaw, fertilizer application, rainfall and rapid changes in soil temperature and moisture.

The magnitude of daily N₂O emission in 2005 was generally higher than in 2006. This is likely because year 2005 was wetter than 2006, while the spring of 2005, as indicated by the soil temperature data, was also warmer than the spring of 2006. The year 2005 was wetter than 2006 as the total rainfall received in fall of 2004 was more than twice that received in fall of 2005, and the snow received from January to May of 2005 was almost 1.5 times higher than that received over the same period in 2006. This type of inter-annual variation in N₂O emission was reported by Corre et al. (1996), in which higher N₂O emission was observed for a Prairie landscape in the spring of 1995 compared to the spring of 1994, due to higher soil moisture in the spring of 1995.

There was a brief burst in N₂O at spring thaw in both 2005 and 2006. This spring-thaw emission of N₂O coincided with when the soil temperature started to steadily warm up above 0°C, and the soil water-filled porosity was still high, predisposing the soil to resumed microbial activities as indicated by dark-chamber CO₂ emission steadily increasing at the same time. This

phenomenon of spring-thaw N₂O emission has been widely reported in literature (Lemke et al. 1998; Wagner-Riddle & Thurtell 1998; Christensen and Tiedje, 1990). Despite the brevity of spring-thaw emission (usually lasting only a few weeks after the onset of spring thaw), it may account for up to 70% of the total annual N₂O emission from agricultural soils of the temperate regions (Röver et al., 1998). The extent of this brief spring-thaw burst might not have been effectively captured in the present study, as gas emission was not intensively monitored during the period, given the frequencies of sampling, especially for 2005. The current study however reiterated the temporal significance of the spring-thaw period to total annual emission of N₂O from agricultural soil.

The emission of N₂O became high again in both 2005 and 2006 immediately after the application of fertilizer (UAN solution and MAP in 2005, UAN solution in 2006). This increase in N₂O emission, which was associated with increasing soil temperature, nitrate and ammonium, is an indication that the application of fertilizer made ammonium and nitrate available to nitrifiers and denitrifiers that transformed the ammonium and nitrate respectively, producing N₂O in the process. This is expected as management practices such as the application of manure and chemical fertilizers are known to lead to dramatic emission of N₂O from agricultural soils, especially when coupled with soil moisture availability (Yates et al., 2006). Also, the fact that N₂O emission increased almost immediately after the application of ammonium-based fertilizers is an indication that nitrification was an important process that produced N₂O from the cropped areas of the landscape during post-fertilizer application period.

This is in line with the observation by Tenuta and Beauchamp (2003), that nitrification was the major process leading to immediate emission of N_2O from wetted soil cores amended with $(NH_4)_2SO_4$, while denitrification only became important after 10 days of fertilizer amendment. This characteristic burst in N_2O emission following fertilizer application to agricultural soil continues to be an important pathway of loss of fertilizer N, resulting in an economic loss to farmers, apart from the environmental implication of N_2O emission.

The emission of N_2O was either low or there was consumption for other periods monitored during the field experiment. The emission of N_2O for instance during mid-summer to fall of 2005 continued to decrease, just as soil temperature, soil water-filled porosity and soil nitrate content were decreasing rapidly. This is expected as the growing crop would be actively scavenging for both nitrate and moisture in the soil, reducing availability to soil micro-organisms involved in N_2O production. This observed temporal pattern in N_2O emission over the course of a season is similar to that reported by Corre et al. (1996), involving a pulse of N_2O emission at spring thaw, an increasing flux towards early summer, a decline in flux at the end of summer and a background level emission by fall. Also, the fact that high field N_2O emissions were associated with prior rainfall events, especially in 2005, coupled with the burst of N_2O at spring-thaw and post-fertilizer application periods in both 2005 and 2006, further reinforces the episodic nature of N_2O emissions from agricultural soils (Brumme et al., 1999).

Also, the cumulative emission of CH_4 in 2005 was generally higher than for 2006. In contrast to N_2O , there was no burst of CH_4 at spring thaw for both

2005 and 2006. This was expected as CH₄ emission from agricultural soil during spring thaw has not been reported in literature. There was however a late-spring to mid-summer burst in CH₄ in 2005 and about few weeks after spring thaw in 2006. This burst in CH₄ occurred mostly when soil water-filled porosity was decreasing and soil temperature was increasing, especially for the Riparian zone. The emission of CH₄ continued for only a few weeks in both cases, confirming the episodic nature of CH₄ emission. Emission of CH₄ otherwise remained low or it was consumed at other times during the period monitored.

2.5.2 Landscape Position's Control on Nitrous Oxide Emission

The spatial variability in N₂O emission within individual landscape position was more frequent than among the different landscape positions. This was because most frequently, only one replicate subset chamber contributed most of the emission from a landscape position with high gas flux values. Though there was no difference in the cumulative emission of N₂O from the Upper, Middle and Lower slope positions for both 2005 and 2006 (Table 2.2), there was disparity in the occurrence of “hotspots” for N₂O emission in these slope positions. The numerically high cumulative N₂O emission from the Lower slope compared to the Upper and Middle slopes was as a result of the frequent occurrence of N₂O emission hotspots at the Lower slope. This high frequency of hotspots for N₂O emission occurring at a specific part of the landscape was reported by Corre et al. (1996), observing that the “hotspots” for N₂O emission was concentrated at the footslope of a Prairie landscape as opposed to the shoulder position. The

disparity in emission N_2O pattern observed in the current study was despite the soil nitrate and soil temperature of the Lower slope being comparable with those of the Upper and Middle slopes (Figures 2.5c and 2.6e), indicating that other soil factors might be responsible.

The soil water-filled porosity of the Lower slope was consistently higher than those of the Upper and Middle slopes (Figures 2.5b and 2.6d), and the emission of N_2O was associated with the soil water-filled porosity only at the Lower slope but not at the Upper and Middle slope positions (Table 2.4). The total organic carbon content of the Lower slope was higher than those for the Upper and Middle slopes (Table 2.1), while the dark-chamber CO_2 emission from the Lower slope was generally higher than from the Upper and Middle slopes (Figures 2.5e and 2.6g). Likewise, the hotspot of N_2O emission at the Lower slope was associated with a replicate subset chamber in section 2 of transect, with 1.2 times the average total organic carbon content for the Lower slope, giving 56% and 65% of total cumulative N_2O from the slope during spring thaw and post-fertilizer application periods of 2006 respectively. These unique features of the Lower slope provide a strong evidence that soil moisture and carbon availability were the soil factors causing the observed disparity with respect to the concentration of hotspots of N_2O emission in the Lower slope as opposed to the Upper and Middle slope positions. While N availability was similar for the Upper, Middle and Lower slope positions (resulting from fertilizer application), soil moisture and carbon availability became limiting factors for the Upper and Middle slopes. This is in agreement with Corre et al. (1996) noting that fertilizer N

application resulted in high N₂O emission only for sites with high soil moisture to match the available N.

There was an increasingly strong association of N₂O emission with soil nitrate content, as well as increasing total organic carbon, in going from the Upper to the Lower slope position (Tables 2.1 and 2.4). Also, N₂O emission was only associated with soil water-filled porosity at the Lower slope, and not at the Upper and Middle slopes (Table 2.4 and Figure 2.7b). These observations, with the numerically highest cumulative N₂O emission being almost consistently from the Lower slope, is an evidence of the intensification of the denitrifying potential in moving from the Upper, through the Middle, to the Lower slope position. This is supported by the observation of Pennock et al. (1992), that the landscape-scale pattern in denitrification results from the difference in the intensities of individual soil processes in each landscape element, the processes being controlled by hydrologic and pedologic processes, as dictated by the landscape.

2.5.3 Landscape Position's Control on Methane Emission

There was distinction in CH₄ emission from the Lower slope compared to emission from the Upper and Middle slope positions. Even though there was no significant difference in cumulative CH₄ emission from the Lower slope compared to the Upper and Middle slopes during the entire duration of the field monitoring, cumulative emission from the Lower slope was numerically high, while low CH₄ emission or consumption was common for the Upper and Middle slope positions (Table 2.2). The Lower slope had soil water-filled porosity and total carbon

content that was higher than those of the Upper and Middle slope positions, suggesting that moisture and carbon availability might be responsible for this difference in CH₄ emission. The high total organic carbon for the Lower slope might be as a result of high soil organic matter, plant root exudates, dead roots and plant residue. The areas within the landscape that are well drained are known to be sinks for CH₄ while emission is usually high in organic C-rich, poorly-drained portions of the landscape (Reiners et al., 1998).

The Lower slope was wetter than the Upper and Middle slope position as a result of moisture redistribution within the landscape, making the water-table at the Lower slope position closer to the surface. Soil redox potential (controlled by soil moisture regime) and depth-to-water-table are known to influence methane emission or consumption (Smith et al., 2003). The drier parts of the landscape (Upper and Middle slopes) provide good aeration that is conducive for the oxidation of methane by methanotrophs (Topp and Pattey, 1997). The Lower slope, being moist and close to the ground water table, provided optimum conditions for the activity of methanogens that are responsible for the production of methane (Le Mer and Rogers, 2001). Therefore, the high soil WFP and possibly higher root consumption of oxygen at the Lower slope likely made the redox potential at this position favorable to methanogens. The repression of methane production resulting from good aeration is evident from the declined methane emission in late summer to fall of 2005 for Lower slope, following decline in its soil WFP.

2.5.4 Nitrous Oxide and Methane Release from Riparian Soil

The Riparian zone behaved differently from the other slope positions in terms of N₂O and CH₄ emission, despite its water-filled porosity (WFP) being comparable to that of Lower slope. The conditions affecting N₂O and CH₄ emission were drastically altered in this zone likely because of the presence of perennial grasses such as *Typha glauca*, *Sochus arvensis*, *Hordeum jubatum*, *Solidago canadensis*, *Carex atherodes*, *Aster simplex* and *Agropyron spp.*

The lowest cumulative N₂O emission was consistently from the Riparian zone for the entire duration of the field study (Table 2.2). This zone had a high dark-chamber CO₂ emission and high total carbon content (indicating high C availability), with high soil electrical conductivity (EC) but low soil nitrate. The low nitrate in this zone may be due to the fact that the zone was not cropped and there was no fertilizer applied to it. Also the perennial grasses growing in the zone might be actively scavenging for the limited nitrate available in the zone. The high soil NH₄⁺ content of this zone, especially for 2005, did not translate to either an increased soil nitrate content or high N₂O emission, indicating a highly anaerobic condition that repressed nitrification. A similar scenario was reported by Corre et al. (1996), with the prolonged saturation of the footslope complex of a clay loam pasture inhibiting nitrification, leading to low emissions of N₂O. The zone's high C availability, high soil WFP (hence reduced oxygen availability), high EC (high salinity) likely resulted in its microbial community being different from those of the Upper, Middle and Lower slope positions. The difference in N₂O emission between the cropped and uncropped portions of the landscape

was reported in the study by Yates et al. (2006) indicating high soil N₂O fluxes were characteristic of the footslopes and depressions of cultivated areas of a Prairie landscape, while the vegetated depressions (Riparian) gave low or negative fluxes.

The high and persistent snow cover at the Riparian zone insulated the soil in the zone and prevented the zone from freezing over the winter, as the lowest soil temperature recorded at 5cm depth for the zone over the winter of 2005/2006 was -2°C. This, apart from the low soil nitrate content of the zone, must have been responsible for the zone not giving a burst of N₂O at spring thaw. On one occasion in late summer (day 220) of 2005, there was a burst of N₂O from the Riparian zone (Figure 2.4a), coinciding with a peak in soil nitrate for the zone. This event occurred when the soil WFP of the Riparian zone was lowest, and the soil temperature was at a peak (Figure 2.5). This event might be due to degassing of aqueous N₂O as the zone which had before then been saturated, became drier (Grant and Pattey, 2003). A field study looking at the effect of lowering the water table on the degassing of dissolved N₂O showed that much more N₂O degassed at a water table of 15cm above the soil compared to a water table of 45cm above the soil (Kliewer and Gilliam, 1995). This was attributed to microbial conversion of N₂O into N₂ during the course of transportation in case of the higher water table. Also, the solubility of N₂O in water is known to decrease with increase in temperature (Weiss and Price, 1980). Therefore, the peak soil temperature on day 220 must have also contributed to the release of N₂O from the Riparian zone.

Also, lowering of the soil WFP of the Riparian zone on day 220 might have led to improved aeration of the zone enhancing nitrification releasing N_2O and possibly making nitrate available to denitrifiers. This is strongly supported by the fact that the peak soil NH_4^+ content on this day was rapidly depleted by day 267 (Figure 2.5d). This sudden improved aeration might have caused a brief shift in the microbial community structure of the zone, in response to changes in the physico-chemical environment of the zone (reduced moisture, higher oxygen availability, and increased nitrate). This strongly suggests that moisture might be the most important modifier of the microbial environment and activities in the Riparian zone, explaining why it behaved differently from the other slope positions. Groffman et al. (1998) argued that the high potential for the Riparian zone to be a hotspot for N_2O production might not be realized, despite its high organic carbon availability, because of its highly anaerobic condition causing the reduction of N_2O to N_2 . This episodic burst in N_2O emission from the Riparian zone with lowered soil moisture and increased soil temperature is however an indication of the potential of the zone for N_2O emission in the event of changing weather conditions (such as unusually dry and warm year).

The Riparian zone was a “hotspot” for CH_4 emission throughout the period monitored (Table 2.2). In contrast to the Upper and Middle slope positions, the Riparian zone was a source of CH_4 emission. The high soil water-filled porosity and high carbon availability at the Riparian zone was conducive to the activities of methanogens. The brief burst in CH_4 emission at the Riparian zone might be due to the release of CH_4 trapped in the saturated soil in the zone as soil

temperature continued to increase weeks after spring thaw. This high emission of CH₄ from the Riparian zone was observed using both the subset chambers as well as the 128 chambers (Table 2.3). There was however a high spatial variability associated with cumulative CH₄ emission from the zone as indicated by CV of 189% and 175% when the replicate subset chambers and 128 chambers were considered, respectively (Table 2.3). This was because one replicate subset chamber located at the Riparian zone of section 3 gave 98% and 66% of the total cumulative CH₄ emission from the Riparian zone in 2005 and 2006, respectively. The fall 2005 soil sulphate content of this particular chamber was 117 times less than the average fall soil sulphate content of all replicate subset chambers located at the Riparian zone. Therefore, high soil sulphate was inhibitory to methane emission in this zone, as sulphate is known to inhibit the activities of methanogens (Jean and Pierre, 2001; Mishra et al., 2003). This inhibitory effect is due to competition between sulphate-reducing bacteria and methanogens for electron donors (such as organic carbon) in sulphate-rich anaerobic environments (Lovely and Klug, 1983). The significant effect of landscape position on methane emission in 2006 attests to the localization of methane emission within the landscape (driven by high moisture and C availability).

2.6 Conclusion

The temporal variation of N₂O and CH₄ was very high. Magnitude of daily emission of N₂O was higher in 2005 compared to 2006, the former being a wetter year. The emission of gases was episodic, with bursts in emission being event-based. The emission of N₂O was high at spring-thaw and post-fertilizer application periods, while high emission of CH₄ was associated with rapid changes in soil moisture and temperature regimes post-thaw. There was no burst in CH₄ emission at spring thaw, not even from the Riparian zone.

There was a distinct pattern of field emission of N₂O and CH₄ over the period of this study, with the hotspots for N₂O emission concentrated at the Lower slope, while the hotspots for CH₄ emission were concentrated at the Riparian zone. These hotspots for N₂O and CH₄ emission were characterized by high moisture and C availability. The uncropped Riparian zone behaved differently from the cropped Upper, Middle and Lower slope positions, with its consistently low or no N₂O emission, despite its C availability and water-filled porosity being comparable to the Lower slope. This pattern in N₂O and CH₄ emission over the landscape was observed using either the subset or 128 chambers.

There are strong indications to suggest that the microbial community structure of the Riparian zone was different from that at the Upland slope positions, considering its organic-C rich, nitrate-depleted, highly anaerobic, perennial grasses-dominated and saline conditions. The high soil water-filled

porosity and C availability of the Riparian zone explained the episodic CH₄ emission from the zone, while the well-drained organic-C depleted Upper and Middle slopes consumed or gave no CH₄. High soil sulphate content at the Riparian zone was inhibitory to CH₄ emission. The emission of N₂O and CH₄ was therefore highly associated with soil factors that promote the activities of nitrifiers and denitrifiers, and methanogens, respectively.

Therefore, the landscape-scale variation in CH₄ and N₂O emission should be factored in when formulating models for estimating greenhouse gas emission, either at a regional or national level. Higher N₂O emission index should be given to cropped areas within the landscape with poor drainage, while higher CH₄ emission index should be assigned to perennially-vegetated areas with poor drainage. The practice of applying N fertilizer in fall should be reviewed, as it predisposes such applied N to losses at spring thaw. Also, appropriate drainage measures should be considered by farmers for the depressional areas of the landscape, in order to optimize applied N for crop use and also reduce the emission of N₂O from this critical area of the landscape. The high water-table at the Lower and Riparian slope positions could be drawn down by the introduction of willows and shrubs. The use of “trap crops” like winter wheat to control spring-thaw nitrate availability should be given serious consideration by farmers. The adoption of “variable-rate” fertilizer N application to positions in the landscape with moisture regimes favorable to N₂O emission, with the goal of matching N availability with crop demand / use would be beneficial to farmers, and friendly to the environment. These management practices, if adopted will not

only improve the value farmers get from the cost incurred on N fertilizers, but also help slow down the current trend of increasing human contribution to greenhouse gas emission and the attendant consequence of climate change.

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CHAPTER 3

**FREEZE-THAW EMISSION OF NITROUS OXIDE FROM SOIL AS AFFECTED
BY LANDSCAPE POSITION**

3.1 Abstract

The spring-thaw period has been recognized as an important small window for the emission of N₂O from temperate agricultural soils. In previous studies by our laboratory, it was shown that increasing the nitrate content and reducing the bulk density of repacked soil increased the freeze-thaw emission of N₂O from soil. In this study, we determined if antecedent soil moisture and landscape position affect the emission of N₂O from soil at spring thaw. The soil factors enhancing the potential of each landscape position for N₂O emission at thaw were also examined.

Soil was taken from the Middle slope position of an undulating landscape in fall of 2005 and treated to determine the effect of antecedent moisture on freeze-thaw emission of N₂O. Drying soil before assaying eliminated the freeze-thaw emission of N₂O. The lack of freeze-thaw N₂O emission from dried soil was associated with drying lowering the denitrifying enzyme activity of soil.

To determine the potential freeze-thaw N₂O emission from different landscape positions, soil samples collected from Upper, Middle, Lower and Riparian slopes were also treated and monitored for freeze-thaw emission of N₂O. The previously frozen soil cores for all landscape positions gave higher N₂O emission compared to previously unfrozen cores. The Riparian zone gave the

highest and earliest N₂O emission, followed by the Lower, Middle and Upper slope positions. This landscape pattern of freeze-thaw emission of N₂O remained the same, even with the addition of 50 mg kg⁻¹ nitrate to all cores. The magnitude of freeze-thaw emission of N₂O however remained unchanged with the nitrate addition for the Upper, Middle and Lower slopes, but magnified three-fold for the Riparian zone.

The pre-assay nitrate contents of all landscape positions were not different, but the antecedent moisture content, denitrifying enzyme activity and total organic carbon content showed a similar trend of increasing from the Upper to the Riparian slope position, as the freeze-thaw N₂O emission. The high freeze-thaw emission of N₂O from the Riparian zone was associated with its high antecedent moisture content, denitrifying enzyme activity and total organic carbon. This high potential of the Riparian zone for freeze-thaw emission of N₂O was however not observed on the field during spring thaw. This was due to snow cover and perennial vegetation insulating the Riparian soil from freezing in winter, as well as saturated conditions of the zone at spring thaw causing it to be highly anaerobic, leading to reduction of N₂O to N₂.

Therefore, positions within the landscape with higher moisture and available C should be assigned a higher spring-thaw N₂O emission quotient if they freeze over winter. Also, the high potential of the Riparian zone for freeze-thaw emission of N₂O should be considered when conducting annual inventory of N₂O emission at the landscape scale in the PPH region, especially where snow cover and moisture levels are low, promoting freezing of these soils.

3.2 Introduction

About 60% of the CO₂ equivalent of all greenhouse gases emitted from agroecosystems is attributable to nitrous oxide (Desjardins and Keng, 1999). In Canada, N₂O is the dominant greenhouse gas emitted from agricultural soils, causing 10% of radiative forcing of gases and accounting for up to 66% of all anthropogenic sources (CGGI, 2002). N₂O is a greenhouse gas which absorbs infra-red radiation (Wang et al., 1976) and causes the destruction of ozone in the stratosphere (Crutzen, 1981). Nitrous oxide is about three hundred times more effective than CO₂ in its heat-trapping and re-radiating capacity (IPCC, 1994), thus having much higher global warming potential than CO₂. The residency time of nitrous oxide in the atmosphere is about 70 years (Beauchamp, 1997), making the current annual atmospheric loading rate of between 0.2 and 0.3% (IPCC, 2001) a disturbing trend. There is therefore the urgent need for mitigation measures that will reduce the current trend in emission of N₂O from agroecosystems.

The spring-thaw period has been identified as an important period of the year for N₂O emission as up to between 40 and 70% of the annual emissions from agricultural soils in Canada can occur within the brief 1 - 3 weeks of soil thawing in spring (Lemke et al. 1998; Wagner-Riddle & Thurtell, 1998), with the peaks of this emission at thaw usually lasting for only a few days (Christensen and Tiedje, 1990).

Several mechanisms like biological denitrification, chemodenitrification and physical release of N₂O in unfrozen subsoil have been suggested as being

responsible for this spring-thaw burst in N_2O from soil. However, chemodenitrification, as described by Christianson and Cho (1983), may not be a significant source of N_2O emission from thawing soil, due to low concentration and instability of soil NO_2^- (Alexander, 1977; Van Cleemput and Samater, 1996). Also, studies by Duxbury et al. (1982) and Teepe et al. (2001) showed that physical release of accumulated N_2O in unfrozen subsoil as suggested by Bremner et al. (1980) and Burton and Beauchamp (1994) may not explain the burst of N_2O at thaw, as frozen subsoil also replicated this burst when warmed in the laboratory. The emission of N_2O at thaw has been identified as a biologically-mediated process (Röver et al., 1998; Teepe et al., 2001; Müller et al., 2003), with biological denitrification being the major mechanism of production (Priemé and Christensen, 2001; Christensen and Tiedje, 1990).

There is some evidence that freezing increases the supply of soil nutrient available for denitrifying organisms. Substrates from the release of intracellular materials from dead micro-organisms, exposure of exchange sites from physical disruption of aggregates and residual fall-applied N are made available to denitrifying organisms (Christensen and Christensen, 1991; Edwards and Cresser, 1992; Christensen and Tiedje, 1990) at spring thaw to produce N_2O . There had been several studies looking at different soil factors and physical conditions that affect the emission of N_2O from thawing soil. Teepe et al. (2004) reported an increase in freeze-thaw N_2O emission resulting from increasing the water-filled porosity (WFP) of soil cores before freezing, as well as subjecting the cores to longer duration of freezing. A combination of high soil moisture,

available N and C concentration was found to stimulate high emission of N₂O at thaw (Müller et al., 2003). Freeze-thaw emission of N₂O was reported to decrease with repeated freeze-thaw cycles of soil cores in the laboratory (Priemé and Christensen, 2001). Previous experiments by our laboratory also showed that the addition of nitrate and use of surface soil, rather than soil at depths, increased emission from thawing soil cores, while compaction reduced the freeze-thaw effect; biological denitrification was observed as the source of N₂O emission (Tenuta et al., 2005).

The spring thaw period is usually characterized by excess moisture from melting ice, snow and frozen soil, as well as poor drainage due to frost layer impeding water percolation (Ferguson et al., 1964). Also in some years, the fall soil moisture is high due to high fall precipitation and / or snow fall. This combination of excess moisture and poor drainage at spring-thaw promotes the poor aeration status of the soil, a condition that is favorable for biological denitrification.

The temporal significance of the spring-thaw period, its brevity notwithstanding, makes it critical for the inventory of the contribution of agricultural soils to annual N₂O emissions. Topography is known to influence the emission of N₂O from agricultural landscapes through its control on the fundamental hydrologic and pedologic processes within the landscape (Pennock et al., 1992). The complexity of the landscapes in the Prairie Pot-hole Region (PPH) may therefore influence the pattern of soil factors driving the spring-thaw emission of N₂O within the landscape, and have serious implications for emission

at this critical period of the year. Izaurre et al. (2004) for instance found the highest nitrate and water-soluble organic C at the depression area of a Prairie toposequence at spring thaw. Previous monitoring of field emission of N₂O at spring thaw (Chapter 2) showed that the Riparian zone was not important for N₂O emission, while the Lower slope had a high concentration of hotspots for N₂O emission. The occurrence of hotspot for N₂O at the Lower slope was associated with its high soil moisture and total organic carbon contents. This pattern of N₂O emission with landscape position observed on the field might not represent the real potential of different landscape elements for freeze-thaw emission of N₂O, given the uncontrolled conditions on the field. Also, a higher magnitude in daily emissions of N₂O at spring thaw was observed in the year 2005 compared to 2006, the former being wetter. This observation underscored the importance of preceding fall soil moisture to spring-thaw emission of N₂O.

An understanding of the landscape-scale distribution of soil factors important for spring-thaw N₂O emission will provide the information about the potential of each landscape position for N₂O emission at spring thaw. This information will be useful in assessing the capacity of different landscape elements for spring-thaw emission of N₂O, in the event of a drastic change in climatic pattern (such as colder winter, drier or wetter fall etc). So far, there is a gap in our knowledge of the potential of each landscape position for N₂O emission at spring thaw. This laboratory study was carried out to: (a) determine how lowering the antecedent soil moisture before freezing will affect freeze-thaw emission of N₂O, (b) determine if landscape position affects the potential for

freeze-thaw emission of N₂O from agricultural soil and (c) determine what soil factor(s) are important for this freeze-thaw effect, and how the factor(s) vary within the landscape.

3.3 Materials and Methods

3.3.1 Soil Sampling, Handling and Processing

Surface soil samples (0-10 cm) were obtained from the Upper, Middle, Lower and Riparian slope positions in the fall of 2005 from the field site (MZTRA) as four independent replicate sample locations. The sampling locations were the same as the subset chambers for the field monitoring of greenhouse gas emission in 2005 (Section 2.3.3). The soil samples were transported to the laboratory in labeled polyethylene bags placed inside a cooler with icepacks. The soil samples were then passed through a 5mm mesh screen and kept at 5°C for 1, 7 and 16 weeks before assaying for Experiments I, II and III, respectively.

3.3.2 Freeze-thaw Assay

The freeze-thaw assay was carried out in order to mimic what happens in the field when winter-frozen soil starts to melt at the onset of spring. The laboratory assay was done under controlled conditions, and thus is considered to be an indication of emission from different landscape positions rather than absolute emission rates as obtainable under field conditions. However, it affords the opportunity to understand the important factors and conditions for the

freeze-thaw emission of N₂O (Tenuta and Sparling, 2004). Processed soil samples were packed to a bulk density of 1.1gcm⁻³ inside a PVC core having 6cm and 5cm internal diameter and height respectively, with a porous sheet attached to the base by means of rubber band to hold the soil inside the PVC core. This was followed by the addition of distilled water to achieve a water-filled porosity of 80% (v v⁻¹), previously determined to be the maximum WFP the soil cores could be brought to without the drainage of water from them. The packed cores were placed inside a polyethylene bag, and half kept at -20°C (Previously Frozen) while the other half were kept at 5°C (Previously Unfrozen) for 2.5 days. Four independent replicate cores per landscape position*treatment combination were prepared from soil samples taken from the field site. The cores were then removed after 2.5 days, placed inside 1.5 L wide-mouth sealer jars. Headspace gas was replaced by ambient air by flushing the jars 15 times by insertion of a 345mL drink can. The jars were then closed with lids fitted with serrated rubber septum (Sigma-Aldrich, Hamilton, ON) for easy access of a PrecisionGlide[®] needle fitted on a 10mL Becton-Dickenson syringe (Fisher Scientific, Nepean, ON) for gas sampling. A blank jar was set up as previously described, but with no soil packed into the PVC core. The closed jars were incubated at 15°C for 2 hours before the first gas sampling. The incubation temperature of 15°C was chosen to mimic the maximum air temperature likely at spring. Gas sampling was done by removing 10mL of the headspace gas from each jar, and injecting the samples into 6mL Labco Exetainer[®] gas vials (Labco Limited, Buckinghamshire, UK). The gas vials had been evacuated and flushed thrice with Helium gas to a

pressure of 500 millitorrs, with the top of the vials sealed with Mastercraft silicone and left to dry prior to gas sampling. The lids of the jars were then removed, the jars covered with parafilm having six holes punctured with a pencil, and the jars returned into the incubator until the next sampling. The parafilm was punctured to prevent build-up of N_2O over the headspace between samplings, which might confound normal emission from the soil cores when jars were closed, and also preventing rapid loss of moisture from soil cores during incubation. The headspace gas of the jars was sampled as previously described at regular intervals for a period of about 4 days. The optimum intervals for gas sampling had previously been determined by running trial experiments before the assay was carried out. The results of the trial experiments showed that peak emission of N_2O occurred within the first 24 hours of placement at $15^\circ C$, necessitating the need for a very intensive sampling scheme (every 6 hours) for the first 30 hours of incubation, and a more relaxed sampling schedule (between 6 – 12 hours interval) thereafter. The gas samples were analyzed using a gas chromatograph (Varian 3800, Mississauga, ON) fitted with ECD, FID and TCD detectors operated at 300 , 250 and $130^\circ C$, respectively. The gas chromatograph was equipped with a Combi-PAL autosampler (CTC Analytics, Switzerland) that injected 2.5 mL volume of sample to the GC to deliver the sample into the three detectors. The volume of each sample loop for the gas chromatograph was 500 microlitres. The flux of N_2O and CO_2 was calculated from the gas sample concentration, oven-dried mass of soil, net volume of jar, volume of water added to soil core, headspace gas concentration of blank jar, molecular mass of gas,

room temperature, incubation time and universal gas constant using the Ideal Gas Law ($PV=nRT$). Dissolved N_2O in the water phase was determined and corrected for according to Moraghan and Buresh (1977). Cumulative N_2O and CO_2 emission from each replicate soil core was calculated by linear interpolation for hours that were not sampled, and adding up the running flux over the entire incubation period. Freeze-thaw N_2O and CO_2 was the difference between the cumulative N_2O and CO_2 emission for corresponding frozen and unfrozen replicate soil cores. Each freeze-thaw experiment was repeated within two weeks of the first trial in order to validate the results.

3.3.3 Extraction and Analysis of Soil Samples

The nitrate, ammonium and extractable dissolved organic carbon (ext. DOC) contents of each soil sample before packing were determined by extracting with 0.5M K_2SO_4 solution. Air-dried and pulverized soil sample (5g) soil was placed inside a 50mL centrifuge tube followed by the addition of 25mL 0.5M K_2SO_4 solution. The mixture was then placed on a reciprocating shaker at 110 rpm for 30 minutes, followed by centrifuging at 3000 rpm ($1,560 \times g$) for 1.5minutes. Using an autopipetter, 10mL of the clear supernatant was transferred into a labeled scintillation vial, while rinsing the tip of the autopipetter with distilled water between transfers. Gravimetric moisture contents of the samples were also determined at the time of extraction. The extracts were kept at $-20^\circ C$ if not analyzed within a week after extraction. The nitrate, ammonium and ext. DOC contents of the extracts were determined by the automated Cadmium reduction

(Method No. 4500-NO₃(F)), Phenate (Method No. 4500-NH₃(G)) and Persulfate-ultraviolet oxidation (Method No. 5310(C)) methods respectively, using Technicon™ Autoanalyzer II system (Pulse Instrumentation Ltd, Saskatoon, SK).

Total organic carbon content (TOC) of soil samples was determined once by using a Truspec Carbon / Nitrogen Determinator (LECO Instruments Limited, Mississauga, ON). Pulverized air-dried 0.25 g of soil samples were placed inside small tin capsules that were then loaded into the instrument for total organic carbon and total nitrogen analysis. The instrument had combustion and secondary furnaces, maintained at 950°C and 850°C, used for combustion and oxidation of samples, respectively. The oxidized samples were then passed through a CO₂ infrared detector to analyze for total organic C content of the soil samples.

3.3.4 Denitrifying Enzyme Activity (DEA) Assay

An assessment of the amount of denitrifying enzymes contained in soil samples from all four landscape positions was done by carrying out a denitrifying enzyme activity (DEA) assay. Soil sample (25g) was weighed into 250 mL Boston amber glass bottles (Fisher Scientific, Whitby, ON), followed by the addition of 25 mL of monobasic potassium phosphate (50 mM)-buffered solution of glucose (10 mM) and potassium nitrate (10 mM), with the pH adjusted to 7 (Murray and Knowles, 2004). The bottles were closed with size 16.5 serrated rubber septa (Sigma-Aldrich, Hamilton, ON) and the headspace made anaerobic

by flushing for 15 minutes with Helium gas. A portion of the headspace (10%) of each bottle was thereafter replaced by pure acetylene gas. The acetylene was passed through a concentrated sulfuric acid wash to remove impurity (acetone) before use. A sample of the headspace gas (10 mL) was taken after flushing bottles with acetylene (time 0) using PrecisionGlide[®] needle fitted on a 10mL Becton-Dickenson syringe (Fisher Scientific, Nepean, ON). This gas sample was injected into 6 mL Labco Exetainer[®] gas vials (Labco Limited, Buckinghamshire, UK) pre-evacuated to 500 millitorrs and sealed dry with silicone as previously described. The bottles were thereafter placed inside a C24KC incubator shaker (New Brunswick Scientific, Edison, NJ) set at 24°C and 200 rpm. The headspace gas was again sampled after 1 hour into pre-evacuated 6 mL Labco Exetainer[®] vials for analysis of N₂O concentration by gas chromatography. Previous laboratory examinations had shown that N₂O accumulation in the headspace is linear over a 1 hour period (Tenuta, Personal Communication). The DEA was calculated as the amount of N₂O evolved over 1 hour, with the amount of N₂O dissolved in water taken into account (Moraghan and Buresh, 1977).

3.3.5 Experiment I: Effect of Drying on Freeze-thaw N₂O Emission from Soil

Our usual freeze-thaw assay involves using soil samples slightly dried just enough to allow freshly collected field soil to pass a 5mm mesh screen (Tenuta and Sparling, 2004). I conducted several preliminary freeze-thaw assays using soil from Upper, Middle, Lower and Riparian slope positions, but had thoroughly

air-dried the soil samples before assaying. With the air-dried soils, there was no evident freeze-thaw effect, with or without the addition of nitrate. Thus, this experiment was conducted to confirm if pre-drying soil eliminates freeze-thaw emission of N₂O. Three independent replicate soil samples were taken from the Middle slope positions of sections 1, 2 and 3 of the 128-chamber transect used for the field monitoring of greenhouse gases in years 2005 and 2006 (Chapter 2). The soil samples were either rapidly air-dried within 12 hours to between 3 and 5% gravimetric moisture content (Dried Pre-treatment), or left as sampled from the field, being between 16 and 20% gravimetric moisture content (Moist Pre-treatment). The air-drying for the dried pre-treatment was done by spreading the soil in trays and placing inside a drying room at a temperature of 24°C for about 10 hours, manually mixing the soil by hand every 15 minutes. A freeze-thaw assay was then carried out on the samples as previously described, with 50 mg N kg⁻¹ nitrate added to all the cores as KNO₃ dissolved in distilled water. The water added was to bring the WFP of all soil cores to 80% v v⁻¹. The denitrifying enzyme activity and extractable dissolved organic carbon of the samples were also quantified as previously described, just prior to the onset of the freeze-thaw assay. This experiment was repeated within 2 weeks of the first trial.

3.3.6 Experiment II: Freeze-thaw Emission of N₂O As Affected by Landscape Position

A freeze-thaw assay was carried out on soil samples from Upper, Middle, Lower and Riparian slope positions. The assays were prepared for each

landscape position using four independent replicate soil samples, each sample taken from sections 1, 2, 3 and 4 of the 128-chamber transect (Chapter 2). The pre-assay soil nitrate content, DEA and extractable dissolved organic carbon of the soil samples was quantified as previously described. The experiment was repeated within 2 weeks of the first trial.

3.3.7 Experiment III: Freeze-thaw Emission of N₂O as Affected by Landscape Position with Non-limiting Nitrate Levels

Nitrate is known to be typically the most important factor affecting N₂O emission from thawing soil. A freeze-thaw assay of the soil samples from the Upper, Middle, Lower and Riparian slope positions was conducted with nitrate supplementation to eliminate nitrate limitation on N₂O emission upon thaw. The addition of 50 mg N kg⁻¹ nitrate to each soil core was done after packing the soil cores, before placing the cores at either -20°C or 5°C. The nitrate was added by dissolving required amount of KNO₃ in the distilled water added to the cores. This was done to remove any potential nitrate limitation of the assayed soil samples, as nitrate may vary with landscape position depending on soil moisture and crop yield. This assay with nitrate supplementation was conducted to clearly understand the potential of each landscape position for freeze-thaw emission of N₂O. This assay was also repeated within 2 weeks of the first trial.

3.3.8 Data Analysis

Statistical analyses of all data was done using SAS statistical package version 9.1 (SAS Institute Inc., Cary, NC, USA). The significance of difference between N₂O emissions of frozen and unfrozen treatments of soil cores for all three experiments was tested using a paired t-test at a $P < 0.05$ level of significance. A generalized linear model (GLM) ANOVA was carried out on the cumulative freeze-thaw N₂O emission from treated cores, pre-assay nitrate and ammonium contents, antecedent moisture content, total nitrogen, total organic carbon, extractable dissolved organic carbon and DEA data. The ANOVA was carried out in order to determine treatment (moisture pre-treatment or landscape position) and block (section of transect) effects. In cases where the treatment effect was significant at $P < 0.05$ level of significance, a Scheffe's grouping of treatment means was carried out. The freeze-thaw N₂O data was tested for normality and homogeneity of error variances using Shapiro-Wilk's and Levene tests, respectively. In cases where the freeze-thaw N₂O data was not normally distributed, a $\log(X + 2)$ transformation was carried out on the raw data before conducting ANOVA. A Spearman rank correlation coefficient was calculated to determine the association of cumulative freeze-thaw N₂O emission to measured soil parameters; DEA, antecedent moisture content, nitrate, ammonium, cumulative freeze-thaw CO₂ emission, total organic carbon, extractable dissolved organic carbon and total nitrogen.

3.4 Results

3.4.1 Effect of Drying Pre-treatment on Freeze-thaw Emission of N₂O from Soil

Drying soil prior to packing and establishment of 80% water-filled porosity (WFP) in cores eliminated a thaw effect of increased N₂O emission for the frozen soil in both trials (Figure 3.1a). There was no N₂O emission from the previously frozen or unfrozen soil cores with the dried pre-treatment. N₂O emission was observed upon the incubation of both the previously frozen and unfrozen soil cores in the case of the undried pretreatment (Figure 3.1b). The emission of N₂O from previously frozen cores for the undried pre-treatment was however significantly higher ($P < 0.05$) than emission from the previously unfrozen cores. The peak emission for the undried pre-treatment cores occurred after 35 and 15 hours of placement at 15°C for the previously frozen and unfrozen cores, respectively (Figure 3.1b). The repeat experiment (Trial II) also showed similar pattern for both dried and undried pre-treatments, except that the previously frozen cores gave slightly less N₂O than the previously unfrozen cores after about 35 hours of incubation (Figure 3.1b). Also, the peak N₂O emission for the repeat experiment occurred after 15 hours of placement at 15°C for both the previously frozen and unfrozen cores, but generally, the pattern and magnitude of emission were similar between both trials.

The combined cumulative freeze-thaw N₂O emission from the undried pre-treatment soil for both trials was higher compared to the dried pre-treatment

soil (Table 3.1). The high cumulative freeze-thaw N₂O emission for the undried pre-treatment soil was variable, with 48% of total cumulative freeze-thaw N₂O emission contributed by the packed core of section 2 of transect. This replicate core had the highest pre-assay soil nitrate content of 10.51mg N kg⁻¹, which is 1.4 times the average soil nitrate content of 7.41mg N kg⁻¹ for all undried pre-treatment replicate soil samples (Table 3.1). The absence of cumulative freeze-thaw N₂O emission observed for the dried pre-treatment was despite the addition of 50 mg N kg⁻¹ nitrate to all the packed cores, and the water-filled porosity of all cores being brought to 80% when assay was prepared.

The pre-assay denitrifying enzyme activity, antecedent moisture content and nitrate content of the undried pre-treatment soil were consistently higher than that of the dried pre-treatment soil (Table 3.1). The pre-assay ammonium and extractable dissolved organic carbon contents of the dried pre-treatment soil were however higher than for the undried pretreatment soil. The DEA and antecedent moisture content of the soil samples were strongly and significantly correlated, with Spearman rank correlation co-efficient of 0.65 at $P < 0.05$ level of significance.

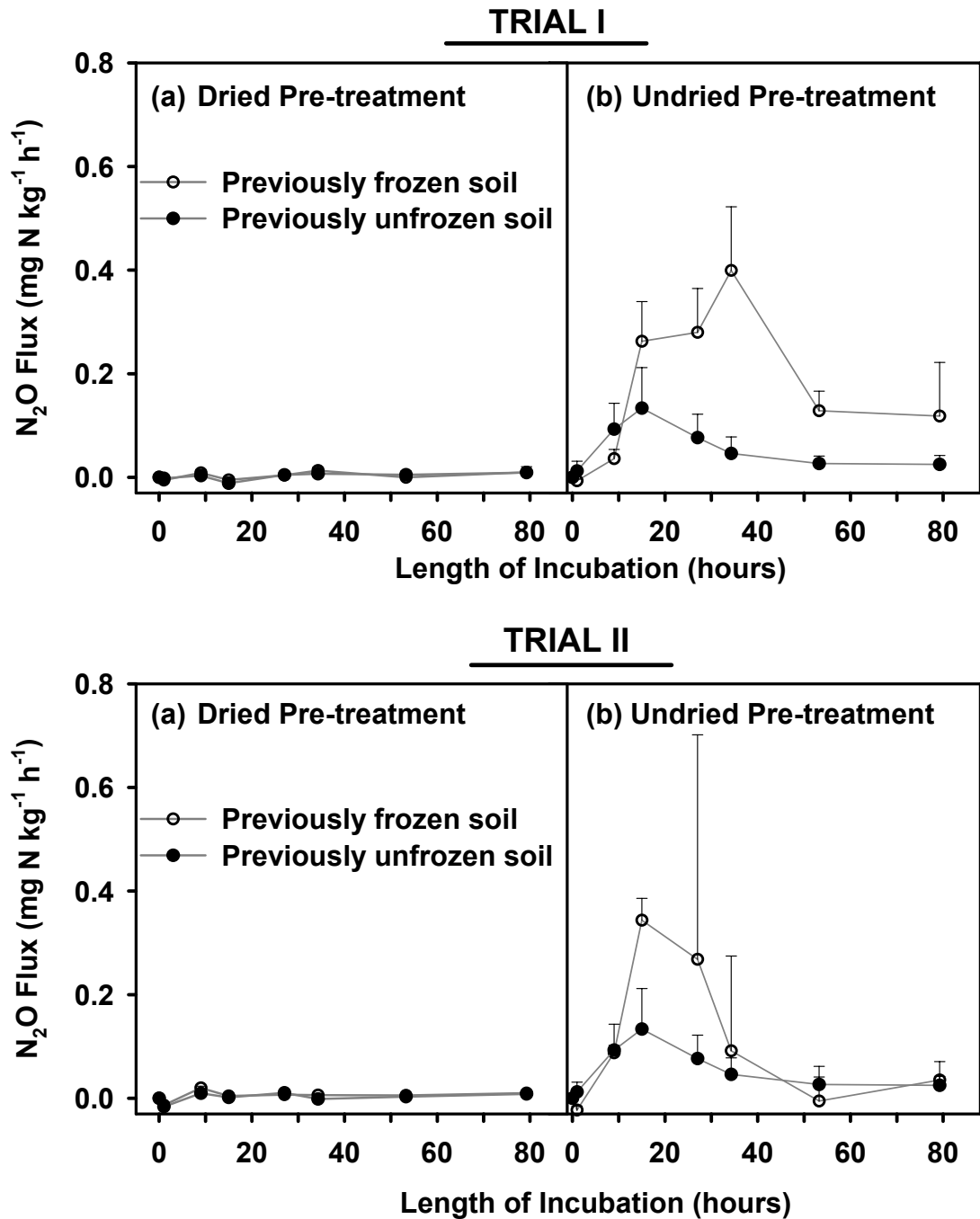


Figure 3.1 Emission of N₂O from previously frozen (-20°C) and unfrozen (5°C) packed soil cores with addition of 50 mg N kg⁻¹ as KNO₃ in Experiment I. Samples were (a) treated after being air-dried rapidly – Dried Pre-treatment, (b) treated as taken from field – Undried Pre-treatment. All soil cores were incubated at 15°C for 80 hours. Trial II was a repeat experiment, and was conducted within 2 weeks of Trial I. Values shown are the mean plus 1 standard error of the mean of 3 independent replicate cores consisting of soil samples taken from the Middle slopes of an undulating field.

Table 3.1 Cumulative freeze-thaw N₂O and associated pre-assay soil parameters of previously undried and previously dried soil samples for Experiment I

Pre-treatment	Freeze-thaw (mg N kg ⁻¹)	DEA (mg N ₂ O kg ⁻¹ min ⁻¹)	Moisture content (g g ⁻¹)	Nitrate (mg N kg ⁻¹)	Ammonium (mg N kg ⁻¹)	Ext. DOC (mg C kg ⁻¹)
Undried	14.78 (3.71) a	1.36(0.05) a	0.19 (0.01) a	37.0 (8.0) a	3.75 (0.05) b	82.9 (9.7)
Dried	0.03 (0.09) b	1.09 (0.03) b	0.04 (0.01) b	21.5 (7.0) b	11.6 (0.50) a	105.8 (17.6)

N.B: Values are the mean of 6 independent replicates for freeze-thaw N₂O, and 3 for denitrifying enzyme activity (DEA), gravimetric moisture content, nitrate, ammonium and extractable dissolved organic carbon (Ext. DOC) data. The freeze-thaw N₂O values are combined means of trials I and II. Values in parentheses are 1 standard error of the mean. Means with different letters (within column) are significantly different, using Scheffe's grouping of treatment means at $P < 0.05$ level of significance. Scheffe's grouping is associated with significant treatment effect using GLM ANOVA at $P < 0.05$ level of significance. The freeze-thaw N₂O was log 10 (X + 2) transformed before doing ANOVA.

3.4.2 Freeze-thaw N₂O Emission Potential of Soil From Different Landscape Positions

There was an increase in N₂O emission from soil cores due to freezing and thawing for all landscape positions (Figures 3.2a and b, trial I). The emission of N₂O from previously frozen cores for Middle, Lower and Riparian slope positions was significantly higher ($P < 0.05$) than emission from the previously unfrozen cores, but not the case for the Upper slope. The highest and earliest N₂O emission was from the previously frozen cores of Riparian zone soil, with emission commencing 6 hours and peak emission occurring 12 hours after placement at 15°C. The freeze-thaw emission from the Lower slope cores was slightly higher than emission from the Upper and Middle slope cores. The Upper and Middle slope positions behaved similarly in terms of freeze-thaw N₂O emission. It is noteworthy that peak emissions for all the slope positions occurred at the same time (12 hours after placement at 15°C). However, commencement of emission was delayed by 6 hours in the other slope positions compared to the Riparian soil. N₂O emission for all the slope positions ceased after 24 hours of placement at 15°C. The repeat experiment (trial II) also showed similar landscape pattern in N₂O emission for both the previously unfrozen and frozen cores, with the peak emission occurring 12 hours after placement at 15°C for all the landscape positions (Figures 3.2a and b, trial II). Also, N₂O emission decreased to zero after 24 hours of incubation for the previously frozen cores for all landscape positions.

The highest and lowest cumulative freeze-thaw N₂O emission was from the Riparian zone and Upper slope, respectively (Table 3.2). The cumulative freeze-thaw N₂O emission from the Upper slope was not different from that of the Middle slope. The high cumulative freeze-thaw N₂O emission from the Riparian zone was as a result of the replicate packed soil core from section 1 of transect emitting 141mg N kg⁻¹, which is 2.8 times the mean cumulative freeze-thaw N₂O emission of 50.4mg N kg⁻¹ from all replicate packed cores from Riparian zone. This select Riparian zone soil core had the highest antecedent moisture content, DEA, total organic carbon and extractable dissolved organic carbon contents of all four replicate soil cores from the zone. The antecedent moisture content, DEA, total organic carbon and extractable dissolved organic carbon contents of this select core was 1.7, 1.8, 1.5 and 1.5 times the respective average for all four replicate packed soil cores for Riparian zone. For the Lower slope, the packed soil core from section 2 of transect gave most (44%) of the total cumulative freeze-thaw N₂O emission from the Lower slope cores. The core had the highest total organic carbon of 6.02%, which was 1.2 times the average of 5.21% for the Lower slope. The chamber located in section 2 of transect was also responsible for 56% of total cumulative N₂O emission during the field monitoring of N₂O emission at spring thaw of 2006. This select chamber had the highest total soil organic carbon, which was 1.2 times the average for all replicate subset chambers located at the Lower slope (section 2.4.1.1).

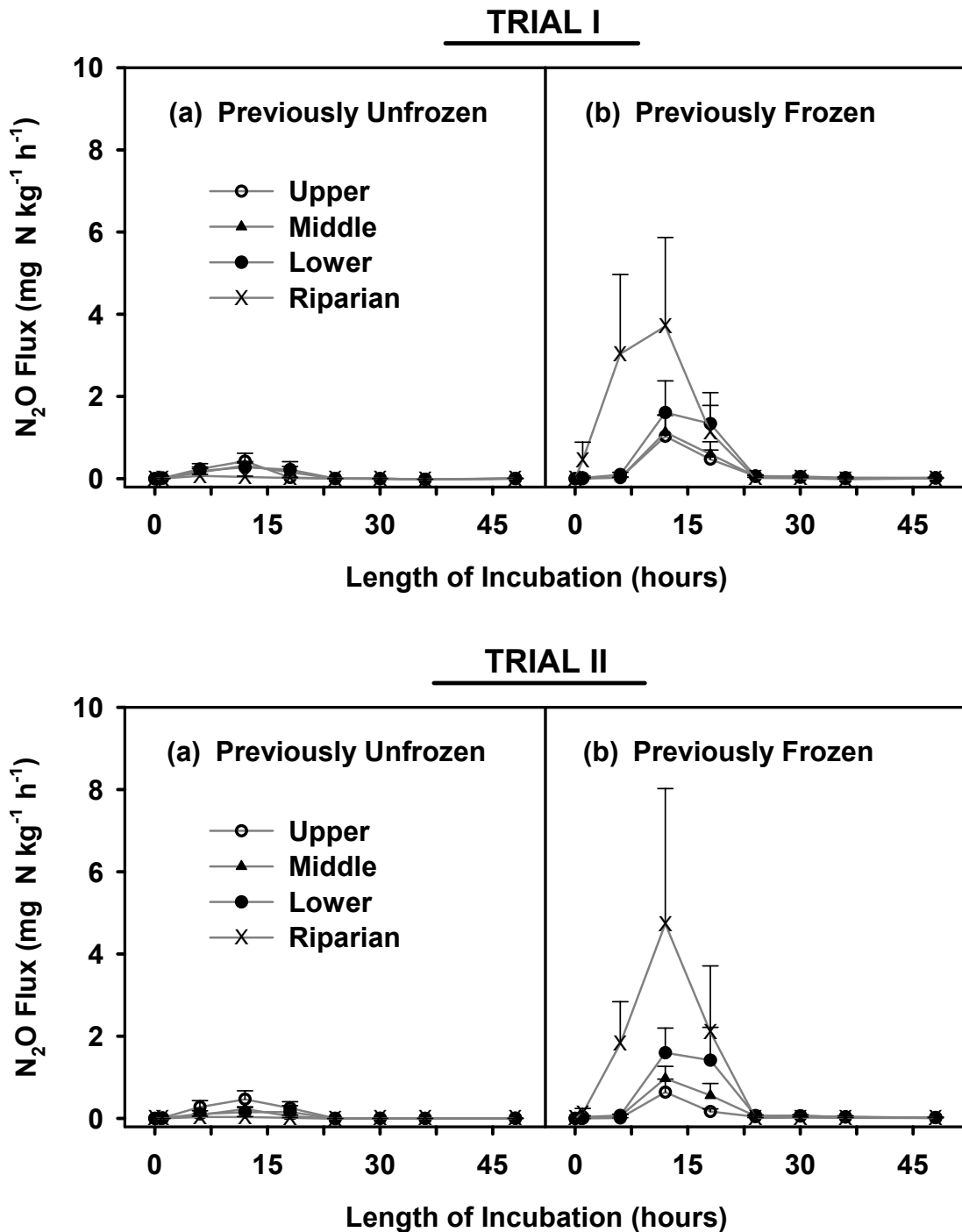


Figure 3.2 Emission of N₂O from repacked cores of independent soil samples in Experiment II, taken from Upper, Middle, Lower and Riparian slopes of an undulating field during fall of 2005, (a) previously kept at 5°C (b) previously frozen at -20°C. All treated cores were then incubated at 15°C for 48 hours. Trial II was a repeat experiment, and was conducted within 2 weeks of Trial I. Values shown are the mean plus 1 standard error of the mean of 4 independent replicate cores for each landscape position.

Table 3.2 Freeze-thaw cumulative emission of nitrous oxide (N₂O) and associated soil parameters of different landscape positions for Experiments II and III

Position	Freeze-thaw N ₂ O		Soil Parameters before Freeze-thaw Assay					
	No Nitrate	With nitrate	Nitrate	Ammonium	Total Org. C	DEA	Moisture content	Extr. Dissolved Org. C
	(mg N ₂ O-N kg ⁻¹)		(mg N kg ⁻¹)	(mg N kg ⁻¹)	(%)	(mg N kg ⁻¹ h ⁻¹)	(g g ⁻¹)	(mg C kg ⁻¹)
Upper	3.0 (1.9) c	3.0 (1.7) b	85 (27)	0.2 (0.2)	4.8 (0.1)	1.6 (0.2)	0.28 (0.02)	154 (18)
Middle	8.0 (1.0) bc	5.3 (1.6) b	79 (5)	0.4 (0.4)	5.0 (0.1)	1.2 (0.5)	0.28 (0.01)	235 (68)
Lower	16.2 (3.9) b	21.2 (3.9) b	92 (31)	0.8 (0.5)	5.2 (0.4)	3.4 (1.9)	0.35 (0.01)	232 (66)
Riparian	50.4 (20.8) a	163.9 (74.1) a	106 (55)	1.1 (0.6)	7.0 (1.4)	5.8 (2.1)	0.59 (0.14)	222 (34)

N.B: Values are the mean of 8 independent replicate packed cores per landscape position for freeze-thaw N₂O, and 4 independent replicate soil samples for nitrate, ammonium, total organic carbon, denitrifying enzyme activity (DEA), gravimetric moisture content and extractable dissolved organic carbon. Values in parentheses are 1 standard error of the mean. The freeze-thaw N₂O values are combined means of Trials I and II for Experiments II (No nitrate) and III (With nitrate). Values represented by different letters (within column) are significantly different, using Scheffe's grouping of treatment means at $P < 0.05$ level of significance. Scheffe's grouping is associated with significant treatment effect using GLM ANOVA at $P < 0.05$ level of significance. The freeze-thaw N₂O was log 10 (X+2) transformed prior to carrying out ANOVA.

The pre-assay nitrate and extractable dissolved organic carbon contents of the soil samples did not explain the observed pattern of increasing freeze-thaw N₂O emission in moving from the Upper to the Riparian slope position (Table 3.2). However, the antecedent moisture content, denitrifying enzyme activity and total organic carbon followed the same trend of increasing from the Upper to the Riparian slope position as the freeze-thaw N₂O emission. No trend in pre-assay ammonium and total nitrogen contents of soil from the landscape positions was observed (Table 3.2).

3.4.3 Freeze-thaw N₂O Emission Potential of Different Landscape Positions With No Nitrate Limitation

With the addition of 50 mg N kg⁻¹ nitrate to the packed soil cores, the previously unfrozen soil still gave no N₂O emission upon thawing (Figure 3.3a, trial I). The landscape pattern in N₂O emission from the previously frozen cores remained the same as when no nitrate was added, only that the effect was significantly amplified, especially for the Riparian zone (Figure 3.3b, trial I). Peak N₂O emission from previously frozen soil cores of the Riparian zone was however delayed until 18 hours after placement at 15°C, while peak N₂O emission remained at 12 hours after placement at 15°C for the Upper, Middle and Lower slope positions (Figure 3.3b, Trial I). Similar trend with landscape position in N₂O emission was observed for the repeat experiment (Trial II), for both the previously frozen and unfrozen soil cores (Figure 3.3a and b, Trial II).

The highest and lowest cumulative freeze-thaw N₂O emission was still from the Riparian and Upper slope positions, respectively (Table 3.2). The cumulative freeze-thaw N₂O emission for the Riparian zone was however over three times the cumulative freeze-thaw N₂O when no nitrate was added to the soil cores (Table 3.2). The cumulative freeze-thaw N₂O emission from the Upper slope was not different from that of the Middle and Lower slopes. The high cumulative freeze-thaw N₂O emission from the Riparian zone was as a result of the replicate packed core of soil from section 1 of transect giving 494mg N kg⁻¹, which is 3 times the mean cumulative freeze-thaw N₂O emission of 163.9mg N kg⁻¹ from all replicate packed cores from Riparian zone. This select Riparian zone soil core had the highest antecedent moisture content, DEA, nitrate content and total organic carbon contents of all four replicate soil cores for the zone. The antecedent moisture content, DEA, nitrate content and total organic carbon content of this select core was 1.7, 1.8, 2.5 and 1.5 times the respective average for all four replicate packed soil cores for Riparian zone. This select core behaved in the same manner for the first and second trials of this experiment, in terms of high cumulative freeze-thaw N₂O emission and the magnitude of its associated soil parameters, relative to the other replicate soil cores of the Riparian zone.

For the Lower slope, the packed soil core from section 2 of transect gave most (38%) of the total cumulative freeze-thaw N₂O emission from the Lower slope cores. The core had the highest total organic carbon of 6.02%, which was 1.2 times the average of 5.21% for the Lower slope.

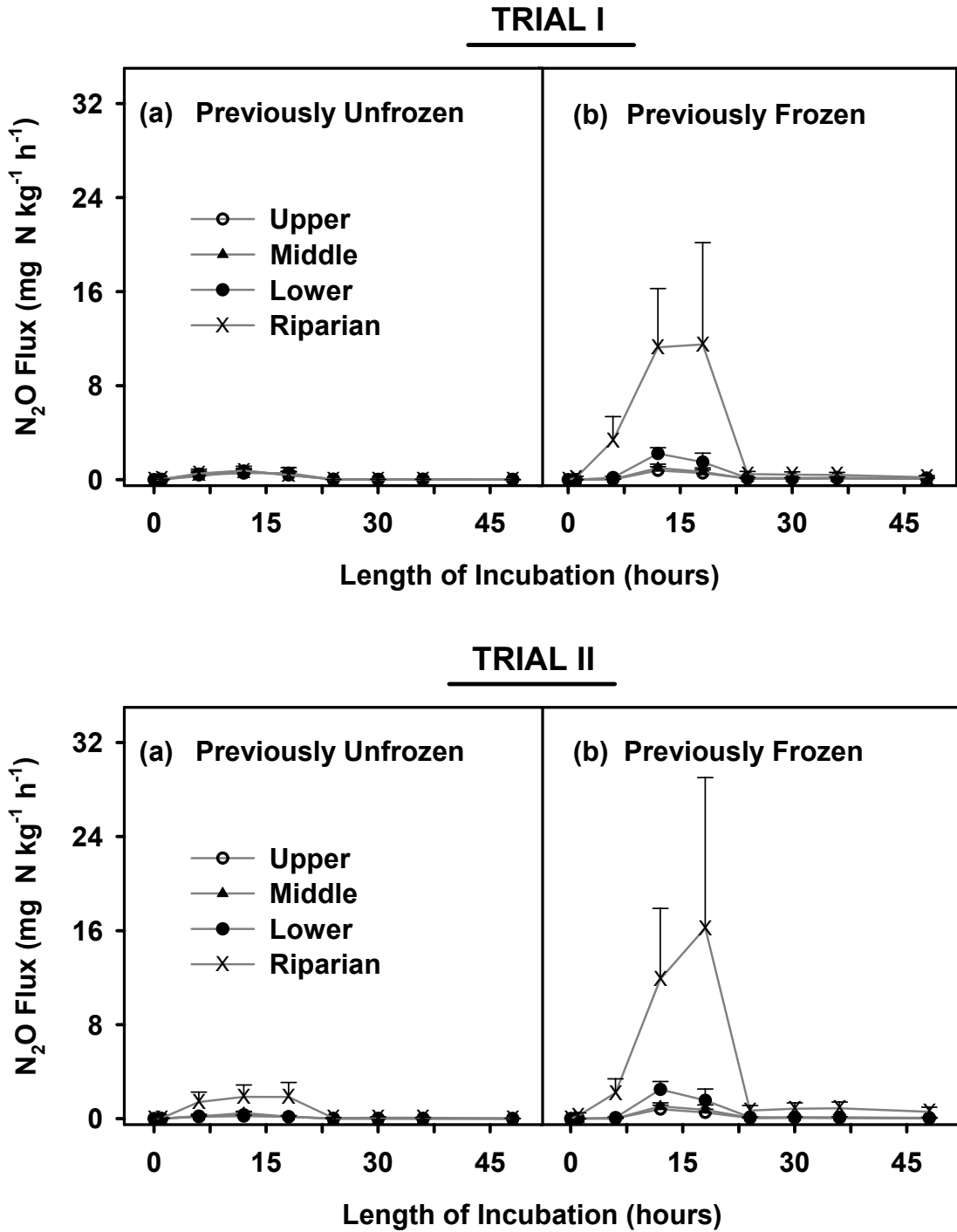


Figure 3.3 Emission of N₂O from cores amended with 50 mg N kg⁻¹ as KNO₃ in Experiment III, packed from soil taken from Upper, Middle, Lower and Riparian slopes of an undulating field during fall of 2005, (a) previously kept at 4°C (b) previously frozen at -20°C. All treated cores were then incubated at 15°C for 48 hours. Trial II was a repeat experiment, and was conducted within 2 weeks of Trial I. Values shown are the mean plus 1 standard error of the mean of 4 independent replicate cores for each landscape position.

The pre-assay nitrate and extractable dissolved organic carbon contents of the soil samples did not explain the observed pattern of increasing freeze-thaw N₂O emission in moving from the Upper to the Riparian slope position (Table 3.2). However, the antecedent moisture contents, denitrifying enzyme activity and total organic carbon followed the same trend of increasing from the Upper to the Riparian slope position as the freeze-thaw N₂O emission. No trend in pre-assay ammonium and total nitrogen contents of soil from the landscape positions was observed (Table 3.2).

3.4.4 Soil Factors Related to the Landscape-scale Pattern in Freeze-thaw N₂O Emission

The cumulative freeze-thaw N₂O emission of soil cores was strongly associated with the antecedent moisture content of the soil samples, both with and without the addition of nitrate (Table 3.3, Figures 3.4a and b). As expected, the cumulative freeze-thaw N₂O was strongly associated with the pre-assay nitrate content for the assay without nitrate addition, but not for the assay with nitrate addition (Table 3.3). The cumulative freeze-thaw N₂O emission was associated with pre-assay denitrifying enzyme activity only for soil cores with nitrate addition. The antecedent moisture content and denitrifying enzyme activity of the soil samples were highly correlated, with a Spearman rank correlation coefficient of 0.69 at $P < 0.05$ level of significance. The cumulative freeze-thaw N₂O was associated with cumulative freeze-thaw CO₂ emission only for soil cores with nitrate addition (Figure 2.4c), and associated with total organic carbon

Table 3.3 Spearman rank correlation coefficients of cumulative freeze-thaw nitrous oxide (N₂O) with soil parameters for landscape freeze-thaw assays in Experiments II (without nitrate) and III (with nitrate addition)

Soil parameter	Cumulative Freeze-thaw N ₂ O (mg N kg ⁻¹)	
	Without nitrate addition	With nitrate addition
Antecedent moisture content	0.53 **	0.77 ***
DEA	0.35	0.51 **
Nitrate	0.51 **	0.24
Ammonium	0.40 *	0.50 **
Total nitrogen	-0.06	-0.34
Total organic carbon	0.48 **	0.33
Freeze-thaw CO ₂	0.02	0.43 *
Extractable dissolved org. carbon	0.42 *	0.29

Note: *, **, *** indicate level of significance of Spearman rank correlation co-efficient at $P < 0.05$, < 0.01 and < 0.001 , respectively. Values in bold are pairs of parameters with significant correlation. There were 32 cores for each pair of parameters. Cumulative freeze-thaw flux was calculated as the difference between cumulative flux from corresponding previously frozen and unfrozen cores. Cumulative flux for each core was calculated by linear interpolation over a 48-hour period.

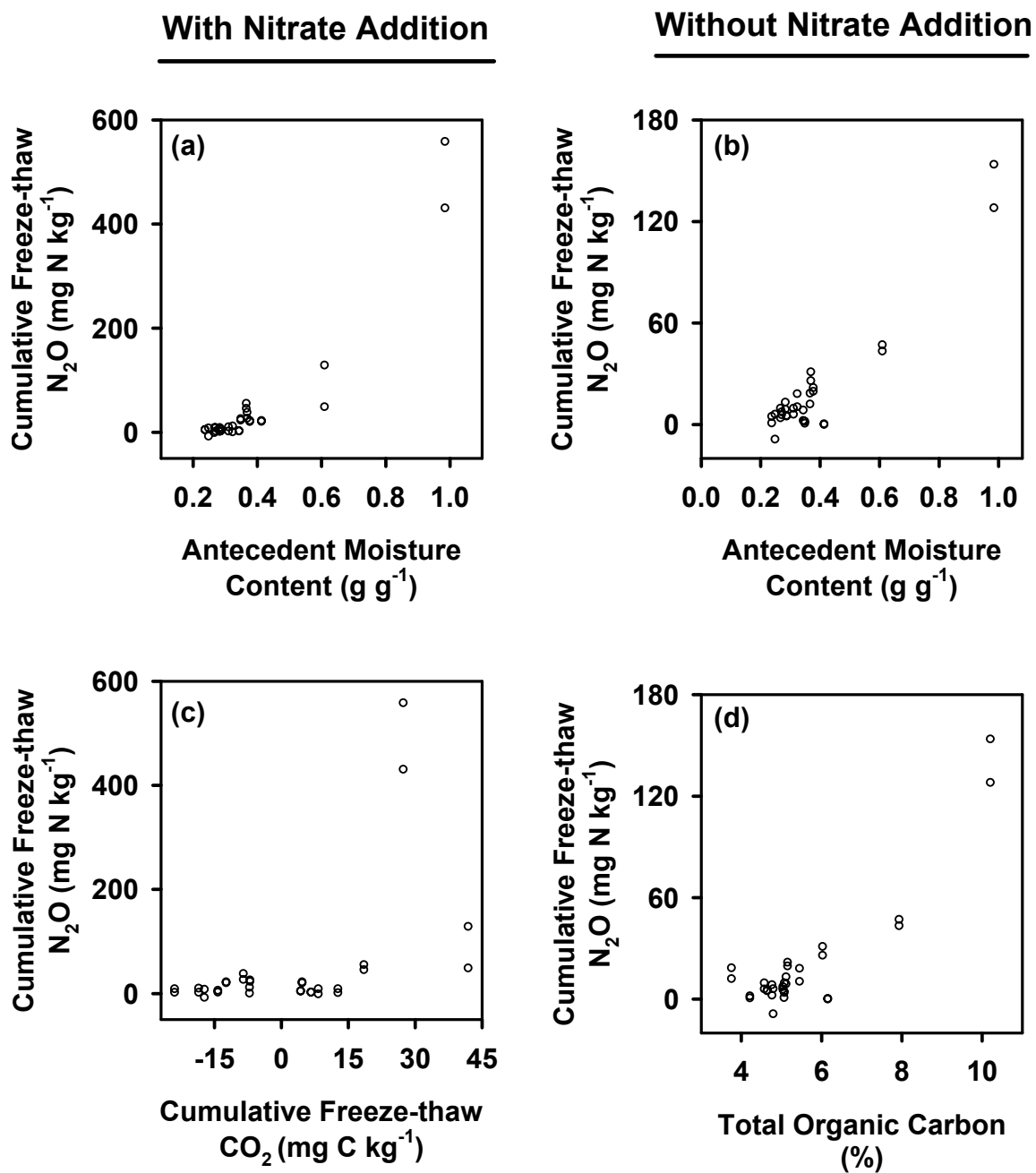


Figure 3.4 Regression of cumulative freeze-thaw N_2O emission on some associated soil parameters for soil cores in trials I and II of Experiments II and III : (a) antecedent moisture content, with nitrate addition; (b) antecedent moisture content, without nitrate addition; (c) cumulative freeze-thaw CO_2 emission, with nitrate addition and (d) total organic carbon, without nitrate addition.

(Figure 3.4d) and extractable dissolved organic carbon only for soil cores without nitrate addition (Table 3.3). The cumulative freeze-thaw N₂O emission was associated with soil ammonium content both with and without nitrate addition to soil cores, but not with total nitrogen for either with or without nitrate addition.

3.5 Discussion

Due to the inherent variation in soil factors at the landscape scale, the potential of different landscape positions for freeze-thaw emission of N₂O might be different. This study was carried out to unravel if different landscape positions differ in their potential for freeze-thaw N₂O emission, and what soil factors are responsible for this difference. This information becomes important as the reality of a change in climate pattern (such as colder winters, drier or wetter falls) due to enhanced greenhouse effect can potentially alter the capacity of different landscape elements for spring-thaw N₂O emission from soil. This study is novel as no previous work looking at the variation with landscape position of the freeze-thaw emission of N₂O exists to the best of our knowledge.

3.5.1 Effect of Antecedent Moisture on Freeze-thaw N₂O Emission Potential of Soil

Results from Experiment I showed that lowering the antecedent moisture of soil (by drying) significantly decreased its potential for freeze-thaw emission of N₂O. Though the water-filled porosity of all the packed cores was brought to the

same level (80%) before the temperature treatment, the dried pre-treatment soil lost its potential for N₂O emission when frozen and thawed. This suggests that the antecedent moisture of the soil before freezing affects the conditions predisposing the soil to freeze-thaw emission of N₂O when thawed. This is reinforced by the fact that significantly lowering the antecedent moisture of the soil before freezing did significantly lower the DEA of the soil. The antecedent moisture status of the soil has been reported to affect the denitrification potential of soil by affecting the initial concentration of reduction enzymes and potential for synthesizing new enzymes (Dendooven et al., 1996), irrespective of the current water and nitrate contents of the soil. The addition of 50 mg N kg⁻¹ of nitrate to the dried pre-treatment soil failed to produce a freeze-thaw effect, implying that nitrate addition on its own does not guarantee a freeze-thaw effect. Drying the samples likely reduced both the initial concentration of N reduction enzymes (as indicated by significant lowering of the DEA), as well as the potential for the synthesis of new enzymes for denitrification and freeze-thaw N₂O emission.

Also, considering the solubility of N₂O in soil solution, drying the soil samples prior to packing would lead to degassing of aqueous N₂O from the soil (Grant and Pattey, 2003). Briefly rewetting the soil to 80% water-filled porosity during the assay preparation and placement at 5°C or -20°C did not leave sufficient time for resumed nitrifying and denitrifying enzyme activity that would have led to the replenishment of dissolved N₂O. Not enough time was allowed for N₂O in soil atmosphere to dissolve in the water briefly added to the dried pre-treatment soil before freezing the cores. These conditions of the dried

pre-treatment soil would have resulted in the elimination of freeze-thaw emission of N_2O upon placement of frozen cores at $15^\circ C$. The drying pre-treatment was brief, likely too brief for loss of considerable amount of denitrifying enzymes, as the DEA values were only slightly (though significantly) depressed by the drying pre-treatment. For the moist pre-treated soil however, part of the N_2O emission upon warming the frozen soil is likely due to release of N_2O dissolved in soil solution before freezing the cores.

This effect of antecedent soil moisture on the potential of soil for freeze-thaw emission of N_2O therefore provides an understanding into why the magnitude of daily field emission of N_2O during the spring-thaw event of 2005 was higher than that for 2006, the latter having a drier fall (Section 2.4.1.1). The fall soil moisture in 2004 was higher than the fall soil moisture in 2005, resulting from a total fall rainfall in 2004 being more than twice the total fall rainfall in 2005 (Section 2.3.2). The strong association between the antecedent moisture content and DEA of soil samples suggests that soil moisture enhances the denitrifying potential of soil, and consequently the capacity of soil for freeze-thaw emission of N_2O .

3.5.2 Potential of Different Landscape Positions for Freeze-thaw Emission of N_2O

Landscape positions differed in their potential for freeze-thaw emission of N_2O , given their pre-assay nitrate contents. The Riparian zone had the highest potential for freeze-thaw emission of N_2O , being related to its high antecedent

moisture content, DEA and available carbon content (from its high total organic carbon content). This confirms previous findings about the high potential of the Riparian zone for denitrification resulting from its high moisture and organic matter status (Cooper, 1990; Ambus and Lowrance, 1991; Groffman, 1994). The pre-assay nitrate contents of the samples did not explain the pattern with landscape position in freeze-thaw emission of N₂O observed, as the nitrate contents of samples from all slope positions were similar.

With the addition of nitrate (50 mg N kg⁻¹ nitrate) to soil from different landscape positions, the landscape pattern of freeze-thaw N₂O emission still persisted. The highest freeze-thaw emission was again from the Riparian zone, further proving that the pre-assay nitrate content of the soil samples was not responsible for the observed pattern of freeze-thaw emission within the landscape. The amplification of the freeze-thaw effect only at the Riparian zone upon the addition of nitrate to the cores confirmed that soil factors other than nitrate content were responsible for the high potential of the Riparian zone for freeze-thaw N₂O emission.

The significantly higher N₂O emission from the frozen cores compared to the unfrozen cores for all the slope positions reinforces the temporal significance of spring thaw period for annual inventory of N₂O emission from agricultural soils (Lemke et al., 1998; Wagner-Riddle and Thurtell, 1998). The freeze-thaw emission of N₂O from all landscape positions was very brief, ceasing after between 18 and 24 hours of thawing the frozen cores by placing them at 15°C.

This underscores the brevity of the burst of N₂O from soil at spring thaw as reported by Christensen and Tiedje (1990).

The high potential of the Riparian zone for freeze-thaw emission of N₂O observed in this laboratory study was not observed from the field monitoring of N₂O emission for spring thaw periods of 2005 and 2006 (Section 2.4.1.1). The Riparian zone is a depressional area, and therefore is saturated, collects snow over winter, and has thick vegetation cover. This condition of the zone is expected to insulate the soil, preventing it from attaining freezing temperature in the field, evident from the lowest over-winter soil temperature for the Riparian zone being -2°C in 2006. The lowest soil temperature at the Riparian zone being -2°C did not ensure the complete freezing of the Riparian zone. Hansson et al. (2004) reported the complete freezing of soil packed inside cylinders by subjecting the soil to a consistent temperature of -6°C for between 12 and 50 hours in the laboratory. Also, the saturated condition of the Riparian zone during spring-thaw (as a result of moisture redistribution within the landscape) makes the zone highly anaerobic, leading to the reduction of N₂O to N₂.

The slightly higher antecedent moisture content, DEA, total organic carbon and cumulative freeze-thaw emission of N₂O for the Lower slope position compared to the Upper and Middle slope positions confirms the intensification of the potential for denitrification in going from the Upper to the Lower slope position (Section 2.5.3.1). The consistent association of the high cumulative freeze-thaw N₂O emission from select Riparian soil core with its high antecedent moisture, DEA and total organic carbon point to biological denitrification being the

dominant process of N₂O production at freeze thaw, as previously reported by Priemé and Christensen (2001).

3.5.3 Soil Factors Responsible for the Landscape-scale Pattern in Freeze-thaw Emission of N₂O

Experiment I clearly showed that lowering the antecedent moisture of soil by drying eliminated the capacity of soil for freeze-thaw emission of N₂O. The failure of the addition of nitrate to cause N₂O emission from the dried pre-treatment soil showed that the low antecedent moisture of the soil eliminated the potential of the soil to reduce the added nitrate to N₂O. The significant reduction in the pre-assay DEA of the soil by drying implies drying reduces the amount of denitrifying enzymes available in soil, and lowers the capacity of the soil for synthesis of new enzymes for denitrification. Results from experiments II and III has shown that the pre-assay nitrate contents of soil samples did not explain the observed landscape pattern of freeze-thaw N₂O emission. There was however a strong association of cumulative N₂O with the pre-assay nitrate content of soil samples when nitrate was limiting, but not when nitrate was added (Table 3.2). This is expected as the emission of N₂O from thawing soil has been reported to be associated with the concentration of soil residual nitrate (Tenuta and Sparling, 2004; Kammann et al., 1998).

The pattern of the antecedent moisture content, DEA, and total organic carbon with landscape position was very comparable to that of freeze-thaw emission of N₂O, with the Riparian zone having numerically, the highest

antecedent moisture content, DEA and total organic carbon, compared to the other landscape positions. The high antecedent moisture of the Riparian zone therefore predisposed the zone to having a high potential for freeze-thaw emission of N_2O compared to the more Upland positions (Upper, Middle and Lower). This high potential for freeze-thaw N_2O (indicated by high DEA) of the Riparian zone was matched by its relatively high carbon availability (from its high total organic carbon). The strong association of the antecedent moisture content with the DEA of the samples underscores the regulatory nature of soil hydrology (imposed by landscape) on the denitrification potential of soil (Pennock et al., 1992). Therefore zones in the landscape where the soil is wet for a prolonged period of time may potentially be zones of high denitrifying activity, and consequently zones of high freeze-thaw N_2O emission potential, especially when matched by high carbon availability and soil freezing over winter.

The Lower slope position had numerically higher antecedent moisture content, denitrifying enzyme activity and total organic carbon content than the Upper and Middle slope positions. The cumulative freeze-thaw emission of N_2O from the Lower slope was slightly higher than from the Upper and Middle slope positions, similar to the pattern of soil water-filled porosity and emission of N_2O observed on the field during the spring thaw period of 2006 (Section 2.4.1.1). The packed soil core from section 2 of transect gave most (38%) of total cumulative freeze-thaw N_2O emission from the Lower slope cores. This is similar to the chamber located in section 2 of transect being also responsible for 56% of total cumulative N_2O emission from Lower slope during the field monitoring of N_2O

emission at spring thaw of 2006. This select chamber had the highest total soil organic carbon, which was 1.2 times the average for all replicate subset chambers located at the Lower slope position on the field.

3.6 Conclusion

Lowering the antecedent moisture of the soil by drying before assaying eliminated the potential of soil for freeze-thaw N₂O emission, reducing the amount of enzymes available or synthesizable for denitrification. The freeze-thaw emission of N₂O was significantly affected by landscape position, with increasing freeze-thaw potential in going from the Upper, through the Middle and Lower slopes, into the Riparian zone. The Riparian zone consistently gave the highest freeze-thaw emission both with and without nitrate limitation. The frozen cores gave significantly higher N₂O emission than the corresponding unfrozen cores for all landscape positions, with emission from the frozen cores being brief, lasting for only between 18 and 24 hours after the onset of thawing. The pre-assay nitrate contents of the soil samples failed to explain the observed landscape pattern in freeze-thaw N₂O emission. The antecedent moisture content, DEA and total organic carbon content however followed the same pattern with landscape as the freeze-thaw N₂O emission. High cumulative freeze-thaw emission of N₂O from the Riparian zone soil was associated with its high antecedent moisture content, DEA and total organic carbon content.

The implication of the strong association between the antecedent moisture content and the DEA of soil is that positions within the landscape with higher

moisture should be assigned a higher spring-thaw N₂O emission quotient, as such positions potentially have the denitrifying enzymes, available carbon and nitrogen required for denitrification. Though field flux data did not depict the Riparian zone as being a “hotzone” for spring-thaw N₂O emission, its potential for emission should not be discountenanced in modeling for N₂O emission at the landscape scale in the PPH region, especially where snow cover and moisture levels are low, promoting freezing of these soils.

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CHAPTER 4

OVERRRAL SYNTHESIS

Knowledge of how landscape position affects the emission of greenhouse gases from the agricultural soils of the Prairie pothole region is important for improving on the reliability of emission estimates for this region. This is because the complex landscapes of this region might affect the type, extent and pattern of greenhouse gas emission due to variability in soil factors and processes along these landscapes. This knowledge of the effect of landscape position on greenhouse gas emission will also help in modifying existing and formulating new management practices needed to reduce emissions. While there are a few past efforts that appraised the seasonal and landscape pattern of denitrification and / or N_2O emission, detailed information on the landscape-scale of the field emission of both N_2O and CH_4 within a year and between years is lacking. Also, while the phenomenon of freeze-thaw N_2O emission has been studied to a limited extent, no information exists on the potential of different landscape positions for freeze-thaw emission of N_2O . This study aimed at determining which areas within the landscape and what periods of the year are critical for N_2O and CH_4 emission, and the soil factors associated with this spatial and temporal variation in emission. The study also sought to determine how lowering the antecedent soil moisture affects the freeze-thaw emission of N_2O , the potential of different landscape positions for freeze-thaw N_2O emission, and the soil factors associated with these differences in potentials.

The field emission of N₂O and CH₄ was characterized by high temporal variation, with bursts in emission associated with events such as spring thaw, fertilizer application, and rapid changes in soil moisture and temperature. Daily emission of N₂O was generally higher in 2005 compared to 2006, the former year being wetter. The emission of N₂O was high only at spring-thaw and post-fertilizer application periods, while CH₄ emission occurred as brief bursts when soil moisture was high and soil temperature was increasing.

A distinct pattern in field emission of N₂O and CH₄ with landscape was observed, with a concentration of the hotspots for N₂O and CH₄ at the Lower and Riparian slope positions, respectively. The hotspot for N₂O emission at the Lower slope was associated with high soil moisture and carbon availability. The Upper and Middle slope positions had lower soil moisture (higher aeration) and carbon availability compared to the Lower slope, and gave numerically lower N₂O emission compared to the Lower slope. There was an intensification of the denitrifying potential in moving from the Upper to the Lower slope position, as moisture and carbon availability increased from the Upper to the Lower slope. There was some CH₄ emission at the Lower slope, but the Upper and Middle slope positions either gave no CH₄ or consumed CH₄, as soil moisture and C availability at the Upper and Middle slope positions were low.

The uncropped Riparian zone was different from the cropped Upper, Middle and Lower slope positions, with its consistently low or no N₂O emission, even though its carbon availability and water-filled porosity were very similar to those of Lower slope position. The organic-rich, nitrate-depleted, highly

anaerobic and saline conditions of the Riparian zone suggest the microbial community structure at the zone might be different from that for the Upland slope positions. The Riparian zone was however a hotspot for CH₄ emission, with the emission being episodic in nature, coinciding with increasing soil temperature and decreasing soil moisture in the zone. The high soil water-filled porosity and carbon availability at the Riparian zone explained the high CH₄ emission observed at the zone. The high production of CH₄ at the Riparian zone is characteristic of poorly-drained and organic carbon-rich parts of the landscape, where organic matter is decomposed and CO₂ is reduced by micro-organisms under highly anaerobic conditions (Reiners et al., 1998). High concentration of sulphate at the Riparian zone was inhibitory to the activities of methanogens, with low CH₄ emission observed for areas within the Riparian zone with high sulphate content. This inhibitory effect of soil sulphate on methane emission in the zone is due to competition between sulphate-reducing bacteria and methanogens for electron donors (such as organic carbon) in sulphate-rich anaerobic environments (Lovely and Klug, 1983). This landscape pattern in N₂O and CH₄ emission was observed using either the 32 subset chambers or the entire 128 chambers on the transect. The emission of N₂O and CH₄ at the landscape scale was therefore associated with soil factors promoting the activities of nitrifiers and / or denitrifiers, and methanogens, respectively.

Due to the temporal significance of spring-thaw emission of N₂O from soil observed from the field, a laboratory investigation of how lowering the antecedent soil moisture affects N₂O emission from thawing soil, and the potential of

individual landscape positions for freeze-thaw emission of N₂O was conducted. Decreasing the antecedent soil moisture content by drying soil before assaying eliminated the potential of the soil for N₂O emission when thawed, even with non-limiting nitrate. The lack of freeze-thaw N₂O emission from dried pre-treated soil was associated with drying reducing the amount of denitrifying enzymes available for denitrification, explaining why the daily emission of N₂O at the spring-thaw period of 2005 was higher in magnitude than for 2006, the latter year being preceded by a drier fall.

The potential for freeze-thaw emission of N₂O was lowest for the Upper slope, and highest at the Riparian zone. The addition of nitrate to soil cores before assaying failed to achieve higher freeze-thaw emission at the Upper, Middle and Lower slope positions, but increased emission more than three-fold for the Riparian zone, implying soil factors other than nitrate was responsible for the high freeze-thaw emission potential of the Riparian zone. The high freeze-thaw potential of the Riparian zone was associated with its high antecedent moisture content, DEA and carbon availability. This high potential of the Riparian zone for freeze-thaw emission of N₂O observed was in contrast to lack of emission at spring thaw from the zone in the field. This was attributed to the lack of soil freezing over-winter at the zone due to snow insulation, vegetation cover and the saturated conditions of the zone as a result of moisture re-distribution within the landscape.

The freeze-thaw emission potential of the Lower slope was higher than those of the Upper and Middle slopes, with the antecedent moisture, DEA and

carbon availability higher at the Lower slope compared to the Upper and Middle slopes. This trend was in agreement with the intensification of denitrifying potential in moving from the Upper, through the Middle to the Lower slope position observed on the field. Freeze-thaw emission of N_2O from all landscape positions was very brief, similar to the brief bursts in N_2O emission observed at spring-thaw on the field.

4.1 General Conclusion and Recommendation

From the results from this study, it is recommended that estimates of N_2O and CH_4 emission from the Prairie pothole region should be landscape-based and not field-based. Higher N_2O emission index should be given to cropped areas within the landscape having poor drainage, as such areas potentially have the denitrifying enzymes and available carbon required for denitrification. The potential of the Riparian zone for freeze-thaw emission of N_2O should not be discountenanced in modeling for annual emission at the landscape scale for the PPH region, especially where snow cover and moisture levels are low, promoting freezing of these soils. Also, higher CH_4 emission index should be assigned to poorly-drained uncropped (vegetated) areas within the landscape, especially when the C availability of such areas is high.

Fertilizer management practices like fall application that predisposes fertilizer N to spring-thaw loss as N_2O should be reviewed, while the use of “trap crops” like winter wheat to keep fall applied N in the soil should be considered for adoption by farmers. Also the adoption of “variable-rate” fertilizer N application

and use of appropriate drainage measures for poorly drained areas within the landscape will be of both economic and environmental benefits.

Future research efforts aimed at unraveling the relative contribution of nitrification and denitrification to N_2O emission at the different landscape positions and different periods over a season will provide further insight into how variation in soil conditions at the landscape scale can determine the pathway of N_2O emission. This will further help to refine the appropriate management practices to reduce N_2O emission. Field monitoring of N_2O and CH_4 emission from different landscape positions throughout the entire year (spring, summer, fall and winter) will be useful in having a complete annual inventory of the spatial and temporal pattern of emission from agricultural soil. This will also help to improve on the current estimates of greenhouse gas emission from agricultural soils of the PPH, and provide a stronger basis for emission mitigation measures.

4.2 References

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6. APPENDIX

List of Abbreviations

PPH- Prairie Pothole Region

WFP- Water-filled porosity

EC- Electrical Conductivity

DEA- Denitrifying enzyme activity

GMC- Gravimetric moisture content

C- Carbon

PVC- Polyvinyl Chloride

TOC- Total organic carbon

DOC- Dissolved organic carbon

Ext. DOC- Extractable dissolved organic carbon