# DYNAMICS OF PROFILES OF SOIL GREENHOUSE GASES IN A TOPOGRAPHICALLY VARIABLE LANDSCAPE IN WESTERN CANADA

BY

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A Thesis
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in Partial Fulfillment of the Requirements
for the Degree of

MASTER OF SCIENCE

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THE UNIVERSITY OF MANITOBA

FACULTY OF GRADUATE STUDIES

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# Dynamics of Profiles of Soil Greenhouse Gases in a Topographically Variable Landscape in Western Canada

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## ABSTRACT

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Greenhouse gas emission studies from temperate soil have received much attention in recent years, particularly freeze-thaw emission and their association with soil conditions. Field and laboratory experiments were conducted in the undulating landscape elements (Upper, Middle, Lower and Riparian) at the Manitoba Zero-Tillage Research Association's farm, to determine the association between seasonal and landscape variation in soil greenhouse gas concentration profiles, greenhouse gas surface emissions and soil conditions. Profile greenhouse gas concentrations, surface emission and soil conditions were monitored from August to November 2005 and then from March to August 2006. Highest nitrous oxide ($N_2O$) profile concentrations (287.3 $\mu L\ L^{-1}$ at 15 cm depth) and highest $N_2O$ surface emission (0.1 $\mu g\ N\ m^{-2}\ s^{-1}$) was recorded in the Lower landscape element. Soil methane ($CH_4$) concentrations ranged between 0.5 and 2,587 $\mu L\ L^{-1}$ and were highest during freeze-thaw period for the Riparian element at 15 cm depth. The $CH_4$ emission was highest in the Riparian (1.2 $\mu g\ C\ m^{-2}\ s^{-1}$) followed by the Lower element (1.2 $\mu g\ C\ m^{-2}\ s^{-1}$). The $CH_4$ concentration was variable in all sections where the $SO_4^{-2}$ levels were high. Carbon dioxide ($CO_2$) concentrations increased with depth in all the landscape elements and were highest in the Riparian element (225,000 $\mu L\ L^{-1}$) at 65 cm depth and unaffected by freeze-thaw but elevated during the cropped period. The $CO_2$ emission was highest in the Riparian element and increased during the cropped period. Oxygen concentrations were highest in the Upper and Middle elements and lowest at the 65 cm depth in the Riparian element. Significant correlations were found between profile greenhouse gas concentrations and surface emission, soil moisture and temperature at all depths in the four landscape elements. The estimated $N_2O$ and $CH_4$ profile emission values derived from greenhouse gas profile concentrations were closer to measured chamber emission values after normalization with $CO_2$ surface emission in all elements and periods except the freeze-thaw period. A laboratory investigation with intact frozen and unfrozen soil cores obtained from the study site revealed that $N_2O$ emissions from unfrozen deeper soils were negligible and the frozen surface (0-5 cm) and shallow depth soils (10-15 and 30-35 cm) recorded highest $N_2O$ emissions during thaw events. In summary, the Lower landscape element had greater field $N_2O$ emissions, profile concentrations and intact soil core freeze-thaw emissions. Further, the results of this study provide more evidence that frozen surface soil and not unfrozen deeper soil is the source of field emissions of $N_2O$ during spring thaw.

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## FOREWORD

This Thesis has been prepared in manuscript format following the guidelines established by the Department of Soil Science at the University of Manitoba. The Thesis begins with a General Introduction chapter providing the scope and rationale for a field investigation presented in Chapter 2 and a laboratory experiment presented in Chapter 3. The format of the two manuscript chapters is that for the Canadian Journal of Soil Science. The Thesis concludes with a General Discussion synthesizing the results of the two manuscripts and provides insight into future research directions. Each chapter is followed by a list of references cited in their respective text.

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## LIST OF ABBREVIATIONS

$\mu g\ m^{-3}$ – microgram per cubic metre
$\mu L\ L^{-1}$ – microlitre per litre
$^{0}C$ – degree Celsius
C – carbon
$CH_4$ – methane
cm – centimeter
$CO_2$ – carbon dioxide
D – diffusion coefficient
$D_0$ – gas diffusion coefficient in free air
$D_{std}$ – gas diffusion coefficient under standard conditions
g – gram
$K_2SO_4$ – potassium sulphate
$kg\ ha^{-1}$ – kilogram per hectare
kPa – kilo pascal
M – molar
$mg\ kg^{-1}$ – milligram per kilogram
$mL\ min^{-1}$ – millilitre per minute
mm – millimeter
$mS\ cm^{-1}$ – milliseimens per centimetre
N – elemental nitrogen
n – number of replicates
$N_2$ – nitrogen gas
$N_2O$ – nitrous oxide
$NH_4^+$ - ammonium
$NO_2^-$ – nitrite
$NO_3^-$ – nitrate
$O_2$ – oxygen
$p$ – pressure
P – probability level
pH – potential of hydrogen
ppb – parts per billion
ppm – parts per million
psi – pound per square inch
S – sulphur
SCL – sandy clay loam
SEM – standard error of mean
SiL – silty loam
$SO_4^{2-}$ - sulphate
$T$ – temperature in kelvin [K]
Tg - teragram
$\alpha$ – probability level
$\varepsilon$ - tortuosity
$\Phi g$ – air-filled porosity function

# CHAPTER 1

# INTRODUCTION

## 1.1 Climate Change and Role of Greenhouse Gases in Climate Change

"Warming of climate system is unequivocal, as is now evident from observations of increases in global average air and ocean temperatures, widespread melting of snow and ice and rising global average sea level" (IPCC 2007). Global climate change has attracted the attention of human kind as it represents a serious threat to human existence and survival. As a consequence of climate change, hydrological system effects such as increased runoff and earlier spring peak discharge in many glacier and snow-fed rivers and warming of lakes and rivers have been observed, with effects on thermal structure and water quality (Bates et al. 2008). In terrestrial biological systems, climate change effects include earlier timing of spring events such as bud break, bird migration and egg laying habit (Both et al. 2009). In fresh water biological systems the effects are associated with rising temperature as well as related changes in oxygen levels and circulation which affect a range of algal, plankton and fish abundance in high latitude lakes (Flanagan et al. 2003). In agricultural ecosystems the alteration in weather patterns have been predicted to result in new pest outbreaks and the spread of crop diseases, lengthening of crop growing season, impacting water and sunlight availability for crop maturation, and result in a restriction of choice of crops (Garrett 2006). Other significant effects of climate change are alterations in forest disturbance due to fires and pests, decrease in snow cover and northern hemisphere sea ice extent, thinner sea ice, shorter freezing season of lake and river ice, glacier melt, decrease in permafrost extent, increase in soil temperature and borehole temperature and sea level rise (IPCC 2007).

The radiative forcing of the climate system, and the resultant change in climate, is dominated by the long-lived greenhouse gases. Changes in the atmospheric concentration of greenhouse gases, aerosols, land cover and solar radiation, all alter the earth's energy balance and climate system and as a result are the main drivers of climate change. Global mean sea level is projected to rise by 0.09 – 0.88m between 1990 and 2100 under different greenhouse gas emission scenarios (IPCC 2007). Global atmospheric concentration of carbon dioxide ($CO_2$), methane ($CH_4$) and nitrous oxide ($N_2O$) have increased markedly as a result of anthropogenic activities. The current atmospheric concentration of $CO_2$ is 379 ppmv which has increased from the pre-determined industrial value of 280 ppmv, the concentration of $CH_4$ is 1,774 ppbv, which is more than twice the pre-determined industrial value of 715 ppbv and the concentration of $N_2O$ in atmosphere is approximately 319 ppbv which has increased from the pre-determined industrial value of 270 ppbv and the major increase occurred within the past 10 years (IPCC 2007). The global increase in $CO_2$ concentrations are primarily due to fossil fuel use and land-use change, the increase in $CH_4$ concentrations are predominantly due to agriculture and fossil fuel use and the increase in $N_2O$ concentration is primarily due to agriculture (IPCC 2007). The increase in atmospheric $N_2O$ concentration has also contributed to destruction of stratospheric ozone (Crutzen 1994).

## 1.2 Greenhouse Gas Emissions from Agricultural Landscapes

Agricultural soils contribute approximately one-third of $CH_4$ emissions and about two-thirds of $N_2O$ emissions, either directly or indirectly (Kulshreshtha et al. 2000). The importance of these gases results impart from the relative radiative forcing potentials,

$N_2O$ and $CH_4$ are 296 and 23 times more powerful than $CO_2$, respectively (IPCC 2007). For the global agriculture industry these two greenhouse gases are of greatest importance as they account for the vast majority (>90%) of agricultural contributions to anthropogenic greenhouse gas emissions.

The Prairie Pot-hole region of North America has undulating landscape encompasses an area of 775,000 $km^2$. Prairie Pot-hole landscapes consist of relatively well drained upper and middle landscape elements and poorly drained lower elements and depressions. The depressions have stagnant water either that persists for the whole year or accumulates seasonally. The vegetation is dominated by short-grass, tall grass and mixed perennial grasses (Brenton et al. 1999). Riparian zones occur between terrestrial and aquatic environments and are known to remove large quantities of N from the vadose zone and shallow ground water (Groffman et al. 1998). The major mechanisms of N retention in riparian zones are plant uptake, denitrification and microbial immobilization. In these landscapes uncultivated lower landscape elements, often richer in soil organic carbon, emit less $N_2O$ compared to cultivated lower elements (Pennock et al. 2005). This observation results from the combined effects of land use and landform on the predominance of nitrate in cultivated lower elements (Pennock et al. 2005). $N_2O$ emissions are generally higher from lower and depression than upper landscape elements (Pennock and Corre 2001). Dunmola et al. (2010) found that hotspots of $N_2O$ and $CH_4$ emission within the landscape are localized and driven by high soil moisture and C availability, and concluded that Riparian areas should be treated separately from cropped areas as their $N_2O$ and $CH_4$ emissions are lower and higher, respectively. The greenhouse gas generating processes such as nitrification and denitrification (for $N_2O$ production), methanogenesis (for $CH_4$ production) and microbial and root respiration (for $CO_2$ production) were therefore expected to vary across the landscape as a result of the variation in soil factors such as soil moisture, soil temperature, bulk density, particle density, air-filled porosity, pH, nutrient contents in soil, which are important in controlling the extent of these processes.

## 1.3 Knowledge Gaps about Greenhouse Gas Production, Consumption and Transport within Soil Profiles as Influenced by Landscape Element and their Relation to Surface Emission

Soil-atmosphere exchange of gases is controlled by production, transport, and transformation processes. Soil temperature, moisture, and aeration are known to control these processes (Jungkunst et al. 2008). Positive effects of temperature on $CO_2$ production, $N_2O$ emission, and $CH_4$ production and oxidation are well documented (Mielnick and Dugas 2000; Avery et al. 2003). Increased temperature stimulates both $CH_4$ formation and oxidation (Prieme and Christensen 2001). Within a soil profile, there occurs a zone between gaseous production and transformation. This zone often arises from the distribution of $O_2$, moisture and substrates, and the interaction of these factors to create favorable habitats for the various microbial groups mediating these processes. Prieme and Christensen (2001) reported that the depth of maximum $CH_4$ oxidation is not in the uppermost soil layers but at 10-20 cm depth range. This depth distribution suggests that oxidation of $CH_4$ is more likely if this gas is produced in the deeper soil layers.

Rolston et al. (1991) has also reported that $N_2O$ evolved in the lower soil horizons is converted into $N_2$ before escaping into the atmosphere. Hosen et al. (2002) monitored

$N_2O$ emissions following application of urea at different depths in an Andisol and concluded that emission rates were not affected by depth of fertilizer application and distance traveled by $N_2O$ within the soil profile. Besides the depth of gas formation, conditions at the soil surface also affected the gas emissions. Accumulation of gases in the profiles of frozen (Burton and Beauchamp, 1994) and compacted (Conlin and Driessche 2000) soils has been reported and vigorous emission of gases occurred during spring-thaw. Bajracharya et al. (2000) measured higher $CO_2$ concentration and emissions in moderately and severely eroded landscapes than in slightly-eroded and depositional areas. These differences were attributed to higher soil temperatures in the erosion-impacted areas, especially during the summer.

Understanding of relationship between greenhouse gas production and surface emission requires a thorough knowledge of greenhouse gas concentration redistribution within soil profile, temporal and spatial patterns of production and soil factors influencing them. A relatively small number of subsurface studies have addressed greenhouse gas emission by measuring $CO_2$ production within the soil profile (Burton and Beauchamp 1994; Davison and Trumbore 1995; Risk et al. 2002; Jassal et al. 2005). The measurements of $CO_2$ efflux and concentrations were used to infer the depth distributions of $CO_2$ production in forest soil and less than 2% of $CO_2$ produced in soil originated from depths below 50 cm and 85% of surface emission from forest soil were originated at depths shallower than 30 cm (Drewitt et al. 2005). To my knowledge, no studies have attempted to estimate the greenhouse gas emission using concentration gradients and diffusion coefficients in topographically variable landscape. Hence, it is essential to estimate the greenhouse gas emission from concentration gradients at different depths and to compare them with the measured greenhouse gas surface emission in order to recognize exactly what proportion of greenhouse gases accumulated at depth within soil profiles are reaching atmosphere as surface emission and which soil depth greenhouse gas concentrations are related directly to surface emission.

Thawing of soil in spring can be a considerable source of annual $N_2O$ emission in temperate climates. More than 70% of the total $N_2O$ emission occurred during winter in southern Ontario (Wagner-Riddle et al. 1997). Freeze-thaw events during winter and spring are known to induce a pulse of $N_2O$ emitted at or shortly after thawing (Dorsch et al. 2004) partly attributable to release of physically trapped $N_2O$ (Burton and Beauchamp 1994) but primarily due to enhanced biological activity (Oquist et al. 2004). Studies by Teepe et al. (2004) and Muller et al. (2002) showed that a combination of high soil moisture, available N and C content were favorable for elevated $N_2O$ emission during freeze-thaw period. The results of Wagner-Riddle et al. (2008) revealed that the source of $N_2O$ burst during spring thaw was mostly the newly produced $N_2O$ in the shallow surface layer, and not by the release of trapped $N_2O$ from unfrozen soil lying below the frozen layers. Also, the phenomenon of freeze-thaw related high $N_2O$ emission events is well known, but the underlying processes and conditions that control the production of $N_2O$ are still poorly known (Rover et al. 1998). To my knowledge no studies have attempted to investigate the effect of freeze-thaw in deeper soil layers and the contribution of soil depth, soil conditions and subsurface soil processes to $N_2O$ emission in an undulating landscape. To obtain a better insight and to fill the above knowledge gaps a field experiment and a laboratory study were performed with the following objectives.

## 1.4 Thesis Objectives and Structure

The objectives of this thesis were:

1. To determine the greenhouse gas concentration profiles and surface greenhouse gas emissions from the Upper, Middle, Lower and Riparian landscape elements of an undulating Prairie Pot-hole landscape (Chapter 2).
2. To explore the relationships between subsurface profile accumulation of $CO_2$, $CH_4$ and $N_2O$, their emissions from the soil surface and soil conditions (Chapter 2).
3. To determine the effect of freeze-thaw, soil depth and landscape element on $N_2O$ production and to relate these findings to the field observations of $N_2O$ surface thaw emissions and soil $N_2O$ gas concentration profiles (Chapter 3).

Field and laboratory experiments were conducted in order to achieve the above objectives. Soil atmosphere, greenhouse gas emission, soil moisture and soil temperature from the Upper, Middle, Lower and Riparian landscape elements of an undulating agricultural landscape were monitored at monthly intervals from August 2005 to November 2005 and at weekly intervals from spring-thaw (April 2006) to post-fertilizer application period (June 2006) and again at monthly intervals from June 2006 to August 2006 periods. Soil samples were collected in May 2005 and analyzed in the laboratory for the physico-chemical properties. Soil cores were collected from all the landscape elements during winter 2006 and the cores were incubated in the laboratory and the freeze-thaw, soil depth and landscape element effects on $N_2O$ emission were determined.

Chapter 2 of this thesis presents the results of the field study examining the influence of landscape element and seasonal variation on greenhouse gas profile concentrations and surface emission and the relationship of profile greenhouse gas concentrations to surface emission and soil conditions. That chapter highlights the landscape element, depth and the periods which are significant for greenhouse gas concentrations and surface emissions, as well as the relationship between the estimated profile greenhouse gas emission and measured surface greenhouse gas emission. Chapter 3 deals with the laboratory investigation of how freeze-thaw, soil depth and landscape element affects the $N_2O$ production potential in soil. That chapter describes how the soil depth, freeze-thaw and landscape element are controlling the $N_2O$ production potential. Chapter 3 also aimed to relate the finding of the winter core incubation to the field $N_2O$ surface thaw emissions and soil $N_2O$ gas concentration profiles of Chapter 2. Chapter 4 is the overall synthesis discussing the findings of the field and laboratory experiments. This thesis as a whole attempts to contribute to our understanding of the importance and contribution of subsurface greenhouse gas concentrations towards surface greenhouse gas emission in a topographically variable landscape.

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## CHAPTER 2

## RELATIONSHIP BETWEEN GREENHOUSE GAS SOIL CONCENTRATION PROFILES AND SURFACE EMISSIONS IN A TOPOGRAPHICALLY VARIABLE LANDSCAPE

### 2.1. Abstract

A field experiment was conducted in the undulating landscape of Manitoba Zero Tillage Research Association farm to determine the association between seasonal and landscape variation in soil greenhouse gas concentration profiles, greenhouse gas surface emissions and soil conditions. Fifteen soil atmosphere and surface emission samplings were done over three periods viz., post-cropped, pre-crop/freeze-thaw and cropped period. Highest nitrous oxide ($N_2O$) profile concentrations (287.3 µL $L^{-1}$ at 15 cm depth) and highest $N_2O$ surface emission (0.1 µg N $m^{-2}$ $s^{-1}$) were recorded in the Lower landscape element. Soil methane ($CH_4$) concentrations were highest during the freeze-thaw period for the Riparian element at 15 cm depth (2,587 µL $L^{-1}$). Methane emissions were also highest in the Riparian (1.2 µg C $m^{-2}$ $s^{-1}$) landscape element. Carbon dioxide ($CO_2$) concentrations increased with depth in all the landscape elements and were highest in the Riparian element (225,000 µL L-1) at 65 cm depth and remain unchanged during freeze-thaw but elevated during the cropped period. Surface $CO_2$ emissions were highest in the Riparian element and increased during the cropped period. The oxygen ($O_2$) concentrations were highest in the Upper and Middle element and were lowest at 65 cm depth in the Riparian element. Significant correlations were found between the profile greenhouse gas concentrations and surface emissions, soil moisture and temperature at all depths in the four landscape elements. The estimated $N_2O$ and $CH_4$ profile emission

values derived from greenhouse gas profile concentrations were closer to measured chamber emission values after normalization with $CO_2$ surface emission in all elements and periods except the freeze-thaw period and further studies are required to validate this approach of calculating $N_2O$ surface emissions from profile concentrations.

## 2.2. Introduction

The concentration of the greenhouse gases, carbon dioxide ($CO_2$), methane ($CH_4$), and nitrous oxide ($N_2O$) in the atmosphere are increasing rapidly and are believed to be contributing to the warming of the earth (IPCC 2007). Nitrous oxide and $CH_4$ are 296 and 23 times more powerful in their warming potential than $CO_2$, respectively (IPCC 2007). The current atmospheric concentration of $CO_2$ is 379 ppmv which has increased from the pre-determined industrial value of 280 ppmv, the concentration of $CH_4$ is 1,774 ppbv, which is more than twice the pre-determined industrial value of 715 ppbv and the concentration of $N_2O$ in atmosphere is approximately 319 ppbv which has increased from the pre-determined industrial value of 270 ppbv and the major increase occurred within the past 10 years (IPCC 2007). The increase in atmospheric $N_2O$ concentration has contributed also to destruction of ozone in the stratosphere (Crutzen 1994). A major share of $N_2O$ and $CH_4$ emissions to the atmosphere is contributed by soils. About one third of $CH_4$ and two-thirds of $N_2O$ emissions to the atmosphere originate from agricultural soil (Prather et al. 1995). Nitrous oxide is primarily emitted from agricultural soils and more than 65% of the atmospheric $N_2O$ comes from soil as a result of nitrification and denitrification processes (Bouwman 1994). Nitrous oxide is produced in soils by bacteria through nitrification in aerobic conditions and through denitrification in anaerobic conditions. These processes are regulated by several soil physical, chemical and biological factors and their interaction. Soil moisture, temperature, mineral N and organic C contents and soil texture are among the most important regulators governing greenhouse gas emission from soils (Smith et al. 1998; Skiba and Ball 2002).

The undulating landscapes of the Prairie Pot-hole region of North America encompass an area of 775,000 $km^2$. Landscapes in the Prairie Pot-hole region are typified by relatively well drained upper and middle landscape elements and poorly drained lower elements and depressions. The depressions have stagnant water either all the time or seasonally and are dominated by short-grass, tall grass and mixed perennial grass vegetation (Brenton et al. 1999) and some depressions can be cropped. Upland soils are an important global sink for methane, consuming nearly 30 Tg of $CH_4$ per year (IPCC 2007). Riparian zones occur between terrestrial and aquatic environments and are known to remove large quantities of N from shallow ground water (Groffman et al. 1998). The major mechanisms of N retention in riparian zones are plant uptake, denitrification and microbial immobilization. The soil in these zones is predominantly anaerobic and contains high amounts of organic matter resulting in conditions conducive to denitrification. The uncultivated lower landscape elements which are often richer in soil organic carbon emit less $N_2O$ compared to cultivated lower elements, illustrating the effect of land use on landform patterns and the predominance of nitrate in cultivated lower elements (Pennock et al. 2005). Nitrous oxide emissions are generally higher from lower and depression than upper landscape elements (Pennock and Corre 2001). Dunmola et al. (2010) found that the hotspots for $N_2O$ and $CH_4$ emission within the landscape are localized and driven by high soil moisture and C availability, and concluded Riparian areas are distinct from cropped areas as their $N_2O$ and $CH_4$ emissions are lower and higher, respectively.

Methane is produced in the anaerobic zones of submerged soils by methanogens and is oxidised into $CO_2$ by methanotrophs in the aerobic zones of wetland soils and in upland soils (Le Mer and Roger 2001). Liblik et al. (1997) reported that the concentration of $CH_4$ in saturated peat was 6,000 times higher than the atmospheric concentration and the production of $CH_4$ in soil was strongly influenced by the quality and amount of substrate, pH and temperature. An environment is a $CH_4$ source when the balance between production by methanogenic bacteria and consumption by methanotrophic bacteria is positive, leading to $CH_4$ emission. When the balance is negative, the environment is a $CH_4$ sink.

In tropical and temperate forest soils, land use change had a greater impact on the $CH_4$ sink because these land use changes had both direct and indirect effects on the soil physical, chemical and biological properties (Dobbie and Smith 2001). Methane oxidation occurred very rapidly in coarse-textured soils with well developed soil structure and surface organic layer through which the gases could diffuse easily to the atmosphere (Smith et al. 2004). About 30 Tg of atmospheric $CH_4$ per year were oxidized to $CO_2$ by aerobic soil bacteria which were capable of living on a very small amount of substrate (Prather et al. 1995). Most published results of $CH_4$ concentration and emissions are for peat systems (Potter et al. 1996; Smith et al. 2004), whereas a limited number are available for $CH_4$ emissions from agricultural soils in undulating landscapes and also a little is understood of the distribution of $CH_4$ within soil profiles in undulating landscapes. Hence, it is essential to determine the depth distribution pattern of $CH_4$

concentrations within the soil profile to understand the relationship between subsurface $CH_4$ concentrations, soil conditions and surface $CH_4$ emissions.

The concentration of $CO_2$ in soil is much higher than in the atmosphere as a result of production of $CO_2$ in the soil by plant roots and microbial respiration (Jassal et al. 2004; Oh et al. 2005). Soil moisture and temperature were found to influence subsurface $CO_2$ concentration because of the relationship between moisture and soil-profile gas diffusivity (Risk et al. 2002). The diffusivity of $CO_2$ in soil is a function of air-filled porosity, which in turn is controlled by soil bulk density and volumetric moisture content. Thus, both soil $CO_2$ concentrations and surface emissions were regulated by the production and transport of $CO_2$ within the soil and were therefore interdependent (Jassal et al. 2005). Several soil studies of $CO_2$ concentration profiles have been conducted in forest and pasture sites in eastern and western Canada (Risk et al. 2002; Jassal et al. 2004; Kellman et al. 2007; Bekele et al. 2007), whereas none have been conducted in undulating agricultural landscapes of the Prairie Pot-hole region.

The variability in environmental conditions such as temperature, water regime, availability of oxygen and energy sources, and the microbial community composition all likely influence the source or sink function describing the greenhouse gas production and consumption processes (nitrification, denitrification, methanogenesis, methane oxidation, decomposition, and respiration) in undulating landscapes. Greenhouse gas production and consumption processes such as nitrification ($N_2O$ production), denitrification ($N_2O$ production and consumption), methanogenesis ($CH_4$ production), methanotrophy ($CH_4$ consumption) and microbial and root respiration ($CO_2$ production) are therefore expected to be variable within the landscape as a result of variability in soil factors (soil moisture, soil temperature, bulk density, particle density, air-filled porosity, pH, nutrient contents in soil) which govern these processes. Hence, examining variation in these factors might allow us to better understand how the landscape variation and depth distribution of production, consumption and transport of these gases influences their emission from the soil surface of topographically variable landscapes.

Greenhouse gases are produced near the soil surface as well as in the subsurface soil extending to parent material including ground water (Rice and Rodgers 1993). In a soil profile, the production, consumption and transport of $N_2O$ gases within soil layers are interconnected to each other and they interact to create changes in $N_2O$ concentration within the soil profile (Hojberg et al. 1994). The production of $N_2O$ in soils is continuous, and is expected to occur in a short span of time (Mosier et al. 1991). Nitrous oxide is produced and consumed continuously in non-frozen soil profiles and this may be produced and accumulated at one site and can be transported to other sites either by upward, lateral or downward movement (Rice and Rodgers 1993).

The emission of $N_2O$ from the soil surface depends mainly on the concentration of $N_2O$ within shallow and deeper soil profiles. If only the sporadic surface gas emission measurements were taken into consideration, then some significant portion of $N_2O$ may be missed that occurred in deeper layers, which could have resulted in underestimation of $N_2O$ (Bowden et al. 1991). Thus measurement of the $N_2O$ concentration gradient in the soil profile should be done to assess the complete $N_2O$ emission (Burton and Beauchamp 1994). Most studies have shown that $N_2O$ concentrations in the soil profile were greater than in the atmosphere and recorded a larger accumulation of $N_2O$ in the lower profiles (Li et al. 2002; Tenuta and Beauchamp 2000). Wagner-Riddle et al. (2008) found that the source of $N_2O$ burst during spring thaw was mostly the newly produced $N_2O$ in the shallow surface layer, and not by the release of trapped $N_2O$ from unfrozen soil lying below the frozen layers. Hence it is imperative to determine the site or depth of $N_2O$ production and accumulation within the soil profile and which soil conditions and processes are altering the $N_2O$ production, consumption and transport within the soil profile before it escapes to the atmosphere as surface emission.

Gaseous movement in soil profiles has been quantified by calculating the diffusive emission from soil gas concentration gradients. In gaseous movement studies, oxygen and carbon dioxide have received greatest attention, but diffusive transport studies of $N_2O$ and $CH_4$ in soil are limited (Rolston et al. 1991). There has been past research efforts directed at investigating greenhouse gas emissions based on greenhouse gas concentration data, which measures the gas diffusion in response to the concentration gradient as described by Fick's law. The gas diffusion coefficient in soil and its variations with soil type and soil air-filled porosity typically control the soil aeration, soil uptake or emission of greenhouse gases (Kruse et al. 1996). Most of the models predicting gas diffusion coefficients (Steele and Nieber 1994; Moldrup et al. 1999) take into account the soil physical characteristics such as pore-size distribution and include several empirical and soil-type-dependent constants.

Low diffusivity can limit gas movement and result in higher accumulation of greenhouse gases in the subsurface and differences in greenhouse gas emission occurs as a result of production change within soil and as a result of variation in soil moisture, organic matter content, temperature, and pH. When emissions were estimated at the surface without identifying the production site within soil profiles, a significant portion may be missed if consumption or other transport process modifies subsurface produced gas on its way to the soil surface. Understanding the relationship between greenhouse gas production and surface emission requires a thorough knowledge of greenhouse gas concentration redistribution within the soil profile, temporal and spatial patterns of production, and soil factors influencing them. A relatively small number of subsurface studies have addressed greenhouse gas emission by measuring $CO_2$ production within the soil profile (Burton and Beauchamp 1994; Davison and Trumbore 1995; Risk et al. 2002; Jassal et al. 2005). The measurements of $CO_2$ emission and concentrations were used to infer the depth distributions of $CO_2$ production in forest soil. Less than 2% of $CO_2$ produced in soil originated from depths below 50 cm and 85% of surface emission from forest soil originated at depths shallower than 30 cm (Drewitt et al. 2005). To my knowledge, no studies have attempted to estimate greenhouse gas emissions using concentration gradients and diffusion coefficients in topographically variable landscapes.

Furthermore, to date, no published studies have attempted to integrate detailed information on the subsurface physical environment with subsurface greenhouse gas concentrations, so relatively little is known about subsurface relationships among temperature, moisture and the subsurface greenhouse gas concentration and its influence on surface emission in a topographically variable landscape. Detailed information on the landscape pattern of the profile greenhouse gas concentrations in a complex topography is also lacking. This information is vital where huge variability in soil conditions and factors within the landscape can potentially have serious implication for greenhouse gas emissions. Also, topography which is a critical factor modifying both the microclimatic and hydrologic conditions of a landscape has important implications for greenhouse gas processes within a landscape (Pennock et al. 1994).

This study was carried out to investigate the relationship between soil profile concentrations of greenhouse gases ($N_2O$, $CH_4$ and $CO_2$) to soil conditions and surface emission in a topographically variable landscape. The objectives of the study were to determine, (i) the pattern of greenhouse gas profile concentrations in Upper, Middle, Lower and Riparian landscape elements, (ii) the seasonal patterns in greenhouse gas concentration profiles and whether the buildup in concentrations over winter occur at depth or at surface (iii) determine the relationship between subsurface greenhouse concentrations to soil conditions and (iv) determine the relationship between subsurface greenhouse gas profile concentrations to the measured and estimated surface emissions.

## 2.3 Materials and Methods

### 2.3.1 Site Location and Description

An experimental field site was located at the Manitoba Zero Tillage Research Association farm, 19 km north of the city of Brandon, Manitoba, Canada ($49^{0}55'$ N, $99^{0}57'$ W, 500-m above sea level). The site is situated within the Aspen Parkland of the Prairies Eco-region of South-West Manitoba, and part of the Prairie Pot-hole region of North Central North America. The landscape of the site is undulating to hummocky with a gentle slope of 2 to 5 per cent and the predominant soil at the site mapped as a Newdale Clay Loam series, being a Black Chernozem formed over calcareous glacial tills (Podolsky and Schindler, 1993). Zero-tillage was adopted in 1992 and the major crops grown alternatively at the site were Canadian Prairie spring wheat (*Triticum aestivum*), flax (*Linum usitatissimum*), alfalfa (*Medicago sativa*), field peas (*Pisum sativum L.*) and canola (*Brassica napus*).

In 2005, the experimental site was planted to Canadian Prairie spring wheat (variety 5701) and the wheat received 74 kg $ha^{-1}$ total N in the form of 28-0-0 urea-ammonium-nitrate (UAN 67 kg N $ha^{-1}$) and 11-52-0 mono-ammonium phosphate (7 kg N $ha^{-1}$) at planting. In 2006, the field was planted to flax (variety Bethune), and the flax received 27 kg $ha^{-1}$ total N as 28-0-0 urea-ammonium-nitrate. In 2005, the mono-ammonium phosphate fertilizer was applied with the seeds whereas, the UAN solution was side-dribbled on the soil surface adjacent to the seed row in both years.

### 2.3.2 Position of Sampling Points

A transect of 444.5 m was established in the experimental field site in the fall of 2004. The transect consisted of 128 sample positions having collars for static-vented chambers installed at 3 m intervals. The transect was oriented to the northwest direction. The transect was set up for a study of wave-let analysis of $N_2O$ emissions with results to be reported elsewhere (principle investigator, Dr. David Lobb). The static-vented chambers were used to determine surface gas emissions. The transect moved through the common landscape elements of Upper, Middle, Lower and depression (cropped and non-cropped Riparians). The approximate co-ordinate distance of the transect was 433141E, 5544815N for the Northwest end and 433517E, 5544582N for the Southeast end. The whole transect was divided into three catenas referred to as section 1, 2, and 3. Each section had a distinct Upper, Middle, Lower and Riparian landscape element.

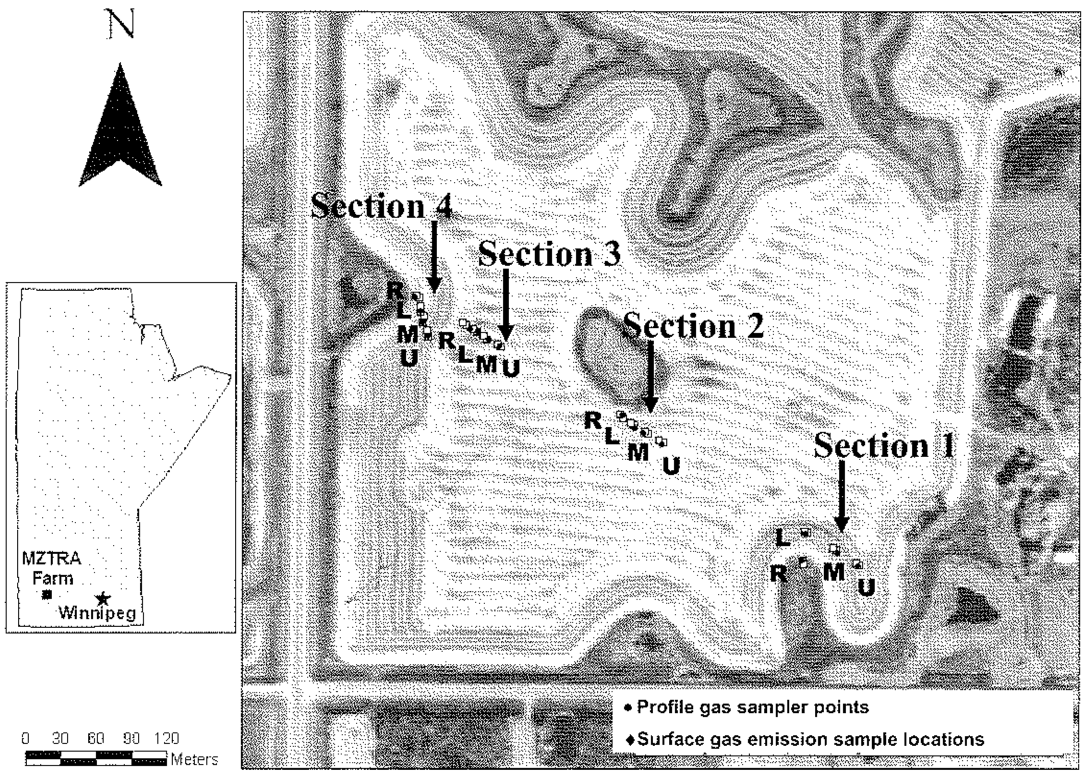


**Figure 2.1** Air photo of the experimental field site at the Manitoba Zero Tillage Research Association Farm (MZTRA) showing the location of catena sections and landscape element positions of the profile gas samplers and sample positions for determining surface gas emissions. The map to the left shows the situation of the site in Manitoba and respective to the City of Winnipeg.

The Riparian landscape element in Section 1 was located off the transect. A fourth section was added at the Northwest end of the transect being a catena from Upper, Middle, Lower to Riparian element (Fig. 2.1). The altitude variation between Upper and Riparian landscape elements ranged between 0.43 and 2.3m. The dominant plant species found in the Riparian element at the Manitoba Zero Tillage Research Association farm were *Typha glauca, Cirsium arvense, Sonchus arvensis, Aster simplex, Hordeum jubatum, Juncus balticus, Carex atherodes* and *Solidago canadensis* (Dunmola 2007).

### 2.3.3 Soil Gas Profile Determinations

The soil gas sampler of Kammann et al. (2001) was used for collecting soil atmosphere. The samplers were made of 18 cm long polyvinyl chloride pipe (Wolseley Plumbing Supply, Winnipeg, MB) of 1.9 cm i.d. with 0.5 cm diameter holes drilled on all sides and containing a 13 cm long peroxide cured silicone tubing (Cole-Parmer Canada, Anjou, QC) of 1.3 cm i.d and 2.4 mm thick wall allowing gases, but not water, to diffuse through. Stainless steel tubing (Winnipeg Fluid System Technologies Inc., Winnipeg, MB) of 0.16 cm i.d. and 0.05 cm wall thickness was inserted into the top of the silicone tubing and was sealed in place using a rubber serum stopper (Suba Seal, #13; Sigma-Aldrich Canada Ltd, Oakville, ON) and sealed with Mastercraft Window and Door Silicone (Canadian Tire Corp.) and Marine Fix Fast Epoxy 2-part Paste (Canadian Tire Corp.). The length of the stainless tubing ranged from 40 to 85 cm depending on the depth of the probe. A Swagelok® fitting 1/4 to 1/8 " reducing union (Winnipeg Fluid System Technologies Inc.) fitted with a 0.95 cm (3/8") M-9 rubber septa (Alltech Canada, Mandel Scientific, Guelph, ON) was inserted onto the end of the stainless steel tubing to serve as a gas sample port. The gas samplers were installed at four depths (5 cm, 15 cm, 35 cm and 65 cm). The samplers were installed into the wall of each soil pit by inserting into holes drilled using an auger drill bit. Each pit was refilled with the soil from the same depth. The profile gas probe sampling ports were buried into the soil (Fig. 2.2) and covered with protective wooden boards during major field operations (seeding, fertilizer application, herbicide application and harvesting) and reinstated to the surface after each operation.

The equilibration time for the profile gas sampler containing 2.4 mm wall thickness silicone tubing was less than 12 hours, which was previously reported by Jacinthe and Dick (1996). Soil atmosphere was collected from August 2005 to November 2005 at monthly intervals, then from March 2006 to May 2006 at weekly intervals and then once again monthly in June, July and August 2006.

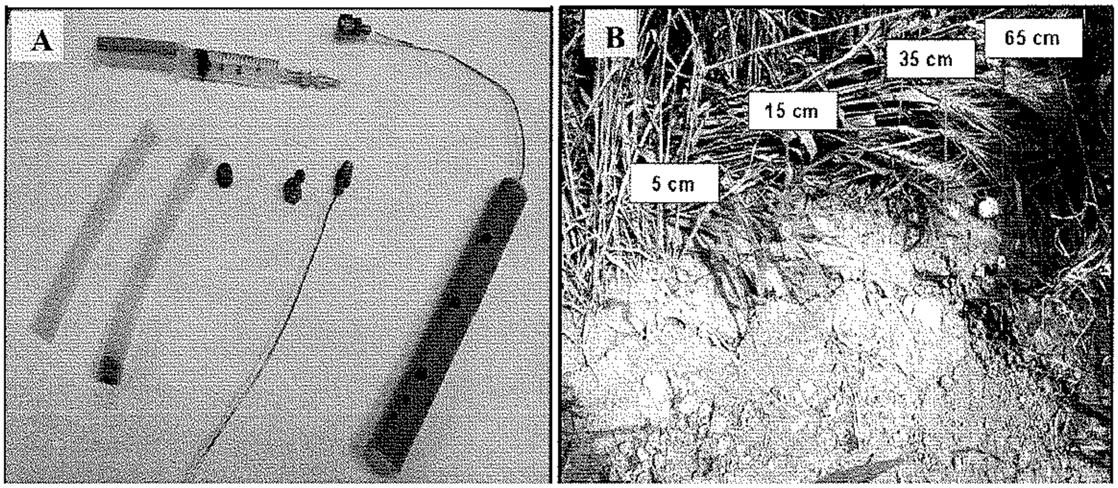


**Figure 2.2** Soil gas samplers for greenhouse gas profile determination; A) its components and gas sampling syringe and B) samplers after installation in profile pits at different depths.

Soil atmosphere was sampled from each gas sampler as well as at the soil surface. The soil atmosphere was collected using a 20-mL Becton-Dickinson syringe (Fisher Scientific Canada, Edmonton, AB), fitted with Becton-Dickinson 23G-2.5 cm needles (Fisher Scientific Canada), and attached to a one-way luer valve (Cole-Parmer Canada). The valves were turned to the "flow" position and the syringe was placed into the gas probe. A 1-mL sample was taken from the gas sampler and then expelled to flush the tubing and sample port dead space. The syringe was reinserted into the sample port and the syringe plunger pulled to the 20-mL mark. A wooden dowel was placed to prevent the syringe plunger from dropping due to the suction created within the gas sampler and allow the gas from the samplers to flow into the syringe. After approximately five minutes, the luer-valve was turned to the "off" position, the wooden dowel removed, the plunger allowed to drop, and the syringe removed from the sample port. The valve was then turned to the "flow" position and a 10-mL of gas sample was placed into 6-mL Exetainer® vials (Labco Ltd., Buckinghamshire, England). Whenever there was less than 10 mL of gas sample (but greater than 4 mL) evacuated 3 mL Labco Exetainer® gas vials were used to store the gas sample.

Surface gas was collected (2.5 cm above ground surface) using the same 20 mL Becton-Dickinson syringe and 25G PrecisionGlide® needle and injected into an evacuated 6 mL vial. All vials used were previously evacuated and flushed three times with helium gas to a final evacuated pressure of less than 400 millitorr. The vials were over-pressurized with sample gas to ensure the gas samples enter into the gas chromatograph syringe without the surrounding air contaminating the sample upon sampling of vials. The septa of the Exetainer vials that had been evacuated had their septa covered with Mastercraft Kitchen and Bath Silicone (Canadian Tire Corp.) before evacuating to maintain an air-tight seal. The integrity of the gas samples during storage was insured by means of low and high standard gas samples (Welders Supplies, Winnipeg, MB) prepared, transported to field and returned to the laboratory for analysis along with the gas samples. The low standard gas sample was 193 ppmv $CO_2$, 1.8 ppmv $CH_4$, 0.35 ppmv $N_2O$, 5% $O_2$ and balance $N_2$ whereas, the high standard gas was 2,980 ppmv $CO_2$, 4.5 ppmv $CH_4$, 0.46 ppmv $N_2O$, 15% $O_2$ and balance $N_2$.

### 2.3.4 Surface Gas Emission Determinations

The surface gas emissions of $N_2O$, $CH_4$ and $CO_2$ from the Upper, Middle, Lower and Riparian landscape elements were determined using a modified static-vented chamber technique of that presented by Hutchinson and Livingston (2002). The static-vented chamber had a circular collar (base), made of white polyvinyl chloride, with an internal diameter of 14.7 cm and a total length of 7.5 cm, with 3 cm of this length driven into the soil through a beveled edge. Covers made of pipe caps were fitted with a rubber-septum sampling port and a vent to ensure that the pressure inside the chamber is in equilibrium with the atmospheric pressure. The collars were held firmly into the soil by means of three 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 lids were made of white polyvinyl chloride 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 covers were placed on the pre-installed collars at the start of gas sampling, and removed after sampling was finished. The total volume occupied by the chamber after placing the cover was 3.81 L, and a smear of grease at the collar-cover interface ensured the chamber was air tight. One position with a static-vented chamber was used at each landscape element of the four field sections during the year 2005, whereas, in 2006 two positions with static-vented chambers were used for surface gas emission determinations.

Headspace gas of chambers (20 mL) was removed at 0, 9, 18 and 27 minutes, using a PrecisionGlide® needle (25G, 5/8") fitted to a 20 mL disposable Becton Dickinson Syringe (Fisher Scientific Canada), and injected into a pre-evacuated 12 mL

Labco Exetainer® gas vials. The gas samples were transported to the laboratory and stored at room temperature until they were analyzed.

### 2.3.5 Gas Analyses

Gas samples collected from chambers and soil profiles were analyzed for $N_2O$, $CH_4$ and $CO_2$ using a gas chromatograph (Varian CP3800; Varian Canada, Mississauga, ON) equipped with an electron capture detector for $N_2O$, flame ionization detector for $CH_4$ and thermal conductivity detector for $CO_2$ and the detectors operated at 300, 250 and 220$^0$C, respectively. The gas chromatograph was equipped with a CombiPAL™ auto-sampler (CTC Analytics AG., Zwingen, Switzerland). A total volume of 2.5 mL of gas sample was removed from each vial by the auto-sampler and injected into the gas chromatograph. The auto-sampler injected a gas sample into the sampling valve, which then transfered the sample to two, 0.5 mL sample loops. One loop introduced the sample to a 80/100 mesh Porapak N pre-column (0.4572 m × 3.18 mm i.d. for $CO_2$ gas analysis; Sigma-Aldrich/Supelco, Mississuaga, ON) and the other introduced the sample to a 80/100 mesh Porapak QS column (1.83 m × 3.18 mm i.d. for $CH_4$ gas analysis; Sigma-Aldrich/Supelco) using He as the carrier gas. Carbon dioxide was then determined using a thermal conductivity detector with a filament temperature of 220°C and $CH_4$ was determined using a flame ionization detector maintained at 250°C. For $N_2O$ analyses, the sample was introduced to a 80/100 mesh HayeSep D column (1.83 m × 3.18 mm i.d.; Sigma-Aldrich/Supelco) using a Ar:$CH_4$ mixture (90:10; flow rate = 30 mL $min^{-1}$) as a carrier gas and $N_2O$ detected using a $^{63}$Ni-electron capture detector. Peak areas were quantified by comparing sample peak areas with laboratory prepared standards from pure gas and laboratory determined concentration of custom mixed standard.

The soil surface emission of gas was calculated from the gas concentration, molecular mass of N or C in the gas of interest, chamber area and volume, air temperature at sampling and atmospheric pressure using the Ideal Gas Law (PV=nRT). The gas emission for each chamber was determined by fitting a linear regression line of best fit through three of the four sampling points in time, removing any outliers to achieve a minimum $r^2$ of 0.85. Values for gas emission were reported as $\mu g\ m^{-2}\ s^{-1}$ with positive values being an emission of gas from soil to atmosphere. Surface emission values used were previously reported by Dunmola (2007).

The oxygen concentrations of soil profile gas samples were also determined. Analysis was done using a micro gas chromatograph (Varian CP4900, Varian Inc., Mississauga) by injecting 1 mL of profile gas sample into the injection port using a 1 mL gas-tight glass syringe (Alltech Canada, Mandel Scientific). The micro gas chromatograph was fitted with a thermal conductivity detector operated at $150^0$C and the sample run time was 3.5 minutes. In between two consecutive samples, 1 mL of lab air was injected to purge residual gas sample in the injection port. Calibration of the micro gas chromatograph was done using commercial custom mixed standards containing 9.96% and 15% $O_2$ (Welders Supplies), atmosphere (20.8% $O_2$) and helium (0% $O_2$). The standards were treated as gas samples being stored in Exetainer® vials and 2.5 mL gas sample was removed prior to analysis for $O_2$.

### 2.3.6 Soil Moisture and Soil Temperature Determinations

Soil monitoring stations were set up in each section and landscape element. Monitoring stations were installed first by digging a pit in spring 2005 down slope from the transect at one landscape element in each of the four sections. Section 1 did not go through a Riparian area, thus a pit was dug in a Riparian element close to the transect. Each monitoring station consisted of profile gas sampler, soil moisture probes (CS616-L water content reflectometer), and temperature probes (thermocouples). Soil samples were taken from pits for determination of soil profile characteristics that could influence greenhouse gas profile concentrations and greenhouse gas production, consumption and transport processes.

In 2006, soil moisture and soil temperature were recorded in all soil monitoring positions to determine how these environmental factors alter the production, consumption and transport of greenhouse gases within soil profiles to the soil surface. Soil temperatures were recorded at 5, 15, 35 and 65 cm depths using thermocouples constructed of copper-constantan (Type T; Cole-Parmer)) embedded into 1" o.d. polyvinyl chloride tubes. Soil volumetric moisture content was determined using CS616-L water content reflectometer (Campbell Scientific Canada, Edmonton, AB) at 15 and 35 cm depths. The soil volumetric moisture content at 0-5 cm depth was measured manually using a Delta-T WET Sensor (Delta-T Devices Ltd., Cambridge, England) at time of gas collection.

Each section had one datalogger station for recording soil moisture and temperature profiles. All the datalogger stations (CR10X and Multiplexer AM16/32, Campbell Scientific Canada) were programmed to record soil moistures and temperature once an hour. The station in section 2 also recorded meteorological conditions using a weather station (Campbell Scientific Canada; rain using a Texas Electronics TE525M tipping bucket gauge, wind speed and direction using a 5103 R.M. Young Wind Monitor, relative humidity and air temperature using a shielded Vaisala HMP45C probe, and photosynthetically active radiation using a LI190SB Li-Cor sensor) and reported average conditions every hour. In 2005, soil volumetric moisture contents and temperature were recorded by soil monitoring stations in sections 3 and 4 only.

The Lower and Riparian landscape elements had salinity and high organic matter which resulted in very high and unreliable measurement of volumetric moisture content. Hence, calibration of CS616-L water content reflectometer probes was done for these high saline and organic matter rich Lower and Riparian landscape elements by determining manually the gravimetric moisture contents of soils at different depths (10-20 and 30-40 cm) during different time periods and calculating the volumetric moisture content using gravimetric moisture content and bulk density. Then the determined volumetric moisture contents were plotted against CS616-L recorded volumetric moisture content and finally calibrated values were obtained by fitting into the regression equation.

### 2.3.7 Soil Analysis

In spring 2005, soil samples were collected from all the profile pits at 0-10, 10-20, 30-40 and 60-70 cm depths prior to installation of gas samplers. Samples were analyzed for pH, electrical conductivity, particle density, texture, 0.5M $K_2SO_4$ extractable $NH_4^+$, $NO_3^-$ and extractable dissolved organic carbon, total organic carbon and water soluble $SO_4^{-2}$. Bulk density measurements were done by removing soil cores using small metallic rings at 0-5, 10-15, 30-35 and 60-65 cm depths. The metal rings had a volume of 90.5 $cm^3$ and the soils extracted from the rings were dried at $105^0C$ for 24 hours.

pH and electrical conductivity of profile soil samples were determined using 1:2 soil-water suspension and the same water extract used for $SO_4^{-2}$ determination. The $NO_3^-$, and extractable $NH_4^+$ nitrogen and extractable dissolved organic carbon contents of the soil cores were determined by extracting 5g of soil with 25mL of 0.5M $K_2SO_4$ solution. The mixture was shaken for 30 minutes and centrifuged at 3000 rpm (1,560 X *g*) for 1.5 minutes and the clear supernatant (10 mL) was transferred into a labeled scintillation vial. The extracts were kept at -20 rather than $5^0C$ if not analyzed within a week after extraction. Texture of the soil samples was determined following the procedure outlined by Loveland and Walley (1991). The particle density of all the depth soil samples was determined using the pycnometer method (Blake and Hartge 1986). Gravimetric moisture contents of soil samples were also determined by drying soil for 24 hours at $105^0C$. The $NO_3^-$, and $NH_4^+$ nitrogen and extractable dissolved organic carbon were determined colorimetricaly by the automated cadmium reduction (Method No. 4500-$NO_3$ (F)), phenate (Method No. 4500-$NH_3$ (G)) and persulfate-ultraviolet oxidation (Method No. 5310 (C)), respectively, using a Technicon™ Autoanalyzer II system (Pulse Instrumentation Ltd., Saskatoon, SK).

Total organic carbon content of soil samples was determined using a TruSpec Carbon/Nitrogen Determinator (LECO Instruments Ltd., Mississauga, ON). 0.25g of air-dried and pulverized soil samples were placed inside small tin capsules for analysis. The organic carbon content of the soil samples was determined by the modified Walkley-Black method. The carbonates content in soil samples were determined by the method outlined by Horvath et al. (2005) and the $SO_4^{-2}$ concentration of water extracts was determined using an ICS 1000 – Ion Chromatography System (Dionex Canada Ltd., Oakville, ON).

### 2.3.8 Estimation of Soil Gas Diffusivity and Surface Emission from Profile Gas Concentrations

The diffusivity and surface emission were estimated from profile gas concentrations by following the steps outlined by Burton et al. (1997). Gaseous diffusion is the major process involved in the exchange of gas between soil and atmosphere (Troeh et al. 1982) and the emission of a given gas can be described under steady-state conditions by Fick's law. Also, when the net primary direction of gas emission from soil is vertical, then the gas concentrations measured at different depths along the vertical axis provide an estimate of the concentration gradient driving the emission. At steady state and in the case of one dimensional diffusion, Fick's law of flux density can be rewritten as a function of diffusion coefficient D, concentration gradient and distance (Campbell 1985).

$$q = D\,(c_2 - c_1)/(x_2 - x_1) \qquad \text{(Eq. 1)}$$

where , $c_1$ = concentration at depth 1 ($\mu g\ m^{-3}$), $c_2$ = concentration at depth 2 ($\mu g\ m^{-3}$), $x_1$ = depth 1 (m) and $x_2$ = depth 2 (m), depth 1 < depth 2.

Gas diffusivity has been estimated as a function of $D_0$ (gas diffusion coefficient in free air) and $\varepsilon\ (\phi_g)$ (air-filled porosity function, Campbell 1985).

$$D = D_0\ \varepsilon\ (\phi_g) \qquad \text{(Eq. 2)}$$

The gas diffusion coefficient in free air ($D_0$) is dependent upon temperature ($T$: °C) and pressure ($P$: kPa):

$$D_0 = D_{std}[(T + 273)/273]^n (101.3/P) \qquad \text{(Eq. 3)}$$

where, $D_0$ is the gas diffusion coefficient in free air, and $D_{std}$ is the gas diffusion coefficient under standard conditions. The value of $D_{std}$ for $CO_2$ is $1.39 \times 10^{-5}$ $m^2 s^{-1}$, $N_2O$ is $1.43 \times 10^{-5}$ $m^2 s^{-1}$, $CH_4$ is $1.86 \times 10^{-5}$ $m^2 s^{-1}$ and $n$ is a constant. n = 2 for $N_2O$ and $CH_4$ and n = 1.75 for $CO_2$ (Campbell 1985).

The air-filled porosity function $\varepsilon(\phi_g)$ was defined by Currie (1965) and given as

$$\varepsilon(\phi_g) = b(\phi_g)^m \qquad \text{(Eq. 4)}$$

where as, $(\phi_g)$ = air filled porosity ($m^3 m^{-3}$), b = Campbell pore size distribution index, m = curve fitting parameter and the values of 'b' and 'm' changes from soil to soil as the tortuosity, porosity and water retention characteristics of soil varied with texture.

**Table 2.1** Campbell pore size distribution index and curve fitting parameter of different soil textures

| Texture | 'b' value | 'm' value |
|---|---|---|
| Clay loam | 8.7 | 3 |
| Sandy clay loam | 11.6 | 3 |
| Loam/Loamy sand | 4.6 | 3 |
| Silty clay loam | 0.81 | 3 |
| Clay | 14.1 | 3 |
| Silty clay | 0.92 | 1.7 |
| Silty loam | 0.9 | 2.36 |

The 'b' and 'm' values used to estimate the air-filled porosity function in the present study were those reported by Campbell (1985) and Moldrup et al. (2001). Air-filled porosity was determined from bulk density and particle density at each monitoring station and depth and from volumetric moisture at the time of sampling.

Gas flux estimates were derived from profile concentrations over the depth intervals of 0-5, 5-15 and 15-35 cm and then compared to surface emission measured on the same day using static vented chambers. The diffusion coefficient 'D' was calculated for each depth using the equation $D = D_0 \, b \, (\phi_g)^m$. The average values of '$D_0$' at 5 and 15 cm and 15 and 35 cm were used for diffusion coefficient determination at 5-15 cm and 15-35 cm, respectively. The same depth volumetric moisture content and temperature averages were also used to determine the gas diffusion coefficient in free air ($D_0$). The volumetric moisture content and temperature recorded at the gas sampling time i.e, 2:00 PM was used for '$D_0$'determinations.

The profile concentration emissions generated using profile concentrations were very high and unreasonable. Thus the relationship between $CO_2$ concentration profiles and surface $CO_2$ emissions was used to provide an *in situ* estimate of diffusivity. $CO_2$ can be considered as a more conservative tracer than $CH_4$ or $N_2O$ as it is less dramatically influenced by consumption processes in aerobic subsurface soil (Risk et al. 2002). The relationship between $CO_2$ profile concentration and surface flux of $CO_2$ was used to estimate the diffusion coefficient. These in situ estimates of diffusivity were applied to gaseous profile concentration to estimate surface emissions.

### 2.3.9. Statistical Analyses

Statistical analyses of all data were done by Proc Generalized Linear Model using the statistical analysis software package (SAS Institute Inc., Ver 9.1, Cary, NC). The basic design was randomized complete block design with 'Site' as block and 'Landscape Element' as treatments applied to units within each block. Landscape element, depth and sampling time were considered as fixed effects and site as a random effect. Analysis of variance was performed on log- transformed concentration ($CO_2$) data (to pass the assumptions of analysis of variance) and untransformed data ($N_2O$ and $CH_4$). The differences in concentrations among depths and landscape elements were evaluated with sampling dates considered as repeated measures. Means among different treatments (landscape element, depth and sampling time) were compared using the least significance difference test at $\alpha = 0.05$. Coefficients of variation were calculated and reported to indicate the relative measures of variability. The association of $N_2O$, $CH_4$ and $CO_2$ emissions to profile greenhouse gas and oxygen concentrations and soil parameters was tested using Spearman rank correlation analysis.

## 2.4 Results

### 2.4.1 Soil Conditions

The soil characteristics such as pH, electrical conductivity, texture, bulk density, particle density, ammoniacal and nitrate nitrogen contents, organic carbon, carbonates and sulfate concentrations all differed with depth and the distribution pattern with depth differed among the four landscape elements (Table 2.2). Soil pH generally increased with depth in all the Upper, Lower and Riparian landscape elements. Highest salinity was observed in the Riparian elements. The electrical conductivity decreased with depth in the Lower and Riparian landscape elements. In the Upper and Middle landscape element the electrical conductivity was low and inconsistent with depth. The texture at shallow depth in all the landscape elements ranged from clay loam to loam whereas, at lower depths the texture ranged from clay loam to sandy clay loam or silty clay loam.

**Table 2.2** Physical and chemical characteristics of soil samples collected from soil profiles in different landscape elements at the field site

| Landscape Element | Depth (cm) | pH ($H_2O$) | Electrical Conductivity (m S cm$^{-1}$) | Texture: Sand (%) | Silt (%) | Clay (%) | Textural class | *Bulk density (Mg m$^{-3}$) | Particle density (Mg m$^{-3}$) |
|---|---|---|---|---|---|---|---|---|---|
| Upper | 0 – 10 | 7.4 (0.1) | 0.26 (0.06) | 36 (3) | 32 (4) | 32 (3) | CL to L | 1.29 (0.03) | 2.22 (0.05) |
| | 10 – 20 | 7.5 (0.2) | 0.23 (0.05) | 35 (2) | 30 (2) | 35 (1) | CL | 1.29 (0.06) | 2.29 (0.05) |
| | 30 – 40 | 7.7 (0.2) | 0.22 (0.04) | 36 (1) | 33 (1) | 31 (2) | CL | 1.27 (0.03) | 2.34 (0.05) |
| | 60 – 70 | 7.8 (0.4) | 0.29 (0.08) | 38 (8) | 36 (5) | 26 (5) | SCL to SiCL | 1.29 (0.08) | 2.38 (0.05) |
| Middle | 0 – 10 | 7.6 (0.2) | 0.19 (0.02) | 37 (4) | 31 (4) | 32 (2) | CL | 1.25 (0.03) | 2.26 (0.05) |
| | 10 – 20 | 7.7 (0.2) | 0.18 (0.02) | 33 (3) | 34 (2) | 33 (4) | CL to C | 1.33 (0.04) | 2.27 (0.01) |
| | 30 – 40 | 7.5 (0.1) | 0.32 (0.12) | 27 (4) | 37 (2) | 36 (3) | CL to SiC | 1.36 (0.06) | 2.30 (0.03) |
| | 60 – 70 | 7.7 (0.2) | 0.45 (0.13) | 33 (5) | 30 (3) | 37 (1) | CL to L | 1.21 (0.05) | 2.35 (0.03) |
| Lower | 0 – 10 | 7.4 (0.1) | 1.65 (0.54) | 35 (4) | 34 (5) | 31 (2) | CL to L | 1.20 (0.03) | 2.22 (0.03) |
| | 10 – 20 | 7.4 (0.1) | 1.36 (0.45) | 36 (4) | 32 (3) | 32 (2) | CL | 1.29 (0.05) | 2.26 (0.03) |
| | 30 – 40 | 7.5 (0.1) | 1.18 (0.42) | 28 (4) | 39 (5) | 33 (2) | CL | 1.35 (0.08) | 2.32 (0.03) |
| | 60 – 70 | 7.5 (0.1) | 0.98 (0.31) | 30 (2) | 40 (3) | 30 (2) | CL | 1.27 (0.05) | 2.36 (0.04) |
| Riparian | 0 – 10 | 7.3 (0.1) | 4.45 (1.42) | 33 (1) | 34 (1) | 33 (1) | CL | 0.87 (0.12) | 2.14 (0.06) |
| | 10 – 20 | 7.4 (0.1) | 3.71 (1.19) | 29 (2) | 38 (5) | 33 (4) | CL to SiL | 1.03 (0.13) | 2.18 (0.05) |
| | 30 – 40 | 7.4 (0.1) | 2.87 (0.93) | 28 (3) | 42 (4) | 30 (2) | CL to SiL | 1.15 (0.16) | 2.18 (0.04) |
| | 60 – 70 | 7.4 (0.1) | 1.94 (0.65) | 32 (4) | 36 (5) | 32 (2) | CL | 1.23 (0.08) | 2.29 (0.01) |

Values are means of four independent replicates of each landscape element and the values in parenthesis are ± one standard error of the mean. L = loam, SCL = sandy clay loam, SiCL = silty clay loam, SiC = silty clay, SiL = silty loam, CL = clay loam, C = clay.
* Bulk density determined at 0-5, 10-15, 30-35 and 60-65 cm depth.

**(Continued….)**

**Table 2.2** Physical and chemical characteristics of soil samples collected from soil profiles in different landscape elements at the field site

| Landscape Element | Depth ( cm) | $NH_4^+$-N (mg N $kg^{-1}$) | $NO_3^-$ -N (mg N $kg^{-1}$) | Dissolved Organic Carbon (mg C $kg^{-1}$) | Total Organic Carbon (%) | Total Carbonate (%) | $SO_4^{2-}$ (mg S $kg^{-1}$) |
|---|---|---|---|---|---|---|---|
| Upper | 0 – 10 | 4.1 (0.3) | 2.7 (0.6) | 258.2 (13.3) | 3.3 (0.4) | 4.3 (2.7) | <0.1 |
| | 10 – 20 | 3.7 (0.5) | 2.3 (0.8) | 226.4 (20.4) | 2.3 (0.3) | 7.4 (3.1) | <0.1 |
| | 30 – 40 | 3.1 (0.2) | 1.7 (0.5) | 142.7 (14.5) | 1.1 (0.2) | 20.6 (6.7) | <0.1 |
| | 60 – 70 | 3.2 (0.3) | 0.6 (0.1) | 106.1 (16.8) | 0.8 (0.3) | 18.8 (4.5) | 0.1 (0.1) |
| Middle | 0 – 10 | 4.3 (0.3) | 5.1 (2.7) | 243.6 (13.8) | 3.8 (0.3) | 1.8 (0.6) | <0.1 |
| | 10 – 20 | 3.7 (0.3) | 3.4 (2.1) | 179.6 (18.7) | 2.3 (0.3) | 0.5 (0.2) | <0.1 |
| | 30 – 40 | 2.8 (0.2) | 10.2 (9.6) | 138.5 (12.6) | 1.3 (0.3) | 9.5 (4.2) | 0.2 (0.1) |
| | 60 – 70 | 2.7 (0.4) | 5.1 (2.7) | 119.6 (7.3) | 0.8 (0.1) | 12.7 (2.5) | 0.3 (0.2) |
| Lower | 0 – 10 | 4.6 (0.2) | 7.0 (1.2) | 297.3 (18.5) | 3.7 (0.2) | 0.8 (0.2) | 2.1 (0.8) |
| | 10 – 20 | 3.8 (0.2) | 7.3 (5.6) | 223.9 (29.9) | 2.7 (0.4) | 1.9 (0.8) | 1.7 (0.6) |
| | 30 – 40 | 3.0 (0.5) | 4.6 (3.7) | 150.1 (35.5) | 1.5 (0.4) | 8.8 (7.8) | 1.4 (0.5) |
| | 60 – 70 | 2.7 ( 0.5) | 4.0 (1.8) | 83.2 (10.5) | 0.7 (0.1) | 13.0 (7.6) | 1.1 (0.4) |
| Riparian | 0 – 10 | 5.5 (1.3) | 8.1 (6.2) | 434.1 (121.9) | 5.5 (1.2) | 0.5 (0.2) | 7.0 (2.3) |
| | 10 – 20 | 4.3 (0.7) | 8.8 (7.5) | 347.7 (77.2) | 5.0 (0.8) | 0.7 (0.2) | 5.8 (1.9) |
| | 30 – 40 | 4.0 (0.5) | 11.1(7.8) | 294.0 (51.4) | 4.5 (0.7) | 0.4 (0.1) | 4.6 (1.7) |
| | 60 – 70 | 2.9 (0.4) | 2.9 (1.4) | 109.1 (7.4) | 0.9 (0.1) | 0.6 (0.4) | 2.5 (0.9) |

Values are means of four independent replicates of each landscape element and the values in parenthesis are ± one standard error of the mean.

The bulk density was lower at the soil surface (0-10 cm) in all the landscape elements and the lowest bulk density of 0.87 was recorded in the Riparian landscape element. The bulk density increased up to 35 cm depth and then decreased at 65 cm depth in Upper, Middle and Lower elements whereas, in the Riparian element the bulk density increased with depth. The particle density increased with depth in all the landscape elements and the highest particle density of 2.38 mg $m^{-3}$ was recorded in the Upper element. The $NH_4^+$-N content decreased with depth in all the landscape elements and the highest $NH_4^+$-N content (5.48 mg N $kg^{-1}$) was recorded in the shallow depth (0-10 cm) of Riparian element. The $NO_3^-$-N content also decreased with depth in the Upper and Lower landscape elements, whereas in the Middle and Riparian landscape element the $NO_3^-$-N was variable. Highest $NO_3^-$-N content of 11.1 and 10.2 mg N $kg^{-1}$ were recorded at 30-40 cm depth in the Riparian and Middle landscape elements, respectively.

The organic carbon and extractable dissolved organic carbon content also decreased with depth in all the landscape elements and were highest at shallow depth in the Riparian landscape elements. The carbonate contents increased with depth in the Upper and Middle landscape elements and highest carbonate content of 20.6% was recorded at 30-40 cm depth in the Upper landscape element followed by 18.8% at 60-70 cm depth in the same landscape element. The $SO_4^{-2}$ concentrations decreased with depth in the Lower and Riparian landscape elements whereas in the Upper and Middle landscape elements there was no trend with depth in $SO_4^{-2}$ concentration. Highest $SO_4^{-2}$ concentration of 7.03 mg S $kg^{-1}$ was recorded at 0-10 cm depth in the Riparian landscape element.

### 2.4.2 Environmental Conditions

The soil temperature varied with depth among all the landscape elements and the average soil temperature increased among the landscape elements in the order Upper > Middle > Lower > Riparian. The soil temperatures at different depth in all the landscape elements reached the frozen state on different dates and started thawing on different days (Fig. 2.3).

The soil temperature at the Upper landscape element ranged between -2.2$^0$C and 19.6$^0$C, -2.2$^0$C and 18.6$^0$C, -1.1$^0$C and 17.8$^0$C and -1.4$^0$C and 16.4$^0$C at 5 cm, 15 cm, 35 cm and 65 cm depth, respectively. In the Upper landscape element the soil temperature at 5 and 15 cm reached below zero degrees on day 340 (Dec 6, 2005) and the frozen state continued until day 460 (Apr 5, 2006) whereas at the depths 35 and 65 cm the soil started freezing on day 350 (Dec 16, 2005) and 355 (Dec 21, 2005) and started thawing on day 460 and 440 (Mar 16, 2006), respectively. The soil temperature at the Middle landscape element ranged between -3.6$^0$C and 21$^0$C, -2.5$^0$C and 19$^0$C, -1.6$^0$C and 18.3$^0$C and 0.1$^0$C and 16.4$^0$C at 5 cm, 15 cm, 35 cm and 65 cm depth, respectively. In the Middle landscape element the soil temperature at 5 and 15 cm reached below zero degrees on day 330 (Nov 26, 2005) and the frozen state continued until day 460 for 5 cm and day 467 (Apr 12, 2006) for 15 cm. At the depths 35 the soil started freezing on day 340 and started thawing on day 450 (Mar 26, 2006). In the Lower and Riparian landscape elements soil temperature increased in winter and decreased in summer with depth.

The soil temperature at the Lower landscape element ranged between -3.2$^0$C and 21.2$^0$C, -3.9$^0$C and 19.2$^0$C, -1.2$^0$C and 17.4$^0$C and 0.1$^0$C and 17.8$^0$C at 5 cm, 15 cm, 35

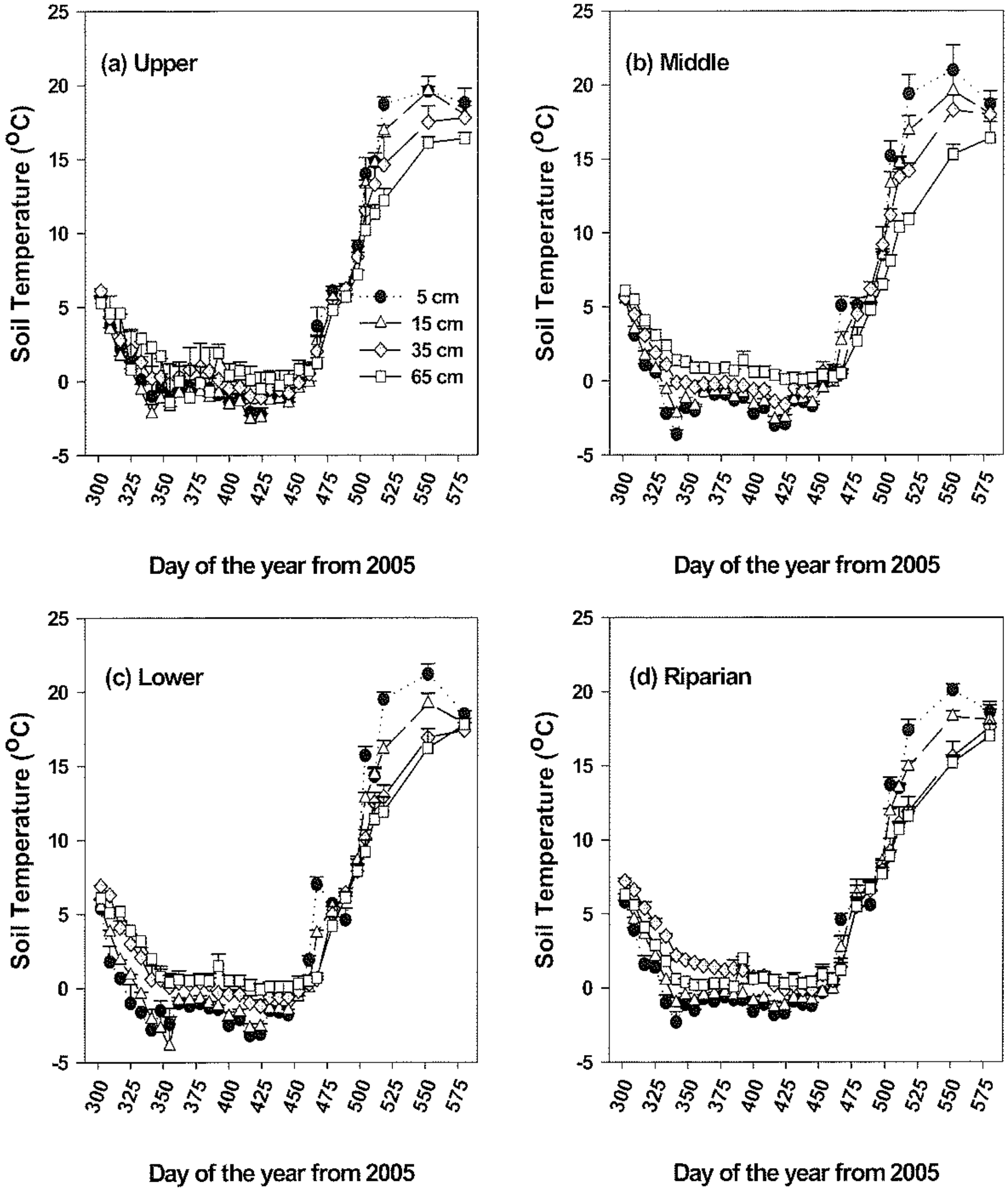


**Figure 2.3** Soil profile temperatures from four landscape elements during various days in 2005 and 2006; (a) Upper, (b) Middle, (c) Lower and (d) Riparian landscape element. Values shown are the mean plus one standard error of the mean of four replicate positions after the day of year 392 and values until the day of year 392 are mean plus one standard error of the mean of two replicate positions.

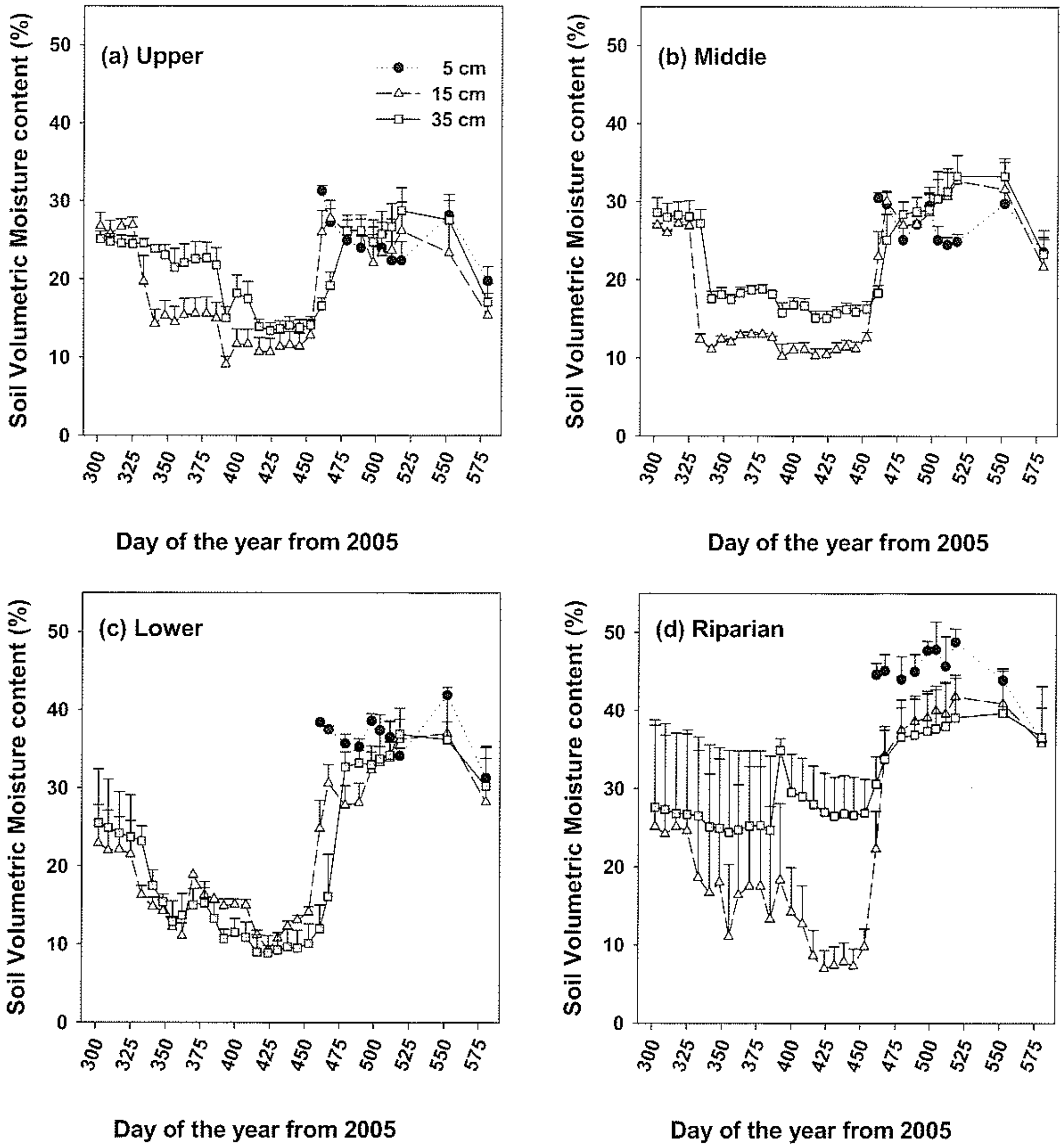


**Figure 2.4** Soil profile volumetric moisture contents from four landscape elements during various days in 2005 and 2006; (a) Upper, (b) Middle, (c) Lower and (d) Riparian landscape element. Values shown are the mean plus one standard error of the mean of four replicate positions after the day of year 392 and values until the day of year 392 are mean plus one standard error of the mean of two replicate positions. (**Note:** Volumetric moisture content values for 5 cm are not recorded until day 453 (March 29, 2006) and only values recorded after day 453 until 575 are presented in the figure).

cm and 65 cm depth, respectively. In the Lower landscape element the soil temperature at 5 and 15 cm reached below zero degrees on day 325 (Nov 21, 2005) and day 333 (Nov 29, 2005), respectively, and the frozen state continued until day 460, whereas at the depths 35 cm the soil started freezing on day 392 (Jan 27, 2006) and started thawing on day 460. Soil temperature at the Riparian landscape element ranged between -1.8$^0$C and 20.1$^0$C, -1.3$^0$C and 18.3$^0$C, -0.1$^0$C and 17.6$^0$C and 0.1$^0$C and 17.0$^0$C at 5 cm, 15 cm, 35 cm and 65 cm depth, respectively. In the Riparian landscape element the soil temperature at 5, 15 and 35 cm reached below zero degrees on day 333, 340 and 424 and the soil started thawing on day 453 (Mar 29, 2006), 467 (Apr 12, 2006) and 445 (Mar 21, 2006), respectively. At the depth 65 cm the soil was never frozen in the Middle, Lower and Riparian landscape elements (Fig. 2.3).

Soil volumetric moisture content varied with depth among all the landscape elements and the average volumetric moisture content decreased among the four landscape elements in the order Upper < Middle < Lower < Riparian (Fig. 2.4). The volumetric moisture content was highest at shallow depth (5 cm) in the Lower and Riparian landscape elements, whereas in the Upper and Middle landscape element, the volumetric moisture content was highest at 35 cm depth. The volumetric moisture content at the Upper landscape element ranged between 22.3 and 31.5%, 9.5 and 28.3% and 14.2 and 29.3% at 5, 15 and 35 cm depth, respectively. The volumetric moisture content at the Middle landscape element ranged between 11.5 and 29.3%, 10.2 and 30.4% and 15.4 and 30.8% at 5, 15 and 35 cm depth, respectively. In the Lower landscape element the volumetric moisture content ranged between 34.3 and 38.4%, 11.2 and 30.5 and 9.6 and 34.3% at 5, 15 and 35 cm, respectively. In the Riparian landscape element the highest volumetric moisture content of 48.8% was recorded at shallow depth (5 cm) on day 455 (Mar 31, 2006), which was immediately after the snow melt.

### 2.4.3 Soil Gas Concentrations

**Nitrous oxide**

Soil atmosphere $N_2O$ concentrations varied significantly at all the landscape elements and at all depths. Soil atmosphere $N_2O$ concentration all followed a trend of lowest concentrations at all depths being observed during the post-cropped period, highest concentrations during the freeze-thaw period followed by a second period of elevated, but slightly lower, concentrations during the post-fertilizer/cropped period in all the landscape elements. Soil atmosphere $N_2O$ concentrations were low in the fall 2005 in all landscape elements and at all depths. During fall 2005, in the Upper landscape element the $N_2O$ concentration increased with depth and the highest $N_2O$ concentration of 1.3 $\mu L\ L^{-1}$ was recorded on day 220 at the 35 cm depth, whereas, in the Middle and Lower landscape elements the 65 cm depth was observed to have the highest $N_2O$ concentration of 1.8 and 11.3 $\mu L\ L^{-1}$, respectively, and there were ambient levels of $N_2O$ accumulation at 65 cm depth in the Riparian element at the same depth. Among, the three periods (post-crop 2005, pre-crop 2006 and crop 2006), the pre-crop 2006 period (freeze-thaw) was observed to have the highest $N_2O$ concentration for all of the landscape elements. The magnitude of $N_2O$ accumulation decreased in the order Riparian > Lower > Middle > Upper. The freeze-thaw $N_2O$ concentrations were greatest at 5 cm depth in the Middle and Riparian landscape elements, whereas in the Lower landscape element the

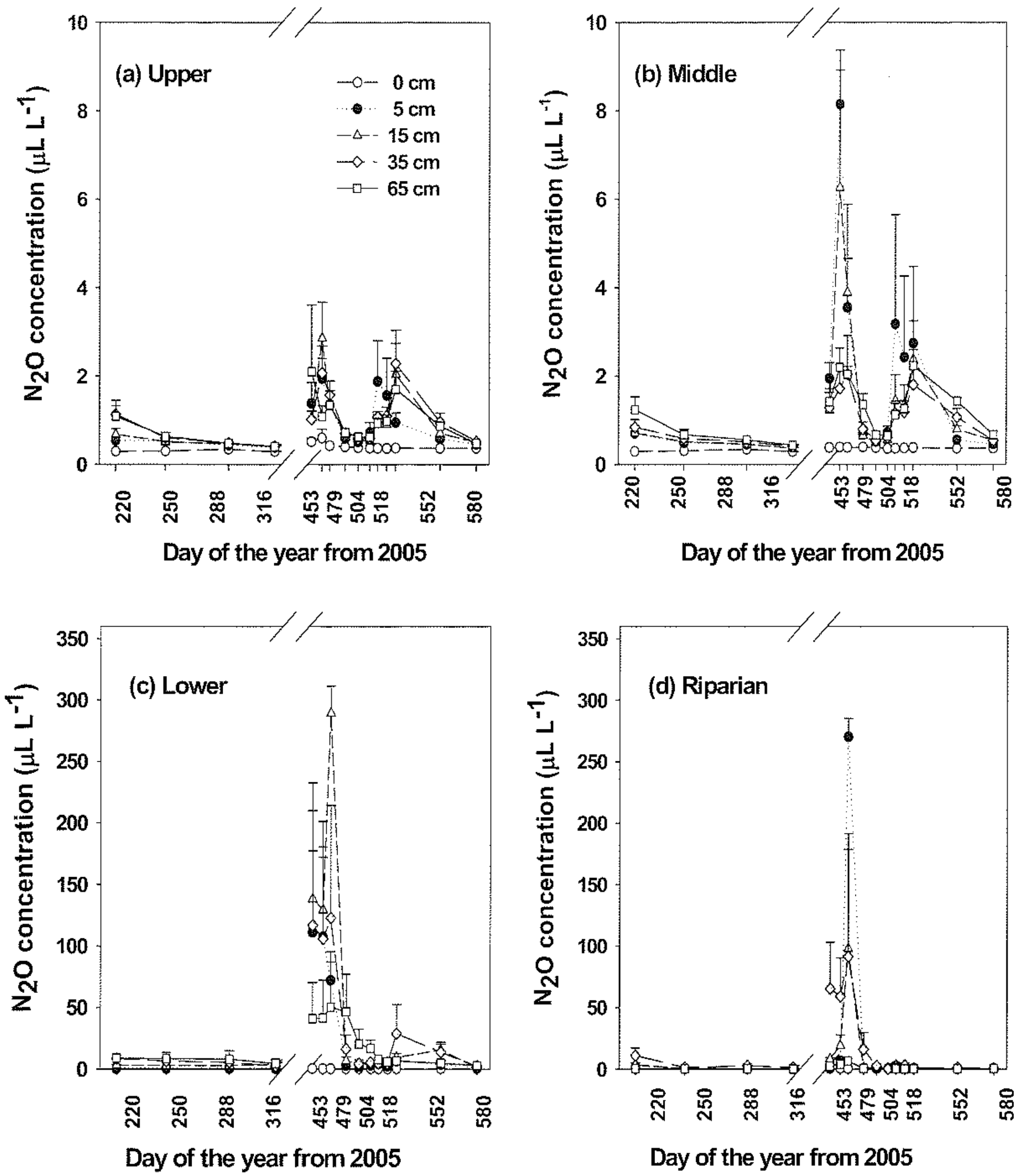


**Figure 2.5** Nitrous oxide ($N_2O$) profile concentration (μL $L^{-1}$ soil atmosphere) at different depths from four landscape elements; (a) Upper, (b) Middle, (c) Lower and (d) Riparian landscape element. Values shown are the mean plus one standard error of the mean of four replicate sample positions.

**Table 2.3** Soil Profile $N_2O$ concentrations at different depths in various landscape elements averaged across three periods.

| Depth | Post-crop period (2005) | | | | Pre-crop period (2006) | | | | Cropped period (2006) | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| (cm) | Upper | Middle | Lower | Riparian | Upper | Middle | Lower | Riparian | Upper | Middle | Lower | Riparian |
| | ---------- $\mu L\ L^{-1}$ ---------- | | | | | | | | | | | |
| 0 | 0.31 aA | 0.31 aA | 0.30 aA | 0.33 aA | 0.45 aA | 0.38 aA | 0.39 aA | 0.42 aA | 0.36 aA | 0.37 aA | 0.37 aA | 0.38 aA |
| 5 | 0.47 aB | 0.51 aB | 0.94 bA | 0.86 abB | 1.08 aB | 2.59 aC | 49.7 bBC | 46.7 bC | 2.81 bC | 1.87 aC | 3.58 bB | 1.03 aB |
| 15 | 0.52 aB | 0.51 aB | 3.19 bB | 1.21 abB | 1.17 aB | 2.18 aC | 95.3 cD | 21.3 bB | 1.03 aB | 1.3 aB | 7.28 bC | 1.09 aB |
| 35 | 0.66 aC | 0.58 aB | 5.74 bC | 4.03 bC | 1.09 aB | 1.17 aB | 62.0 cC | 39.1 bBC | 1.19 aB | 2.07 bC | 10.9 cD | 1.16 aB |
| 65 | 0.65 bC | 0.73 bC | 7.49 cC | 0.28 aA | 1.08 aB | 1.39 aB | 36.1 bB | 3.46 aA | 0.99 aB | 1.34 aB | 5.75 bBC | 0.29 aA |

Note: Mean values followed by the same lower case letter (within the rows - landscape elements) and same upper case letter (within the columns - depths) are not significantly different using least significant difference ($P > 0.05$). Post crop period (8th Aug. – 12th Nov. 2005, 4 dates), pre crop period (29th March – 13th May, 2006, 6 dates), and cropped period (19th May – 3rd Aug., 2006, 5 dates).

highest $N_2O$ concentrations were observed at a 15 cm depth. In all landscape elements and at all depths, $N_2O$ profile concentrations were high during pre-snow melt with the highest being at Lower landscape elements (though variable). The $N_2O$ concentrations peaked during snow melt (Day 467) and then decreased thereafter. A secondary increase of $N_2O$ concentrations occurred immediately following fertilizer application in Upper, Middle and Lower positions for 5, 15, 35 and 65 cm depths but not in the Riparian landscape elements, which did not receive fertilizer (Fig. 2.5, Table 2.3).

There was considerable variation among sections on sampling day 518 in the Upper and Middle landscape elements. The section 2 always recorded very high $N_2O$ concentrations and this section had the highest nitrate nitrogen content. The maximum $N_2O$ concentration of 395.4 $\mu L\ L^{-1}$ was recorded for this section at the 35 cm depth in the Lower landscape element, whereas in all the other sections, the observed maximum $N_2O$ concentrations were 54.3 $\mu L\ L^{-1}$, 30.4 $\mu L\ L^{-1}$ and 65.1 $\mu L\ L^{-1}$. In the Riparian element on day 467 a very high $N_2O$ concentration of 289.4 $\mu L\ L^{-1}$ was observed, contributing to the high variability among sections. This higher variability is reflected in high coefficients of variation ranging from 1 to 131%. Subsurface buildup of $N_2O$ during winter occurred at different depths in all the landscape elements. The soil atmosphere sampling on day 453, a week before snow melt showed that in the Upper, Middle, Lower and Riparian landscape elements, $N_2O$ accumulation was greatest at 65 cm, 5 cm, 15 and 35 cm depths, respectively. Consistently, highest $N_2O$ accumulation occurred in the Lower landscape elements followed by the Riparian landscape elements.

## Methane

The pattern of $CH_4$ in soil profiles was different from that of $N_2O$. Subsurface $CH_4$ concentrations ranged between 0.5 μL $L^{-1}$ and 2,587 μL $L^{-1}$ over the sampling period. Soil $CH_4$ concentration profiles increased in the order Upper < Middle < Lower < Riparian (Fig. 2.6) and there was large variability among sections which resulted in a very high standard error of the mean on sample day 220 for the Upper and Lower landscape elements. The Riparian element of section 3 always recorded highest $CH_4$ concentration when compared to other sections. This is attributed to a low $SO_4^{-2}$ content at 0-10 cm depth in this section (0.06 mg $kg^{-1}$). In other sections $SO_4^{2-}$ contents of 10.2, 8.6 and 9.2 mg $kg^{-1}$ were observed.

In the Upper and Middle landscape elements $CH_4$ concentrations were initially higher at 5 and 35 cm depth, respectively, during the post-crop period and then in the late post-crop period, the $CH_4$ concentrations at 5 cm decreased to below ambient levels (<0.25 μL $L^{-1}$) and at the 35 cm depth all concentrations were below 0.9 μL $L^{-1}$. A similar pattern was observed for other positions in the post-crop 2005 period except for the Riparian position at 65 cm in the late post-crop 2005 period. In the Pre-crop/ freeze-thaw period the $CH_4$ concentrations were elevated and the highest concentrations were recorded at 5 cm depths in both Upper and Middle landscape elements and again the $CH_4$ concentrations decreased during the cropped period. In the freeze-thaw/pre-cropped period the concentrations of $CH_4$ were highest at the 35 cm depth in the Lower elements (18 μL $L^{-1}$) and at the 15 cm depth in the Riparian landscape elements (2,587 μL $L^{-1}$).

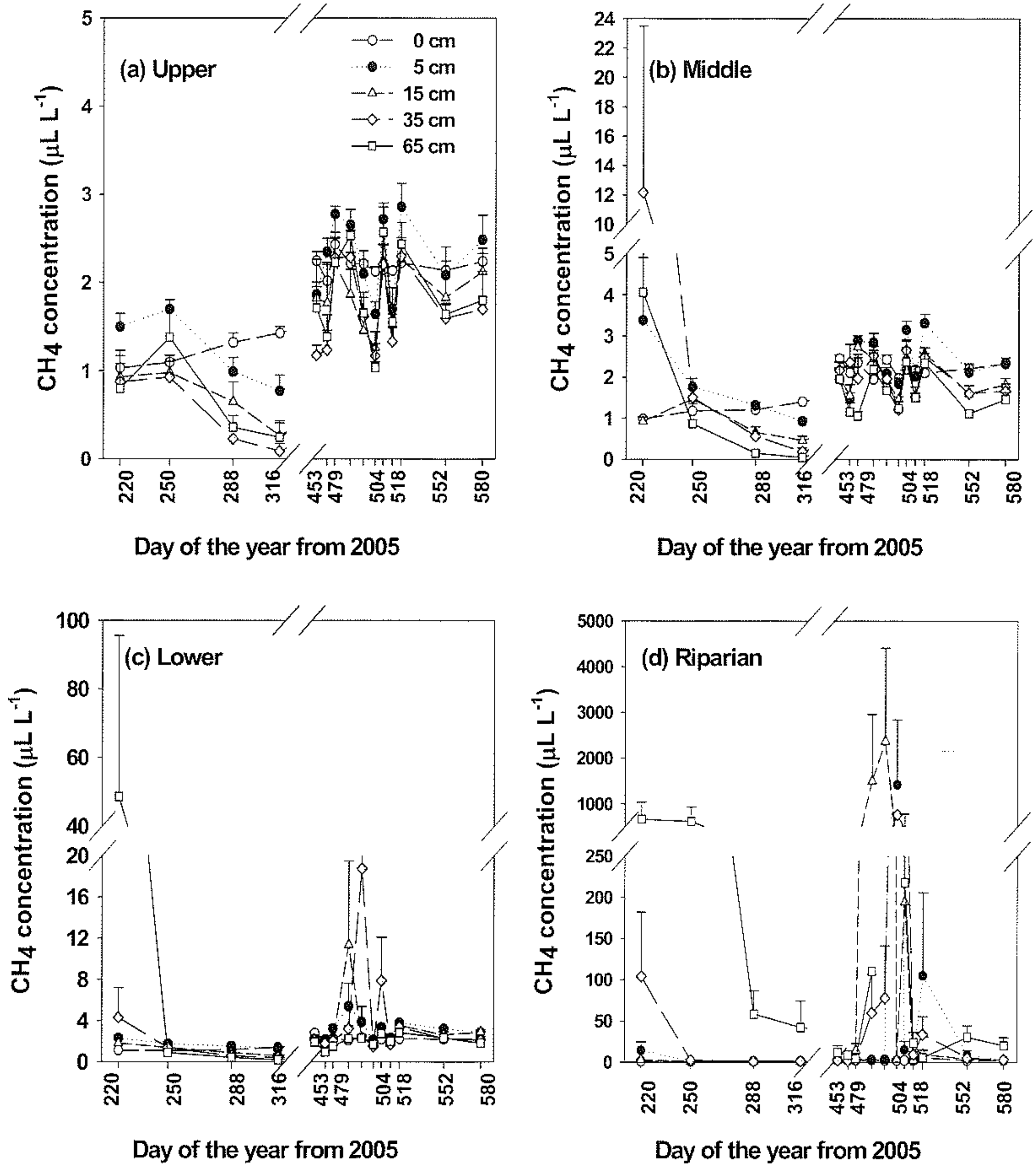


**Figure 2.6** Methane ($CH_4$) profile concentration (µL $L^{-1}$ soil atmosphere) at different depths from four landscape elements; (a) Upper, (b) Middle, (c) Lower and (d) Riparian landscape elements. Values shown are the mean plus one standard error of the mean of four replicate sample positions.

**Table 2.4** Soil Profile $CH_4$ concentrations at different depths in various landscape elements averaged across three periods.

| Depth (cm) | Post-crop period (2005) | | | | Pre-crop period (2006) | | | | Cropped period (2006) | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Upper | Middle | Lower | Riparian | Upper | Middle | Lower | Riparian | Upper | Middle | Lower | Riparian |
| | $\mu L\ L^{-1}$ | | | | | | | | | | | |
| 0 | 1.22 aB | 1.19 aA | 1.18 aA | 1.13 aA | 2.21 aB | 2.21 aA | 2.28 aA | 2.39 aA | 2.18 aA | 2.20 aA | 2.19 aA | 2.94 aA |
| 5 | 1.24 aB | 1.85 aA | 1.69 aA | 4.69 bA | 2.23 aB | 2.18 aA | 3.11 aAB | 240.2 cC | 2.37 aA | 2.59 aA | 3.09 aAB | 27.08 bB |
| 15 | 0.66 aA | 0.88 aA | 1.15 abA | 1.59 bA | 1.73 aA | 2.02 aA | 3.55 aB | 648.1 bD | 2.00 aA | 1.90 aA | 2.74 aA | 42.82 bBC |
| 35 | 0.48 aA | 3.60 aB | 1.59 aA | 27.13 bB | 1.63 aA | 2.03 aA | 4.88 aC | 150.9 bC | 1.83 aA | 1.99 aA | 3.46 aB | 102.4 bD |
| 65 | 0.67 aA | 1.28 aA | 12.5 bB | 344.5 cC | 1.76 aA | 1.55 aA | 1.76 aA | 34.01 bB | 2.00 aA | 1.76 aA | 2.33 aA | 59.6 bC |

Note: Mean values followed by the same lower case letter (within the rows - landscape elements) and same upper case letter (within the columns - depths) are not significantly different using least significant difference ($P > 0.05$). Post crop period (8$^{th}$ Aug. – 12$^{th}$ Nov. 2005, 4 dates), pre crop period (29$^{th}$ March – 13$^{th}$ May, 2006, 6 dates), and cropped period (19$^{th}$ May – 3$^{rd}$ Aug., 2006, 5 dates).

The $CH_4$ concentrations then decreased during the cropped period in both the Lower and Riparian landscape elements resulting in higher concentrations (23 $\mu L\ L^{-1}$) persisting at 65 cm depths in the Riparian landscape elements. In the Upper landscape elements the $CH_4$ accumulation was higher during the pre-crop period (2006). The pattern of $CH_4$ accumulation within depths in different landscape element was not similar (Table 2.4). The varying levels of $SO_4^{-2}$ in all four Sections and landscape elements resulted in higher variability of $CH_4$ accumulation (Sections 1, 2 and 4 had very high $SO_4^{-2}$ content at the Upper, Middle and Lower landscape elements, Section 3 had very low $SO_4^{-2}$ content at Riparian landscape element). For instance, on day 220, for the Lower element at the 65 cm depth in Section 1 there was 0.4 $\mu L\ L^{-1}$ of $CH_4$, Section 2 recorded 189.5 $\mu L\ L^{-1}$ of $CH_4$, Section 3 recorded 3.5 $\mu L\ L^{-1}$ of $CH_4$ and Section 4 recorded 0.7 $\mu L\ L^{-1}$ of $CH_4$. In another landscape element (Middle), Section 4 on the same sample day had 46.2 $\mu L\ L^{-1}$ of $CH_4$ at 35 cm depth whereas the other sections at the same depth and the same landscape element had 0.8, 0.9 and 1.5 $\mu L\ L^{-1}$ of $CH_4$. The higher variability among the sections $CH_4$ concentration resulted in very high coefficient of variation and the coefficient ranged from 3 to 111%.

**Carbon dioxide**

The pattern of $CO_2$ accumulation was similar to $N_2O$, where highest accumulation was observed at lower depths. The subsurface $CO_2$ concentrations ranged between 396 and 225,000 $\mu L\ L^{-1}$ (Fig. 2.7). The extent of $CO_2$ accumulation in the soil profiles varied among landscape elements, decreasing in the order Riparian > Lower > Middle = Upper. The accumulation of $CO_2$ increased with depth in the order 5 <15 <35 < 65 cm. The $CO_2$

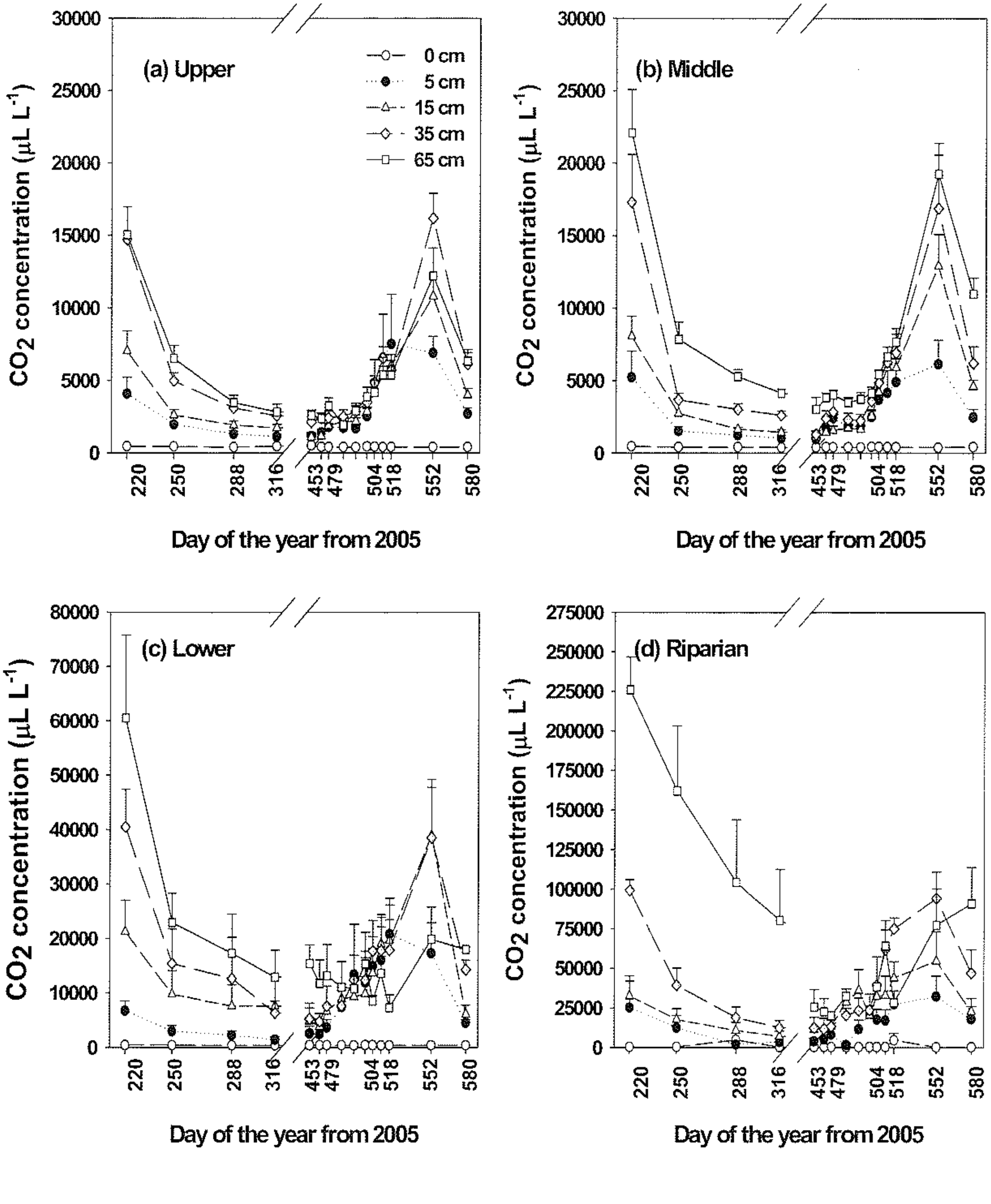


**Figure 2.7** Carbon dioxide ($CO_2$) profile concentration at different depths from four landscape elements during various sampling dates; (a) Upper, (b) Middle, (c) Lower and (d) Riparian landscape element. Values shown are the mean plus 1 standard error of the mean of four replicate sites.

**Table 2.5** Soil Profile $CO_2$ concentrations at different depths in various landscape elements averaged across three periods.

| Depth ( cm) | Post-crop period (2005) | | | | Pre-crop period (2006) | | | | Cropped period (2006) | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Upper | Middle | Lower | Riparian | Upper | Middle | Lower | Riparian | Upper | Middle | Lower | Riparian |
| | ------------ $\mu L\ L^{-1}$ ------------ | | | | | | | | | | | |
| 0 | 435 aA | 406 aA | 400 aA | 1,499 bA | 423 aA | 398 aA | 408 aA | 404 aA | 406 aA | 400 aA | 396 aA | 1,244 bA |
| 5 | 2,117 aB | 2,243 aAB | 3,338 abAB | 10,804 bB | 1,716 aB | 1,874 aB | 6,903 bB | 8,766 cB | 5,711 aB | 4,267 aB | 14,710 bB | 22,502 bB |
| 15 | 3,315 aB | 3,467 aBC | 11,536 bBC | 17,000 bB | 1,886 aB | 1,664 aB | 7,227 bB | 20,279 cC | 6,092 aB | 6,701aBC | 19,480 bC | 37,350 cB |
| 35 | 6,331 aC | 6,641 aCD | 18,703 bC | 42,550 cC | 2,633 aC | 2,434 aB | 8,329 aB | 17,547 bC | 7,882 aB | 8,218 aCD | 21,223 bC | 63,492 cC |
| 65 | 6,967 aC | 9,831 aD | 28,404 bD | 143,123 cD | 2,819 aC | 3,692 aC | 12,922 cC | 25,306 bD | 6,701 aB | 9,997 aD | 13,462 aD | 59,835 bC |

Note: Mean values followed by the same lower case letter (within the rows - landscape elements) and same upper case letter (within the columns - depths) are not significantly different using least significant difference ($P > 0.05$). Post crop period (8th Aug. – 12th Nov. 2005, 4 dates), pre crop period (29th March – 13th May, 2006, 6 dates), and cropped period (19th May – 3rd Aug., 2006, 5 dates).

concentrations decreased from the early post crop 2005 to the late post crop 2005 period. Neither the snow melt nor the post fertilization period increased the $CO_2$ concentrations, rather it steadily increased up to harvest (day 552) and then declined by day 580. The $CO_2$ concentrations were higher in the Riparian and the Lower landscape elements, while the Middle and the Upper positions were generally similar throughout the study. Very high concentrations of $CO_2$ were recorded in the Riparian landscape element (225,000 $\mu L\ L^{-1}$) followed by the Lower landscape elements (60,000 $\mu L\ L^{-1}$) at 65 cm depth. The $CO_2$ concentrations were highest at 65 cm depth in all the landscape elements (except Middle element) during the cropped period (Table 2.5). The variability for a sample element of high $CO_2$ concentrations was slightly less than that of $N_2O$ and $CH_4$ and the coefficient of variation of $CO_2$ ranged between 3 and 97%.

**Oxygen**

The $O_2$ concentration increased among landscape elements in the order Riparian < Lower < Middle < Upper and in all the landscape elements, the $O_2$ concentration at the 5 cm depth decreased during the snow melt period. The $O_2$ concentrations in the Upper and Middle landscape elements ranged between 18 and 20% at all the depths during all the three periods. But at 5 cm depth, in the Middle landscape element the $O_2$ concentration decreased to 16% during snow-melt/ pre-crop period. There was a clear pattern of decreasing $O_2$ concentrations with depth in soil for the Lower and Riparian positions. The $O_2$ levels increased from early post crop 2005 to late post crop 2005 for the Lower and Riparian landscape elements. The decrease in $O_2$ concentration with depth was greater in the Riparian (4%) and the Lower element (13%) during the snow melt period, but with no

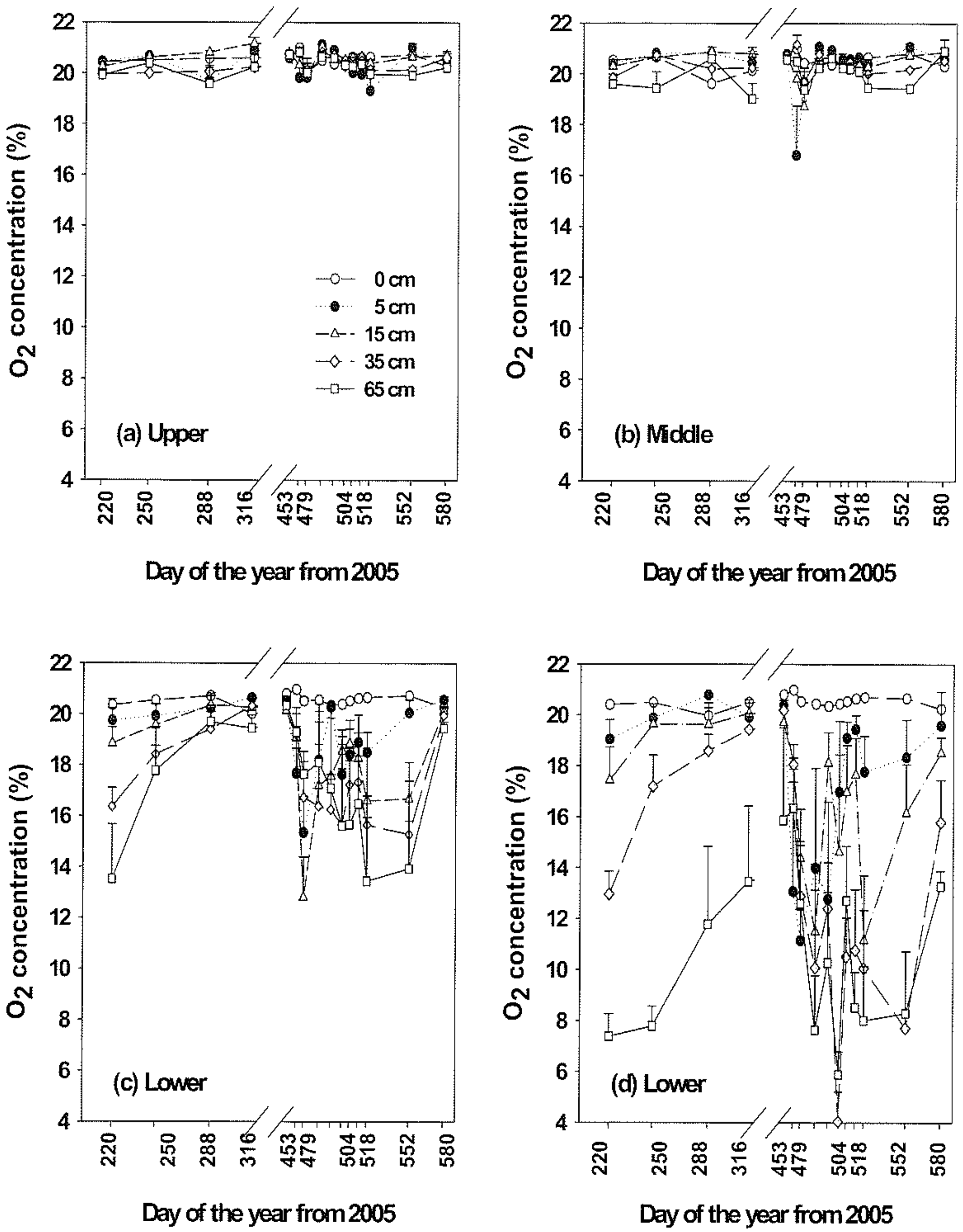


**Figure 2.8** Oxygen profile concentrations (%) in different depths from four landscape elements at various sampling dates: (a) Upper landscape element, (b) Middle landscape element, (c) Lower landscape element and (d) Riparian landscape element. Values shown are the mean plus 1 standard error for 4 replicate sites.

**Table 2.6** Soil Profile $O_2$ concentrations at different depths in various landscape elements averaged across three periods.

| Depth (cm) | Post-crop period (2005) | | | | Pre-crop period (2006) | | | | Cropped period (2006) | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Upper | Middle | Lower | Riparian | Upper | Middle | Lower | Riparian | Upper | Middle | Lower | Riparian |
| | $\mu L\ L^{-1}$ | | | | | | | | | | | |
| 0 | 20.5 aA | 20.2 aA | 20.4 aB | 20.3 aC | 20.5 aA | 20.6 aA | 20.6 aB | 20.6 aC | 20.6 aA | 20.6 aA | 20.6 aC | 20.6 aD |
| 5 | 20.4 bA | 20.6 bA | 20.1 abB | 19.9 aC | 20.4 bA | 20.0 bA | 18.3 abA | 15.6 aB | 20.2 bA | 20.6 bA | 19.3 aBC | 18.9 aB |
| 15 | 20.7 bA | 20.7 bA | 19.8 aB | 19.2 aC | 20.6 bA | 20.2 bA | 17.6 aA | 16.1 aB | 20.6 bA | 20.5 bA | 18.1 aB | 16.1 aC |
| 35 | 20.1 bA | 20.3 bA | 18.6 aA | 17.0 aB | 20.6 cA | 20.6 cA | 17.4 bA | 13.0 aA | 20.3 cA | 20.3 cA | 17.1 bAB | 11.0 aA |
| 65 | 20.2 cA | 19.7 cA | 17.6 bA | 10.1 aA | 20.5 cA | 20.3 cA | 18.0 bA | 11.4 aA | 20.2 bA | 20.0 bA | 16.0 aA | 18.8 abB |

Note: Mean values followed by the same lower letter (within the rows - landscape elements) and same upper case letter (within the columns - depths) are not significantly different using least significant difference ($P > 0.05$). Post crop period (8th Aug. – 12th Nov. 2005, 4 dates), pre crop period (29th March – 13th May, 2006, 6 dates), and cropped period (19th May – 3rd Aug., 2006, 5 dates).

clear profile gradient evident. The decrease was greater for the Riparian element and a gradient of decreasing $O_2$ concentration with depth was again evident during the post-fertilization period with levels declining (less than 8%) at the 35 cm and 65 cm depths in the Riparian landscape element (Fig. 2.8, Table 2.6). The variability for a sample position of high $O_2$ concentrations were generally less than that of $N_2O$, $CH_4$ and $CO_2$ and the coefficient of variation of $O_2$ ranged between 0.3 and 43%.

### 2.4.4 Soil Surface Emissions of Gases

The daily emissions of $N_2O$, $CH_4$ and $CO_2$ showed high temporal and spatial variability. Among the four landscape elements, the $N_2O$ emissions decreased in the order Lower < Riparian < Upper < Middle and there were two prominent periods of $N_2O$ emission; spring thaw and post-fertilizer application periods (Fig.2.9) in all the landscape elements. There was either no emission or consumption of $N_2O$ at other times. $N_2O$ emission was initially higher at the Riparian (0.12 $\mu g$ N $m^{-2}$ $s^{-1}$) and the Lower landscape elements (0.03 $\mu g$ N $m^{-2}$ $s^{-1}$) during the post-crop 2005 period, whereas the $N_2O$ emission was near zero during the post-crop 2005 period for the Upper and Middle landscape elements.

The $N_2O$ emission increased slightly for the Upper and Middle landscape element during snow-melt then declined and remained low until after the seeding and fertilizer application period. The emission of $N_2O$ increased shortly after the seeding and fertilizer application period for the Upper, Middle and Lower landscape element. There was a burst in $N_2O$ emission (0.1 $\mu g$ N $m^{-2}$ $s^{-1}$) in the Lower landscape element on day 511. The $N_2O$ emission gradually declined towards the end of the cropped period, with crop maturity and eventual harvest of the flax crop. Emission of $N_2O$ at the Upper, Middle and

Riparian landscape elements remained low for the spring-thaw and post-fertilizer application periods. The replicate chamber in the Middle landscape element of section 2 and the replicate chambers in the Lower and Riparian landscape elements of section 4 of the transect always emitted the highest $N_2O$ emissions and were observed to have higher soil nitrate contents (690 mg N $kg^{-1}$). The greenhouse gas surface emission showed high variability among the landscape elements. The coefficient of variation of $N_2O$ emission ranged between 63 and 157%.

The $CH_4$ emission among the landscape elements decreased in the order Riparian < Lower < Upper < Middle. There was no difference in $CH_4$ emission in the Upper and Middle landscape elements during spring-thaw and post-fertilizer application periods in 2006. There was either no emission or there was consumption of $CH_4$ at the Upper, Middle and Lower landscape elements for the entire sampling period. The Riparian and Lower landscape elements however, gave the highest $CH_4$ emissions of 1.2 μg C $m^{-2}s^{-1}$ and 0.4 μg C $m^{-2}s^{-1}$, respectively, during the spring-thaw and post-fertilizer application periods (Fig. 2.9). The high emission of $CH_4$ from the Riparian element was mostly the result of emissions from a single replicate in section 3. This replicate chamber also had the lowest soil sulfate of 0.06 g S $kg^{-1}$ concentration (Table 2.2) which was 117 times lower than that of the average sulfate concentration in the other Riparian locations (7.02 g S $kg^{-1}$). The Upper and Middle landscape elements recorded the highest $CH_4$ emissions during the late cropped period. The variability in $CH_4$ emission was high with a coefficient of variation ranging from 113 to 343%.

Surface $CO_2$ emissions showed a strong seasonal variation among landscape elements, with values between 26 and 173 μg $m^{-2}$ $s^{-1}$. The $CO_2$ surface emissions

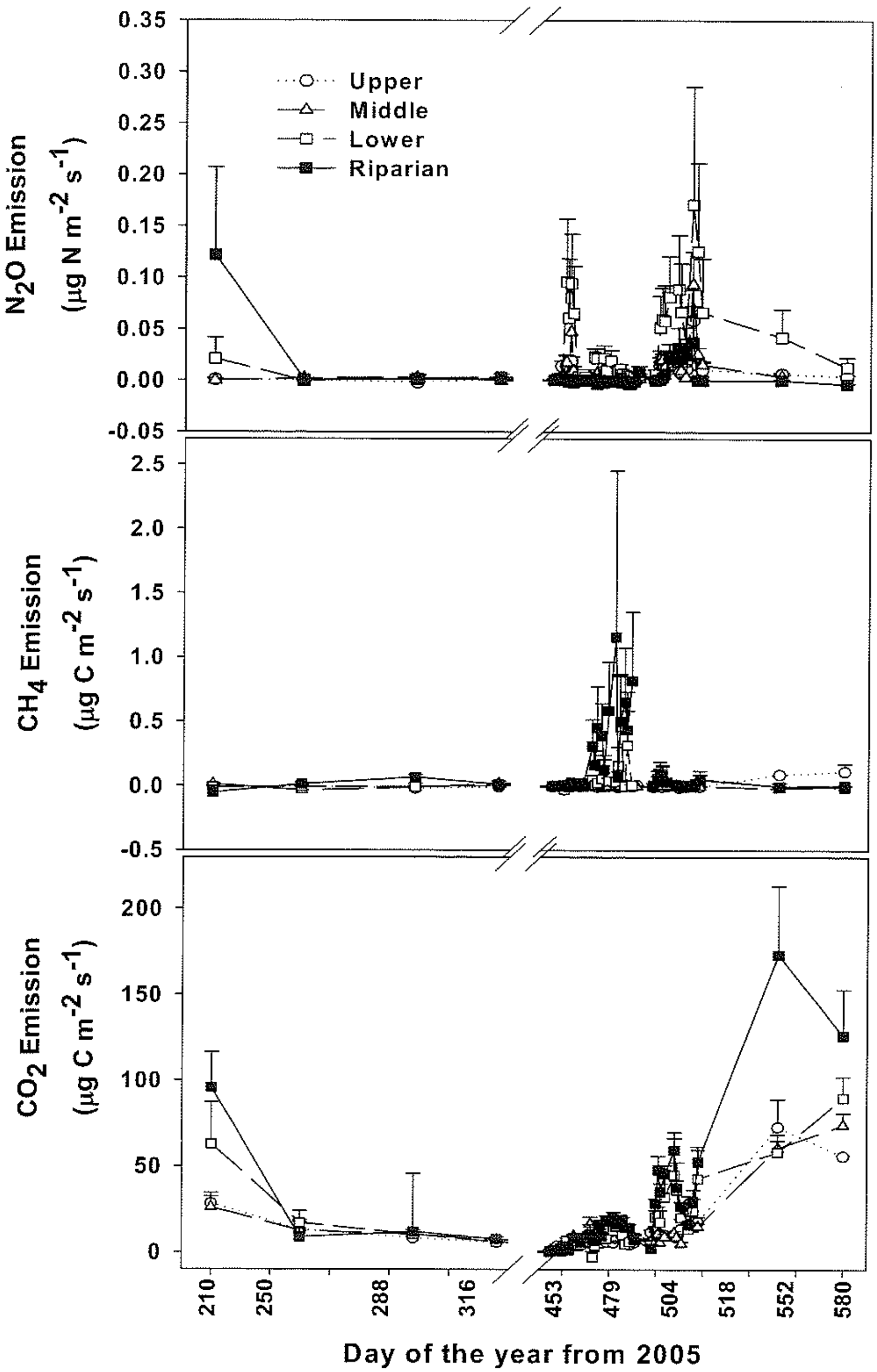


**Figure 2.9** Greenhouse gas surface emissions (µg $m^{-2}s^{-1}$) from four landscape elements at various sampling dates: (a) $N_2O$, (b) $CH_4$ and (c) $CO_2$ emission. Values shown are the mean plus one standard error of the mean of four replicate sites.

decreased among landscape elements in the order Riparian < Lower < Upper < Middle. $CO_2$ emissions were consistently highest in the Riparian landscape elements and were higher initially (98 μg $m^{-2}$ $s^{-1}$) during the post-crop season (August 2006) and then declined (16 μg $m^{-2}$ $s^{-1}$) until spring-thaw. Again $CO_2$ emissions increased in spring-thaw and were highest during the seeding and post-fertilizer application period. $CO_2$ emissions were steadily increasing in all landscape elements as the crop growth proceeds to maturity (Fig. 2.9). The variability in $CO_2$ emissions was less than the variability observed in $N_2O$ and $CH_4$ with a coefficient of variation ranging between 26 and 112%.

### 2.4.5 Relationship between Profile Greenhouse Gas Concentrations, Measured Soil Parameters and Surface Emissions

General trends were found when comparing the soil gas concentrations, soil parameters and surface emissions among all landscape elements at all the depths. At all landscape elements and depths, decreased $O_2$ concentrations led to increased $CH_4$ and decreased $N_2O$ concentrations while lower $CO_2$ concentrations were related to higher $CH_4$ concentrations. In the Upper and Middle landscape elements, the $N_2O$ concentration at 5, 15 and 35 cm depth and $N_2O$ surface emission were positively correlated (Tables 2.7, 2.8, 2.9 and 2.10). In the Upper and Middle landscape elements, the $N_2O$ emissions were elevated when soil $N_2O$ concentrations were higher. In the Lower landscape elements very high $N_2O$ concentrations for five sampling days (three during freeze-thaw period and two during post-fertilizer application period) yielded very high N2O emissions. In the Riparian landscape elements the $N_2O$ concentrations and $N_2O$ emissions were not significantly correlated though the concentrations were very high (Fig. 2.10). Unlike $N_2O$, the $CH_4$ concentrations at depth were not related to $CH_4$ surface emission

(Fig. 2.11) in all landscape elements except at 65 cm in the Upper landscape element (Table 2.10). Generally, there was a strong relationship found between $CO_2$ concentrations at all depths and $CO_2$ surface emission in all the landscape elements and the stronger depth relationship to emission were in the sequence 15 cm > 35 cm > 65 cm> 5 cm (Fig. 2.12). Positive correlations were found for $CO_2$ concentrations at all depths and $CO_2$ surface emission in all the landscape elements (Tables 2.7, 2.8, 2.9 and 2.10).

In the Upper and Middle landscape elements, near ambient $O_2$ concentrations, at just below 21%, were associated with $N_2O$ accumulation. When the $O_2$ concentration decreased below 19%, there was either no $N_2O$ or little $N_2O$ in these landscape elements. Similarly, in the Lower and Riparian landscape elements, $N_2O$ accumulations above ambient only occurred where $O_2$ concentrations was just below 21%. There was a drastic reduction in $N_2O$ concentration when the $O_2$ concentrations in these landscape elements fell below 12% (Fig. 2.13). In the Middle and Riparian landscape element at 35 cm and 65 cm depths these two gases were positively correlated (Tables 2.7, 2.8, 2.9 and 2.10). There was no relationship between $O_2$ and $CH_4$ concentrations at any depth for the Upper and Middle landscape elements as the $O_2$ concentrations were not low enough (>17%) for $CH_4$ production. In the Lower and Riparian landscape elements at the 65 cm depth, $CH_4$ concentration increased with lower $O_2$ concentration (Fig. 2.14). Significant negative correlations were found for $CH_4$ and $O_2$ concentrations at the 65 cm depth in the Lower and Riparian landscape elements. In all the landscape elements and at all depths, the $O_2$ concentrations and $CO_2$ concentrations were negatively correlated (Tables 2.7, 2.8, 2.9 and 2.10).

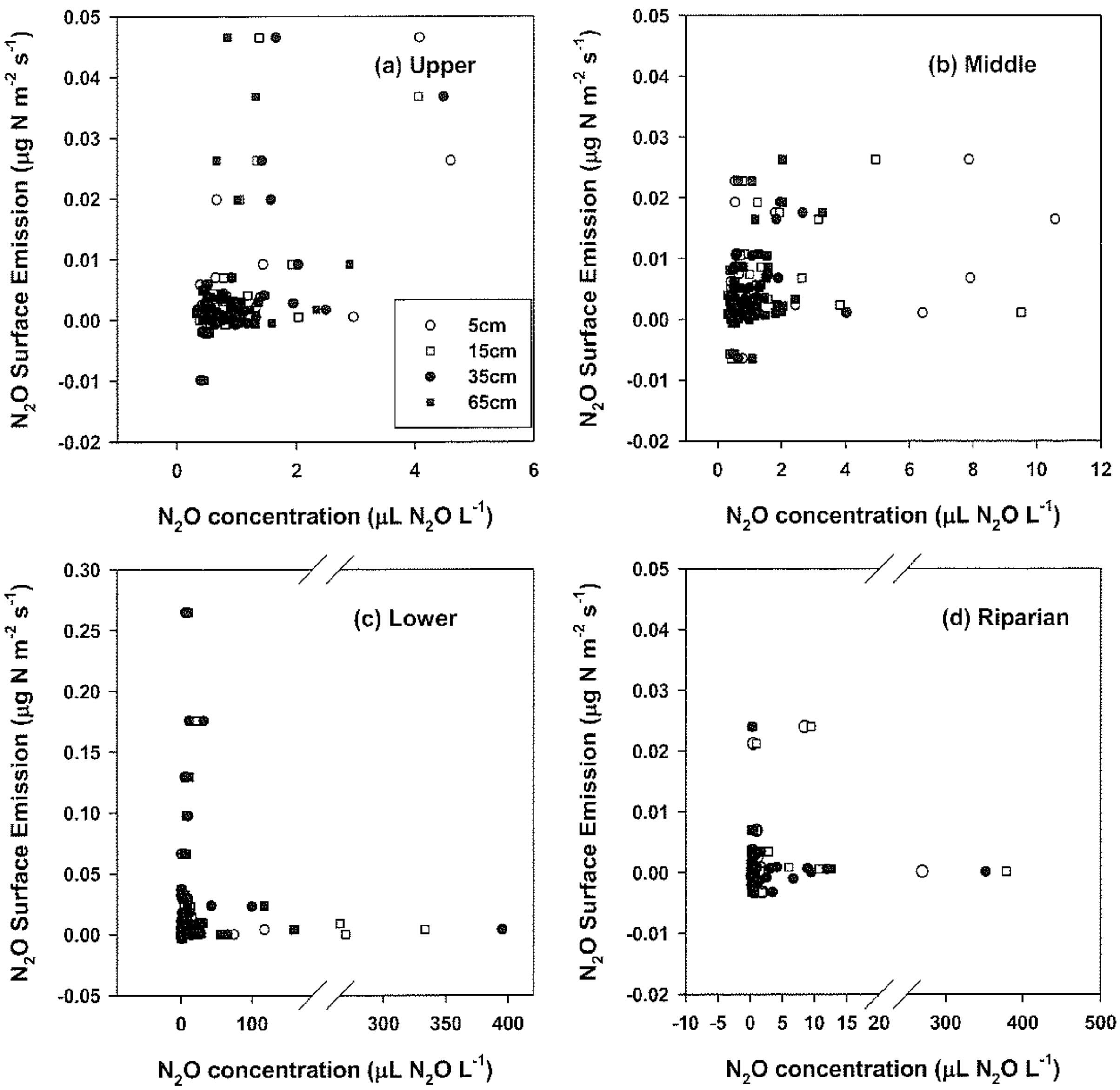


**Figure 2.10** Scatter plots of nitrous oxide ($N_2O$) profile concentration at different depths (5 cm, 15 cm, 35 cm and 65 cm) to $N_2O$ surface emission in different landscape element, (a) Upper element $N_2O$ profile concentration and Upper element $N_2O$ surface emission, (b) Middle element $N_2O$ profile concentration and Middle element $N_2O$ surface emission, (c) Lower element $N_2O$ profile concentration and Lower element $N_2O$ surface emission and (d) Riparian element $N_2O$ profile concentration and Riparian element $N_2O$ surface emission. (**Note:** n=52 for $N_2O$ concentration at each depth and n=13 for $N_2O$ surface emission, the scatter plots are presented with 13 sampling date values having four replicates).

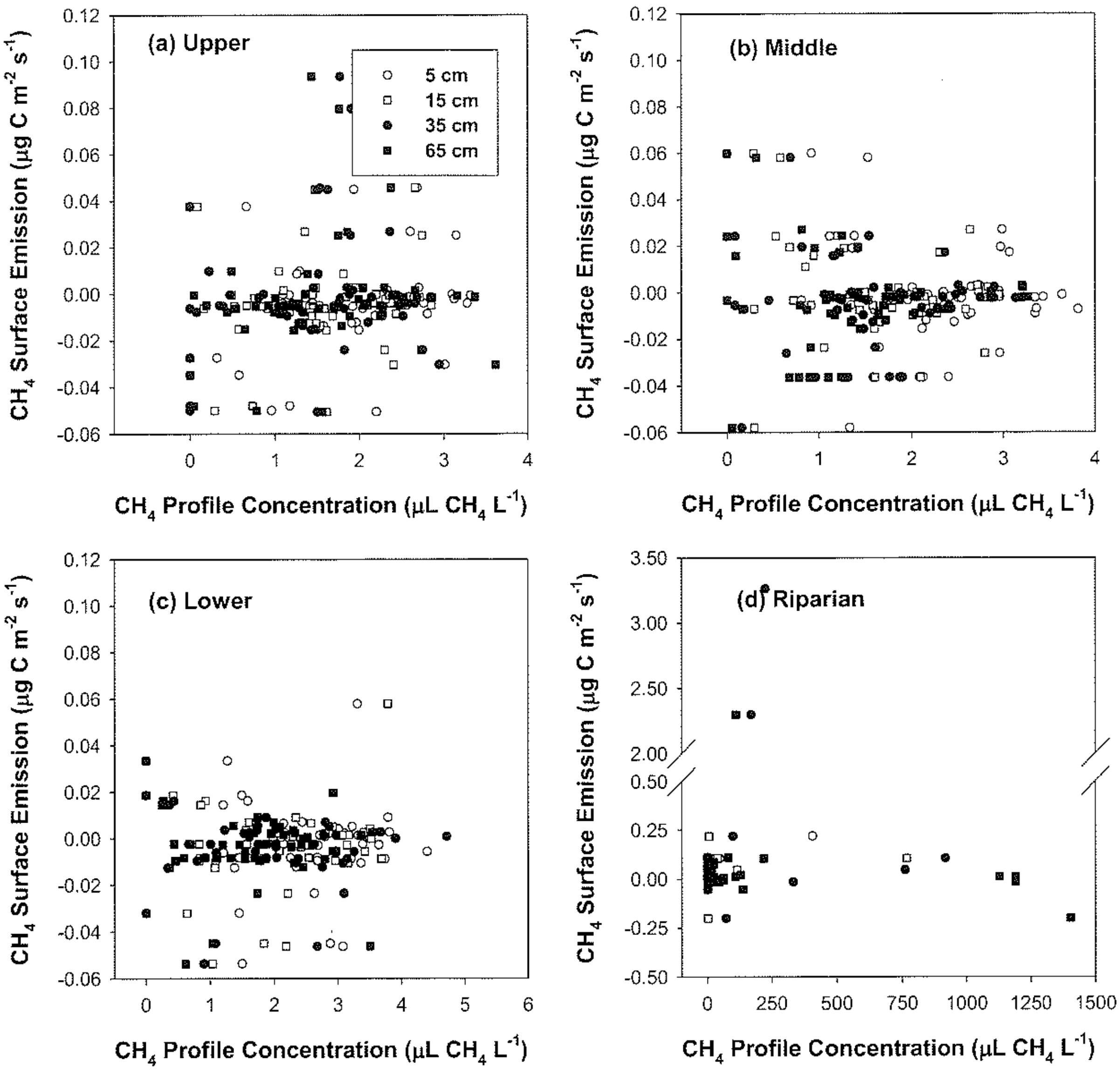


**Figure 2.11** Scatter plots of methane ($CH_4$) profile concentration at different depths (5 cm, 15 cm, 35 cm and 65 cm) to $CH_4$ surface emission in different landscape elements, (a) Upper $CH_4$ profile concentration and Upper $CH_4$ surface emission, (b) Middle $CH_4$ profile concentration and Middle $CH_4$ surface emission, (c) Lower $CH_4$ profile concentration and Lower $CH_4$ surface emission and (d) Riparian element $CH_4$ profile concentration and Riparian element $CH_4$ surface emission. (**Note:** n=52 for $CH_4$ concentration at each depth and n=13 for $CH_4$ surface emission, the scatter plots are presented with 13 sampling date values having four replicates).

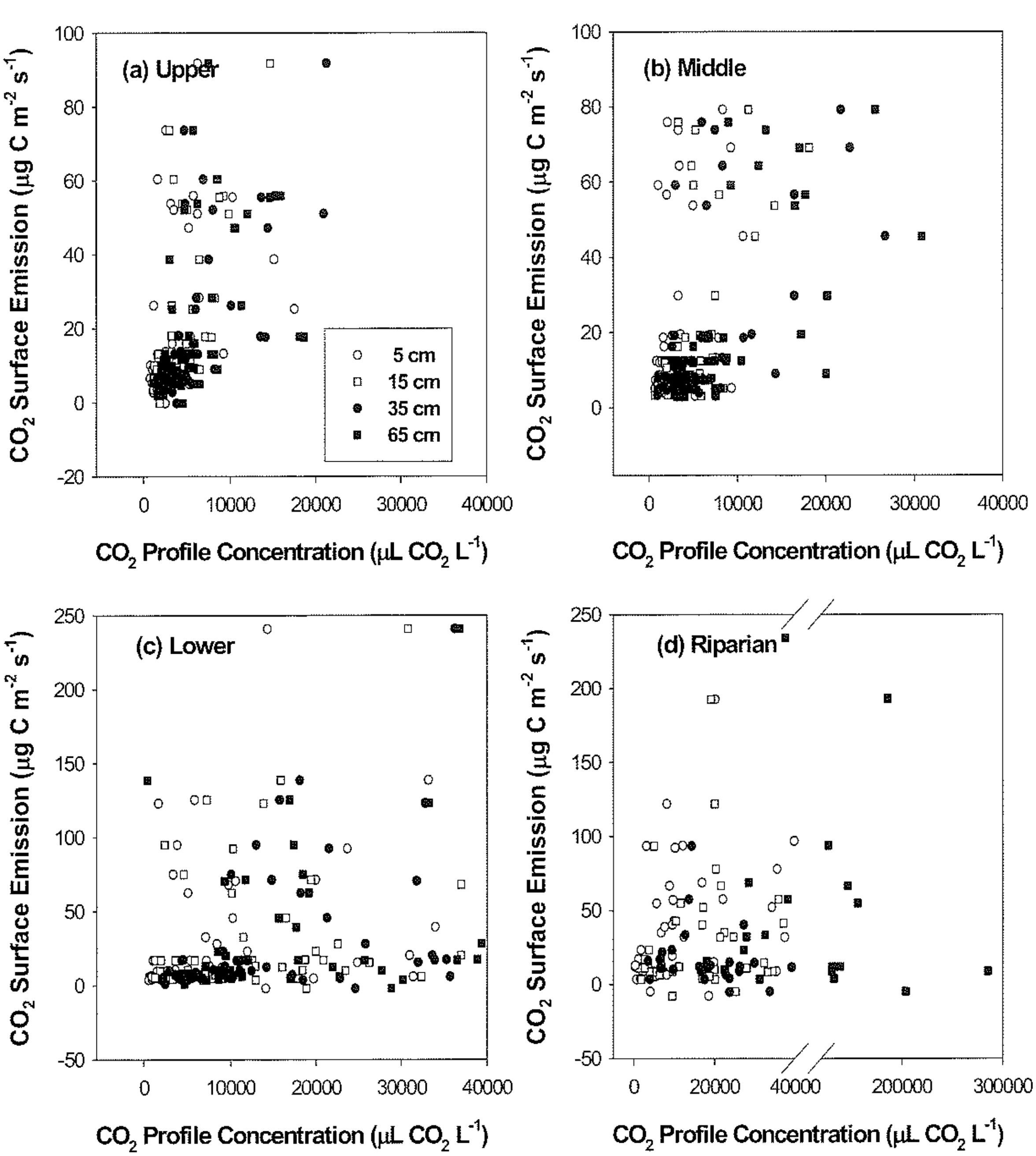


**Figure 2.12** Scatter plots of carbon dioxide ($CO_2$) profile concentration at different depths (5 cm, 15 cm, 35 cm and 65 cm) to $CO_2$ surface emission in different landscape elements, (a) Upper $CO_2$ profile concentration and Upper $CO_2$ surface emission, (b) Middle $CO_2$ profile concentration and Middle $CO_2$ surface emission, (c) Lower $CO_2$ profile concentration and Lower $CO_2$ surface emission and (d) Riparian element $CO_2$ profile concentration and Riparian element $CO_2$ surface emission. (**Note:** n=52 for $CO_2$ concentration at each depth and n=13 for $CO_2$ surface emission, the scatter plots are presented with 13 sampling date values having four replicates).

In the Upper and Middle landscape elements for 5, 15 and 35 cm depths when the $CH_4$ concentrations were 3μL $L^{-1}$, the $N_2O$ concentrations were elevated and in the Lower and Riparian landscape elements for the same depth the $N_2O$ concentrations increased when $CH_4$ reached 4μL $L^{-1}$ and above 5μL $L^{-1}$ $CH_4$ there was no $N_2O$ in all the landscape elements (Fig. 2.15). $CH_4$ concentrations and $N_2O$ concentrations were negatively correlated in the Lower and Riparian landscape elements at the 35 and 65 cm depths respectively, and in other landscape elements and depths the correlations were not significant (Tables 2.7, 2.8, 2.9 and 2.10). In the Upper and Middle landscape elements, $CO_2$ concentrations increased when the $CH_4$ concentrations were between 1 and 3μL $L^{-1}$ and the $CO_2$ concentrations decreased when the $CH_4$ concentrations were below 1μL $L^{-1}$ and above 3μL $L^{-1}$. In the Riparian landscape element, the relationship between $CO_2$ concentration and $CH_4$ concentrations was more closely correlated (Fig. 2.16) and a positive correlation was found at 65 cm depth (Tables 2.7, 2.8 2.9 and 2.10).

Significant correlations were found between greenhouse gas concentrations and soil volumetric moisture content and soil temperature (Tables 2.7, 2.8, 2.9 and 2.10). Volumetric moisture content and $N_2O$ concentrations at 5 and 15 cm depth in the Upper and Middle landscape elements were positively correlated. Volumetric moisture content and $N_2O$ concentrations were negatively correlated for Riparian element. In other landscape elements and depths $N_2O$ concentrations and volumetric water content were not significantly correlated. Volumetric moisture content and $CH_4$ concentrations were not correlated in any depth or landscape element except the 5 cm depth in the Middle landscape element. Volumetric moisture content and $CO_2$ concentrations at 35 cm depth

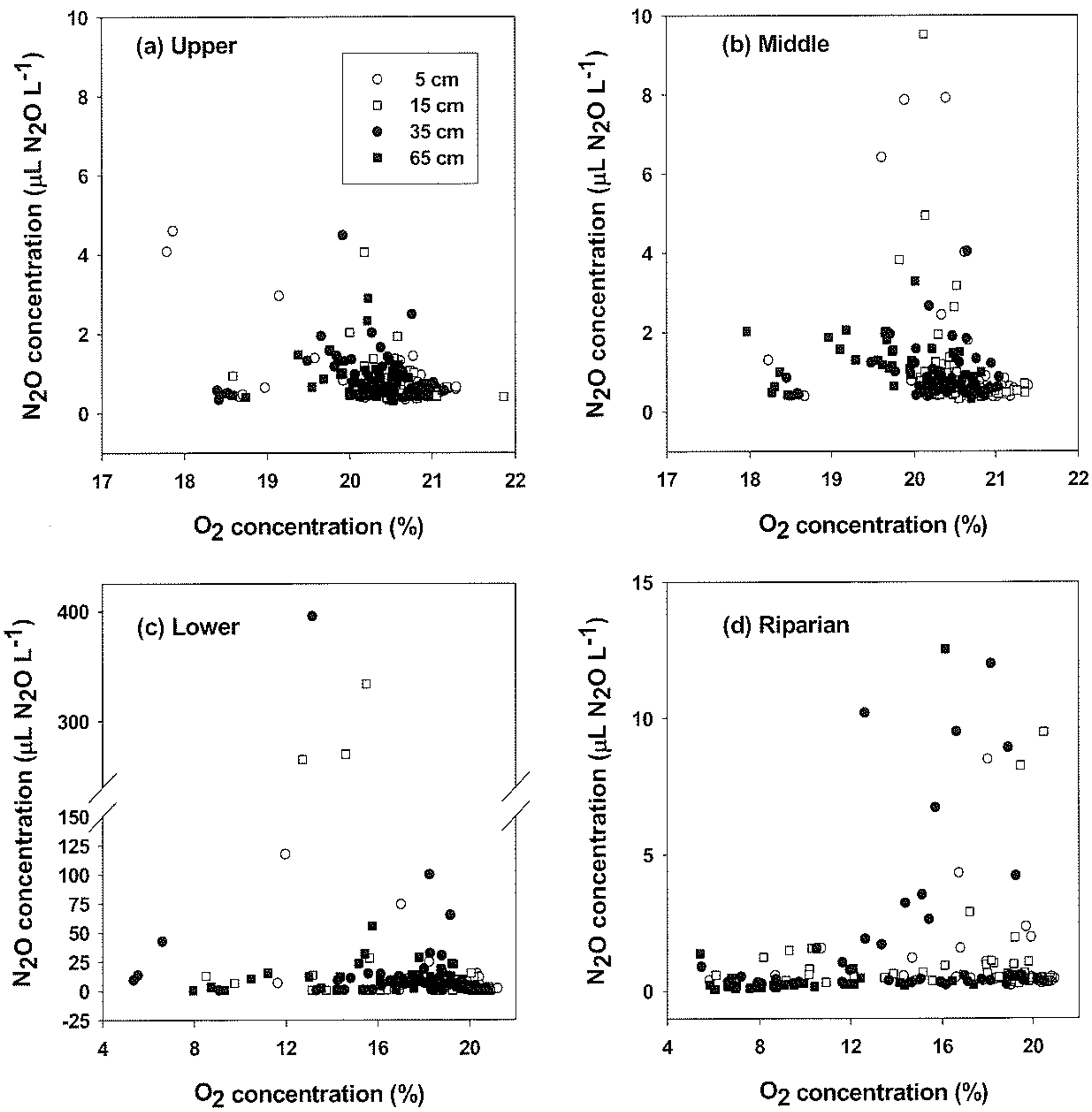


**Figure 2.13** Scatter plots of nitrous oxide ($N_2O$) profile concentration to oxygen ($O_2$) profile concentration at various depths (5 cm, 15 cm, 35 cm and 65 cm) in different landscape elements, (a) Upper $N_2O$ profile concentration and Upper $O_2$ profile concentration, (b) Middle $N_2O$ profile concentration and Middle $O_2$ profile concentration, (c) Lower $N_2O$ profile concentration and Lower $O_2$ profile concentration and (d) Riparian element $N_2O$ profile concentration and Riparian element $O_2$ profile concentration. (**Note:** n=52 for $N_2O$ and $O_2$ concentrations at each depth, the scatter plots are presented with 13 sampling date values having four replicates).

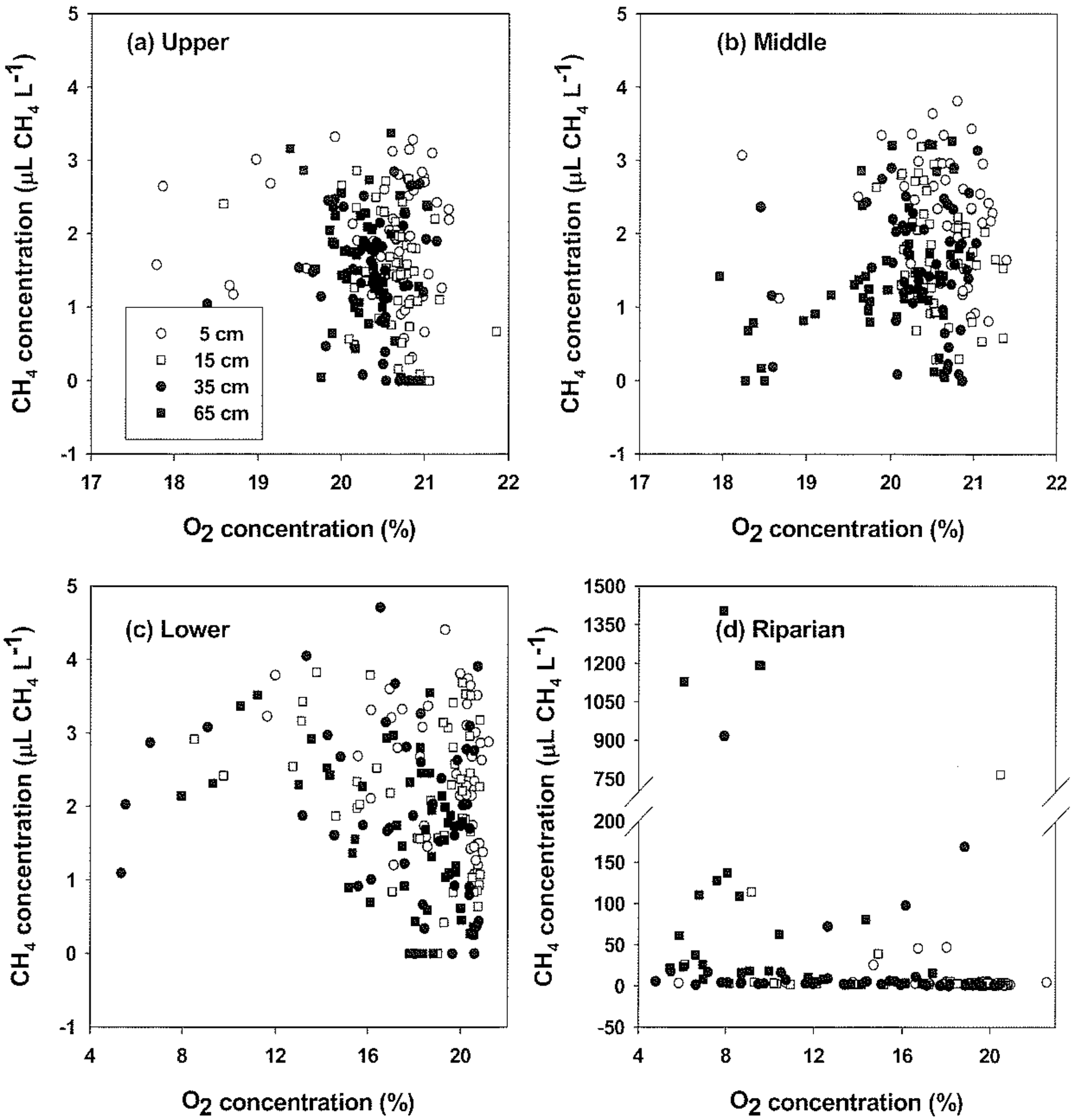


**Figure 2.14** Scatter plots of methane ($CH_4$) profile concentration to oxygen ($O_2$) profile concentration at various depths (5 cm, 15 cm, 35 cm and 65 cm) in different landscape elements, (a) Upper $CH_4$ profile concentration and Upper $O_2$ profile concentration, (b) Middle $CH_4$ profile concentration and Middle $O_2$ profile concentration, (c) Lower $CH_4$ profile concentration and Lower $O_2$ profile concentration and (d) Riparian element $CH_4$ profile concentration and Riparian element $O_2$ profile concentration (**Note:** n=52 for $CH_4$ and $O_2$ concentrations at each depth, the scatter plots are presented with 13 sampling date values having four replicates).

in all the landscape elements were positively correlated but were not strongly associated in any other depths or landscape positions. Soil temperature and $N_2O$ concentrations in all landscape elements and at all depths were negatively correlated whereas the soil temperature and $CO_2$ concentrations in all the landscape elements and at all depths were positively correlated. Soil temperature and $CH_4$ concentration were not strongly associated at any depth (except 65 cm) in the Upper and Middle landscape element. In the Lower and Riparian landscape elements and at 65 cm depth, the soil temperature and $CH_4$ concentration were positively correlated.

### 2.4.6 Relationship between the Measured Surface Greenhouse Gas Emissions and Estimated Profile Greenhouse Gas Emission in Soil

The emission values generated from profile concentrations and depth using calculated diffusion coefficient were 1,000 times more than the measured greenhouse gas emission values. The highest estimated emissions were likely due to over estimation of the actual diffusion coefficient. In order to attain more reasonable estimates of surface flux from profile concentration gradients, static chamber $CO_2$ surface emission values and $CO_2$ concentration profiles were used to estimate the actual gaseous diffusion co-efficient. After normalization with $CO_2$ surface emission, the estimated greenhouse gas emission values were within an order of magnitude to measured greenhouse gas emission. The estimated $N_2O$ emission showed a similar trend as measured emission in all landscape elements (Fig. 2.17). The profile concentration emissions estimated at different depths 0-5, 5-15 and 15-35 cm were well within the range of static vented chamber surface emission measurements. The 5-15 cm estimated profile emissions on sample day 96 were not similar to chamber emission in all the landscape elements. In the

Upper and the Riparian positions this particular depth profile emission was underestimated 10 times whereas in the Middle and Lower landscape elements the same depth profile emission was overestimated by 15 times. The estimated profile emission and measured static vented chamber emission behaved differently only during the freeze-thaw period and post-fertilizer application periods. During the remaining periods the estimated emission values were closer to measured emission values. The scatter plots of the measured surface chamber $N_2O$ emission and estimated profile $N_2O$ emission from 0-5 cm, 5-15 cm and 15-35 cm at all the landscape elements showed no consistent relationship between the measured and estimated values (Fig. 2.19).

The $CH_4$ profile emission values calculated from profile concentration showed similar trend as $N_2O$ but the static chamber values were higher for some sample dates indicating the tendency for profile-based estimates to underestimate emissions for low to medium effluxes. The 15-35 cm profile emissions were highest in the Lower landscape elements for sample day 187. The $CH_4$ emissions estimated from profile concentrations were within the range of measured surface $CH_4$ emissions in the Upper, Middle and Lower landscape elements, but in the Riparian landscape element the 15-35 cm profile emission were negative for two sample occasions, indicating a tendency to underestimate high effluxes. The 0-5 cm profile emissions were also negative in the Riparian landscape element for two sampling days (Fig. 2.18). The scatter plots for the measured surface chamber $CH_4$ emissions and estimated profile $CH_4$ emissions from 0-5 cm, 5-15 cm and 15-35 cm at all the landscape elements showed no consistent relationship between the measured and estimated values (Fig. 2.20).

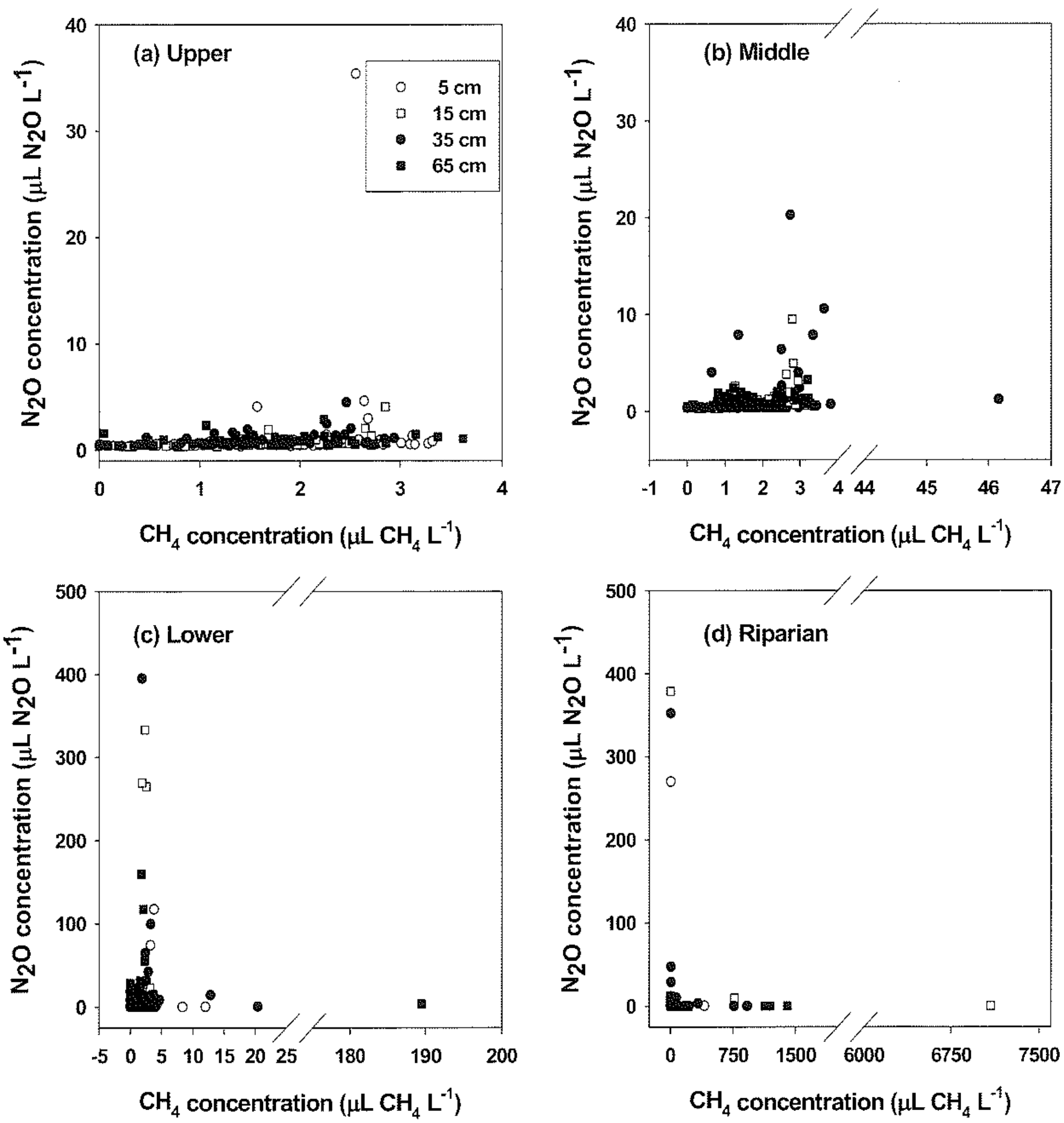


**Fig. 2.15** Scatter plots of methane ($CH_4$) profile concentration to nitrous oxide ($N_2O$) profile concentration at various depths (5 cm, 15 cm, 35 cm and 65 cm) in different landscape elements, (a) Upper $CH_4$ profile concentration and Upper $N_2O$ profile concentration, (b) Middle $CH_4$ profile concentration and Middle $N_2O$ profile concentration, (c) Lower $CH_4$ profile concentration and Lower $N_2O$ profile concentration and (d) Riparian element $CH_4$ profile concentration and Riparian element $N_2O$ profile concentration (**Note:** n=52 for $N_2O$ and $CH_4$ concentrations at each depth, the scatter plots are presented with 13 sampling date values having four replicates).

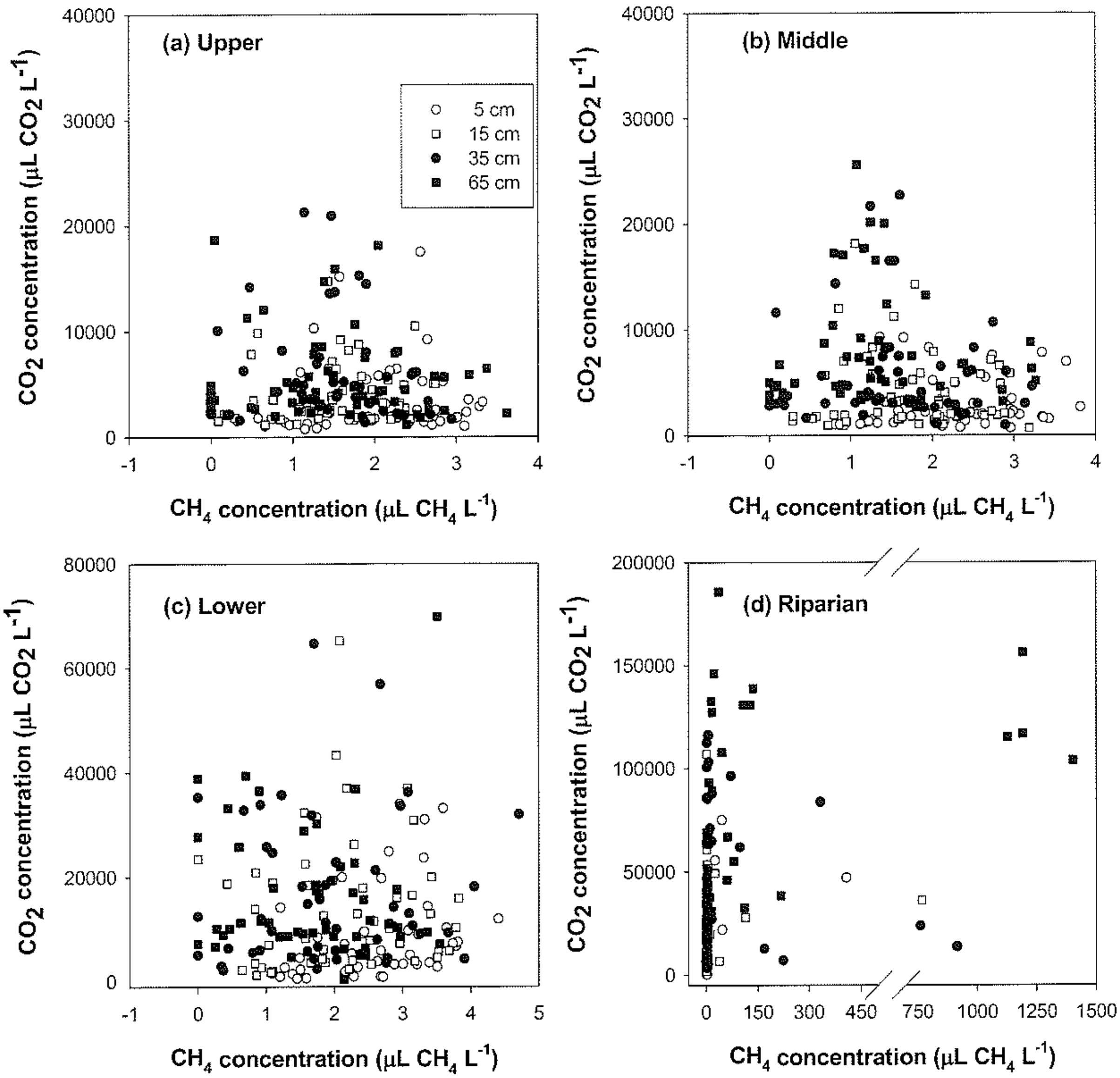


**Fig. 2.16** Scatter plots of methane ($CH_4$) profile concentration to carbon dioxide ($CO_2$) profile concentration at various depths (5 cm, 15 cm, 35 cm and 65 cm) in different landscape elements, (a) Upper $CH_4$ profile concentration and Upper $CO_2$ profile concentration, (b) Middle $CH_4$ profile concentration and Middle $CO_2$ profile concentration, (c) Lower $CH_4$ profile concentration and Lower $CO_2$ profile concentration and (d) Riparian element $CH_4$ profile concentration and Riparian element $CO_2$ profile concentration (**Note:** n=52 for $CO_2$ and $CH_4$ concentrations at each depth, the scatter plots are presented with 13 sampling date values having four replicates).

**Table 2.7** Spearman rank correlation coefficients for $N_2O$, $CH_4$ and $CO_2$ concentrations with $CH_4$, $CO_2$ and $O_2$ concentrations, soil volumetric moisture, soil temperature at 5 cm depth and surface emissions in different landscape elements.

| Variable | Landscape Element | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Upper | | | Middle | | | Lower | | | Riparian | | |
| | $N_2O$ Conc. | $CH_4$ Conc. | $CO_2$ Conc. | $N_2O$ Conc. | $CH_4$ Conc. | $CO_2$ Conc. | $N_2O$ Conc. | $CH_4$ Conc. | $CO_2$ Conc. | $N_2O$ Conc. | $CH_4$ Conc. | $CO_2$ Conc. |
| $CH_4$ Conc. (5 cm) | -0.01 | - | -0.11 | -0.17 | - | -0.01 | -0.25 | - | **0.36*** | 0.19 | - | **0.33*** |
| $CO_2$ Conc. (5 cm) | 0.19 | -0.11 | - | **0.30*** | -0.01 | - | **-0.34*** | **0.36*** | - | **-0.10** | **0.33*** | - |
| $O_2$ Conc. (5 cm) | **-0.37**** | 0.05 | -0.10 | **-0.38*** | 0.02 | -0.16 | -0.09 | 0.01 | **-0.35*** | **-0.40*** | -0.25 | -0.23 |
| VMC (5 cm) | **0.53**** | -0.26 | 0.05 | **0.50**** | **0.33*** | **0.28*** | 0.08 | -0.23 | -0.01 | 0.18 | 0.21 | 0.22 |
| Temperature (5 cm) | -0.25 | 0.15 | **0.75***** | **-0.48**** | **0.40**** | **0.38*** | **-0.44**** | **0.50**** | **0.57**** | -0.28 | 0.08 | **0.53**** |
| $N_2O$ emission | **0.40**** | 0.002 | **0.53**** | 0.07 | **0.29*** | **0.59***** | 0.20 | 0.10 | 0.23 | 0.07 | **-0.32*** | -0.01 |
| $CH_4$ emission | 0.16 | 0.18 | 0.07 | **0.38*** | -0.04 | 0.19 | -0.21 | 0.20 | **0.32*** | 0.13 | 0.19 | 0.08 |
| $CO_2$ emission | -0.24 | -0.06 | **0.69***** | **-0.43**** | **0.31*** | **0.38*** | **-0.47**** | **0.45**** | **0.42**** | -0.14 | 0.16 | **0.46**** |

**Note:** *, ** and *** indicate the correlation is significant at $P < 0.05$, 0.01 and 0.001 level of significance, respectively. The correlation was done with 11 sampling date values of 2006 and there were four replicates for each landscape element for greenhouse gas concentrations, soil volumetric moisture content, soil temperature and surface emissions (n=44).

**Table 2.8** Spearman rank correlation coefficients for $N_2O$, $CH_4$ and $CO_2$ concentrations with $CH_4$, $CO_2$ and $O_2$ concentrations, soil moisture, soil temperature at 15 cm depth and surface emissions in different landscape elements.

| Variable | Landscape Element | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Upper | | | Middle | | | Lower | | | Riparian | | |
| | **$N_2O$ Conc.** | **$CH_4$ Conc.** | **$CO_2$ Conc.** | **$N_2O$ Conc.** | **$CH_4$ Conc.** | **$CO_2$ Conc.** | **$N_2O$ Conc.** | **$CH_4$ Conc.** | **$CO_2$ Conc.** | **$N_2O$ Conc.** | **$CH_4$ Conc.** | **$CO_2$ Conc.** |
| $CH_4$ Conc. (15 cm) | 0.22 | - | 0.03 | 0.18 | - | -0.08 | **-0.41**** | - | 0.07 | -0.19 | - | 0.15 |
| $CO_2$ Conc. (15 cm) | -0.18 | 0.03 | - | 0.16 | -0.08 | - | -0.06 | 0.07 | - | **-0.44**** | 0.15 | - |
| $O_2$ Conc. (15 cm) | -0.21 | -0.09 | **-0.28*** | **-0.48**** | -0.13 | 0.08 | -0.08 | -0.07 | **-0.46**** | -0.06 | 0.21 | -0.25 |
| VMC (15 cm) | **0.41**** | -0.08 | 0.20 | **0.14*** | 0.11 | **0.43**** | 0.15 | 0.01 | 0.18 | **-0.41*** | -0.04 | 0.22 |
| Temperature (15 cm) | **-0.38*** | 0.08 | **0.89***** | -0.20 | -0.08 | **0.86***** | **-0.40*** | **0.29*** | **0.53**** | **-0.64***** | 0.16 | **0.54**** |
| $N_2O$ emission | **0.29*** | 0.17 | **0.42**** | **0.41**** | 0.19 | **0.70***** | 0.16 | 0.16 | **0.47**** | 0.25 | 0.04 | 0.01 |
| $CH_4$ emission | 0.18 | 0.07 | 0.01 | **0.25*** | 0.20 | -0.10 | -0.06 | 0.17 | 0.24 | -0.10 | **0.40*** | 0.21 |
| $CO_2$ emission | **-0.32*** | 0.03 | **0.81***** | -0.11 | 0.05 | **0.63***** | **-0.44**** | **0.49**** | **0.42**** | **-0.60***** | **0.29*** | **0.44**** |

**Note:** *, ** and *** indicate the correlation is significant at $P < 0.05$, 0.01 and 0.001 level of significance, respectively. The correlation was done with 11 sampling date values of 2006 and there were 4 replicates for each landscape element for greenhouse gas concentrations, soil volumetric moisture content, soil temperature and surface emissions (n=44).

**Table 2.9** Spearman rank correlation coefficients for $N_2O$, $CH_4$ and $CO_2$ concentrations with $CH_4$, $CO_2$ and $O_2$ concentrations, soil moisture, soil temperature at 35 cm depth and surface emissions in different landscape elements.

| **Variable** | **Landscape Element** | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | **Upper** | | | **Middle** | | | **Lower** | | | **Riparian** | | |
| | **$N_2O$ Conc.** | **$CH_4$ Conc.** | **$CO_2$ Conc.** | **$N_2O$ Conc.** | **$CH_4$ Conc.** | **$CO_2$ Conc.** | **$N_2O$ Conc.** | **$CH_4$ Conc.** | **$CO_2$ Conc.** | **$N_2O$ Conc.** | **$CH_4$ Conc.** | **$CO_2$ Conc.** |
| $CH_4$ Conc. (35 cm) | 0.09 | - | -0.01 | **0.31*** | - | **-0.28*** | **-0.32*** | - | 0.04 | -0.25 | - | 0.11 |
| $CO_2$ Conc. (35 cm) | 0.03 | -0.01 | - | **0.30*** | **-0.28*** | - | 0.03 | 0.04 | - | -0.19 | 0.11 | - |
| $O_2$ Conc. (35 cm) | -0.09 | -0.09 | **-0.35*** | 0.03 | 0.14 | -0.23 | -0.07 | -0.10 | **-0.63***** | 0.24 | -0.26 | **-0.37*** |
| VMC (35 cm) | 0.06 | 0.22 | **0.47**** | -0.06 | -0.02 | **0.43**** | **-0.34*** | 0.15 | **0.52**** | 0.26 | -0.02 | **0.59**** |
| Temperature (35 cm) | **-0.26*** | 0.20 | **0.83***** | -0.18 | **-0.30*** | **0.76***** | **-0.32*** | 0.09 | **0.69***** | -0.28 | 0.23 | **0.71***** |
| $N_2O$ emission | **0.37*** | 0.14 | **0.49**** | **0.34*** | 0.07 | **0.60***** | 0.21 | 0.09 | 0.45 | -0.01 | 0.12 | 0.10 |
| $CH_4$ emission | 0.11 | 0.01 | 0.09 | 0.19 | 0.17 | -0.13 | -0.09 | 0.10 | 0.15 | **-0.37*** | **0.36*** | **-0.33*** |
| $CO_2$ emission | -0.14 | 0.16 | **0.75***** | -0.16 | -0.08 | **0.52**** | **-0.38*** | 0.43 | **0.54**** | **-0.34*** | 0.19 | **0.66***** |

**Note:** *, ** and *** indicate the correlation is significant at $P < 0.05$, 0.01 and 0.001 level of significance, respectively. The correlation was done with 11 sampling date values of 2006 and there were four replicates for each landscape element for greenhouse gas concentrations, soil volumetric moisture content, soil temperature and surface emissions (n=44).

**Table 2.10** Spearman rank correlation coefficients for $N_2O$, $CH_4$ and $CO_2$ concentrations with $CH_4$, $CO_2$ and $O_2$ concentrations, soil temperature and surface emissions at 65 cm in different landscape elements.

| Variable | Landscape Element | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Upper | | | Middle | | | Lower | | | Riparian | | |
| | **$N_2O$ Conc.** | **$CH_4$ Conc.** | **$CO_2$ Conc.** | **$N_2O$ Conc.** | **$CH_4$ Conc.** | **$CO_2$ Conc.** | **$N_2O$ Conc.** | **$CH_4$ Conc.** | **$CO_2$ Conc.** | **$N_2O$ Conc.** | **$CH_4$ Conc.** | **$CO_2$ Conc.** |
| $CH_4$ Conc. (65 cm) | -0.24 | - | 0.11 | -0.15 | - | -0.25 | -0.13 | - | 0.01 | **-0.36*** | - | **0.65**** |
| $CO_2$ Conc. (65 cm) | -0.19 | 0.11 | - | 0.16 | -0.25 | - | 0.18 | 0.01 | - | **-0.50*** | **0.65**** | - |
| $O_2$ Conc. (65 cm) | 0.24 | -0.26 | **-0.37*** | **-0.37*** | **0.32*** | **-0.36*** | 0.14 | **-0.57**** | -0.07 | **0.70**** | **-0.29*** | -0.30 |
| Temperature (65 cm) | -0.28 | 0.23 | **0.71***** | -0.18 | -0.02 | **0.86***** | **-0.44**** | **0.49**** | 0.23 | **0.58**** | **0.40*** | **0.76***** |
| $N_2O$ emission | -0.01 | 0.13 | 0.10 | **0.33*** | 0.01 | **0.66***** | 0.13 | **0.30*** | 0.24 | -0.30 | 0.23 | 0.11 |
| $CH_4$ emission | **-0.37*** | **0.36*** | **-0.33*** | **0.38*** | 0.11 | -0.18 | -0.03 | 0.14 | -0.14 | 0.11 | 0.28 | 0.01 |
| $CO_2$ emission | **-0.34*** | 0.19 | **0.66***** | 0.03 | 0.02 | **0.67***** | **-0.48**** | **0.48**** | 0.11 | **-0.61**** | **0.41*** | **0.57**** |

**Note:** *, ** and *** indicate the correlation is significant at $P < 0.05$, 0.01 and 0.001 level of significance, respectively. The correlation was done with 11 sampling date values of 2006 and there were four replicates for each landscape element for greenhouse gas concentrations, soil moisture, soil temperature and surface emissions (n=44).

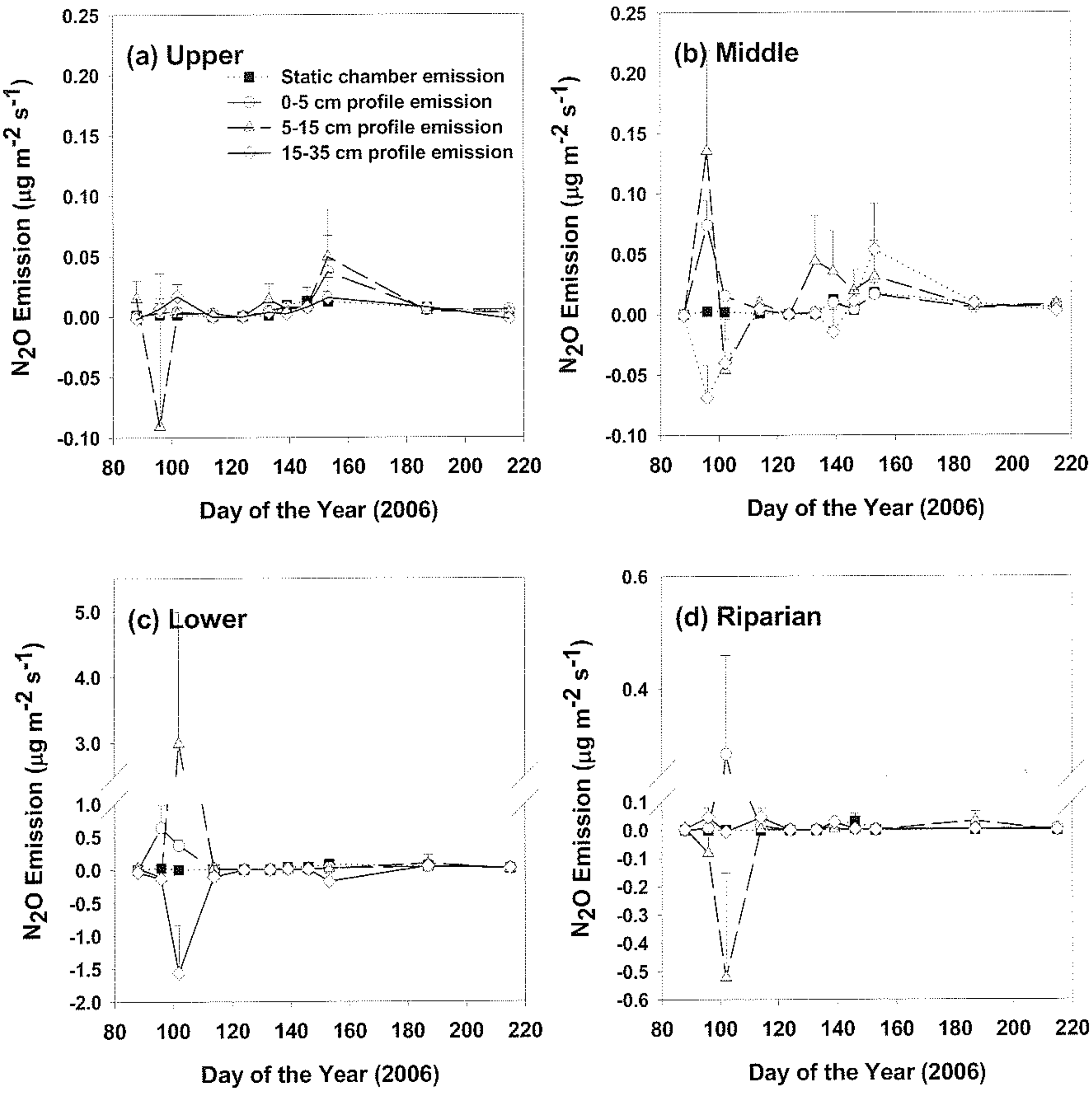


**Figure 2.17** Measured static vented chamber $N_2O$ emission (µg N $m^{-2}s^{-1}$) and estimated profile emission at 0-5 cm, 5-15 cm and 15-35 cm depths in 2006 for various landscape elements; (a) Upper, (b) Middle, (c) Lower and (d) Riparian landscape element. Values are means of four replicate sections and plus one standard error of the mean is shown.

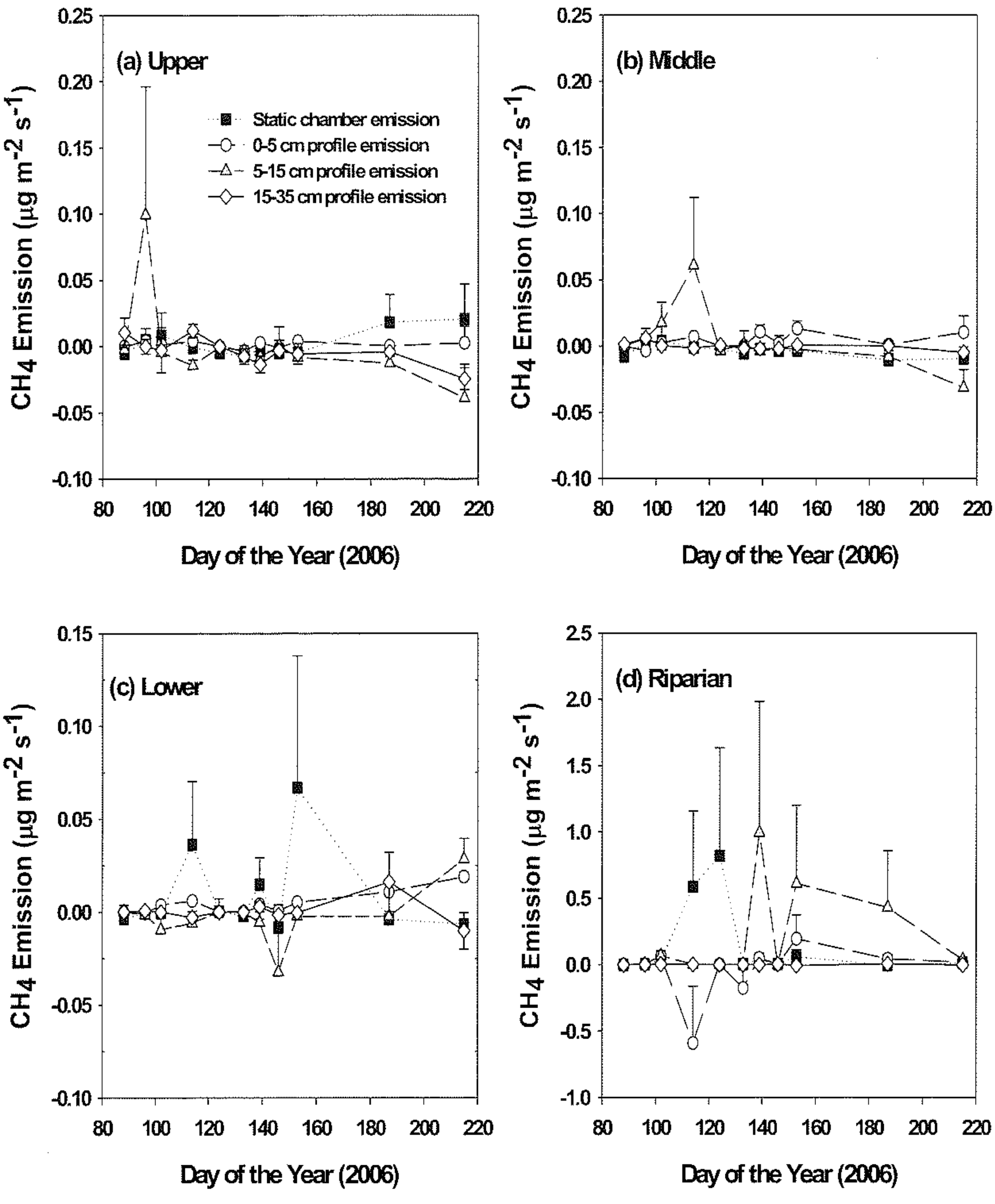


**Figure 2.18** Measured static vented chamber $CH_4$ emission (μg C $m^{-2}s^{-1}$) and estimated profile emission at 0-5 cm, 5-15 cm and 15-35 cm depths in 2006 for various landscape elements; (a) Upper, (b) Middle, (c) Lower and (d) Riparian element. Values are means of four replicate sections and plus one standard error of the mean is shown.

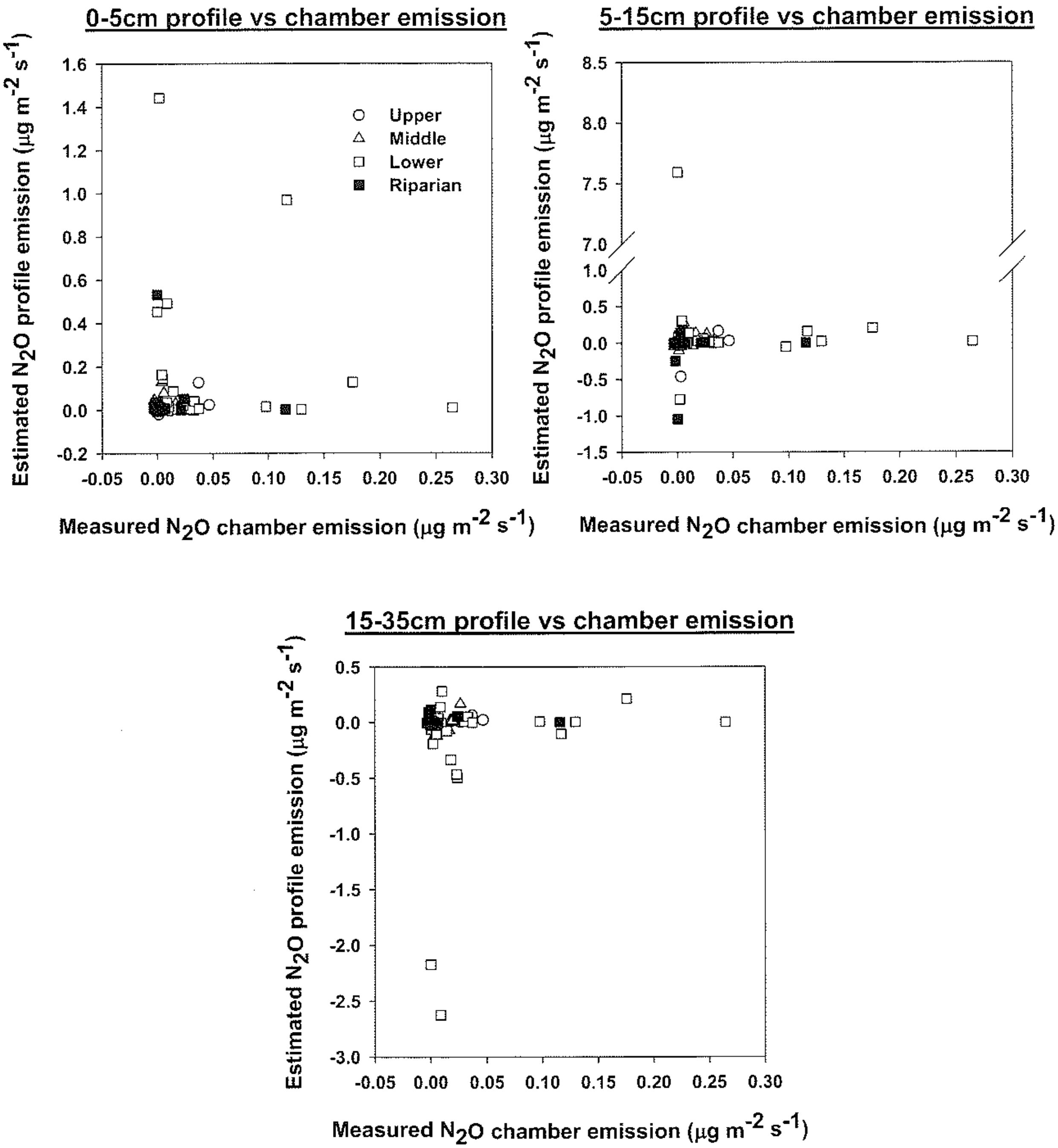


**Figure 2.19** Scatter plots of measured surface chamber $N_2O$ emission (μg N $m^{-2}s^{-1}$) and estimated profile $N_2O$ emission from 0-5 cm, 5-15 cm and 15-35 cm at Upper, Middle, Lower and Riparian landscape elements in 2006 (**Note:** n=44 for estimated $N_2O$ profile emission at each depth and measured $N_2O$ chamber emission, the scatter plots are presented with 11 sampling date values of 2006 having four replicates for each landscape element).

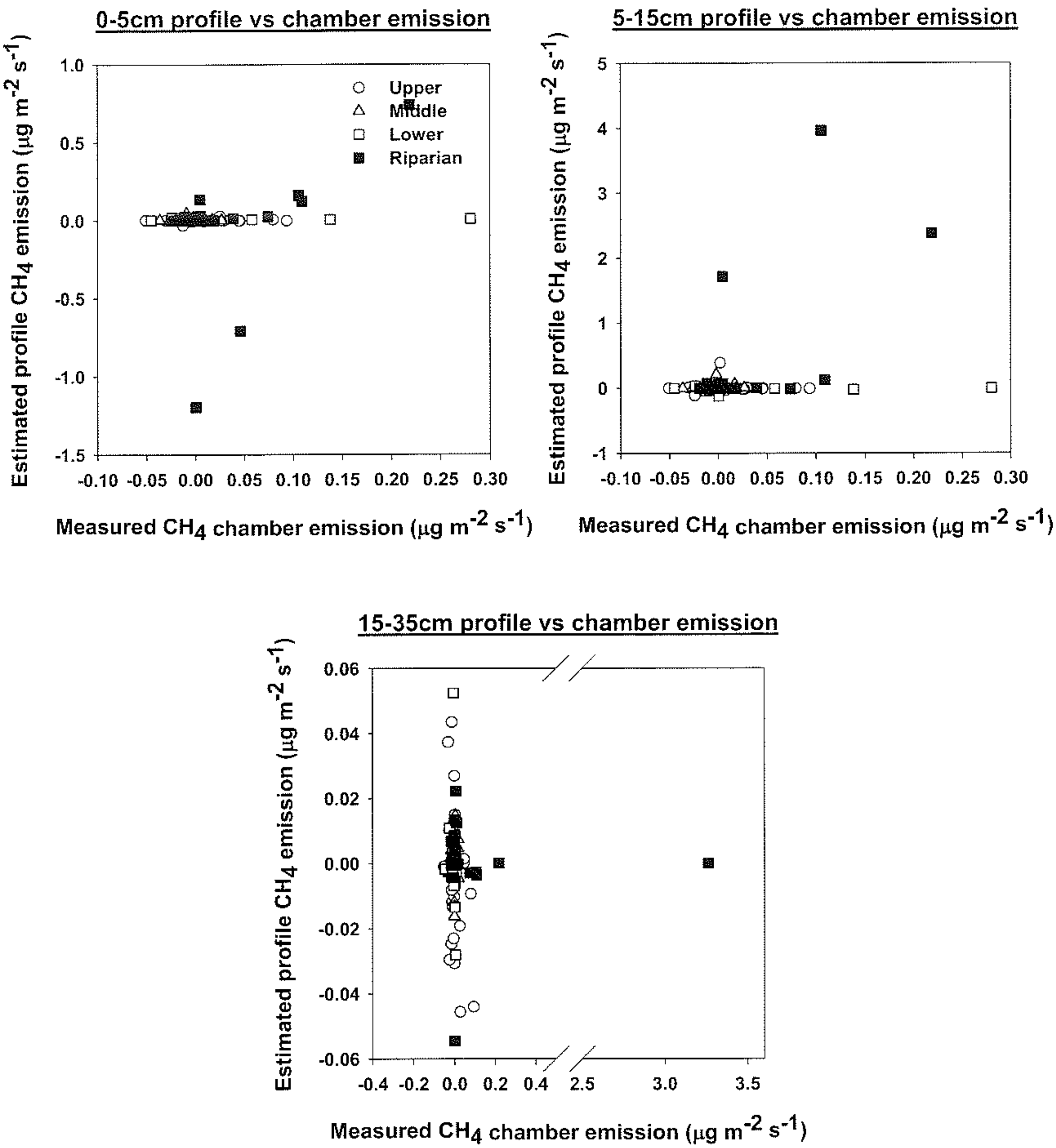


**Figure 2.20** Scatter plots of measured surface chamber $CH_4$ emission (μg C $m^{-2}s^{-1}$) and estimated profile $CH_4$ emission from 0-5 cm, 5-15 cm and 15-35 cm at Upper, Middle, Lower and Riparian landscape elements in 2006 (**Note:** n=44 for estimated $CH_4$ profile emission at each depth and measured $CH_4$ chamber emission, the scatter plots are presented with 11 sampling date values of 2006 having four replicates for each landscape element).

## 2.5 Discussion

### 2.5.1 Seasonal and Landscape Effects on Subsurface Greenhouse Gas Concentrations

The greenhouse gas profile concentrations in the Upper, Middle, Lower and Riparian landscape elements varied temporally and spatially. Soil $N_2O$ concentration profiles differed significantly during the study period across landscape elements and with depth (Fig. 2.5 and Table 2.3). Spatially and temporally episodic increases in $N_2O$ accumulation resulted in maximum $N_2O$ concentrations being observed at 5 and 15 cm depth. The $N_2O$ concentrations in the soil profiles were greatest during pre-snow melt in the Lower and Riparian landscape elements and the highest concentrations were recorded at 5 and 15 cm depth. Highest $N_2O$ concentration of 289.4 $\mu L\ L^{-1}$ was recorded in the Lower landscape element at 15 cm depth which is in contrast to the published data of others (Egginton and Smith 1986; Burton and Beauchamp 1994; Li et al. 2002; Tenuta and Beauchamp 2003). These authors found highest $N_2O$ concentrations at the lower depths. Others have also recorded the $N_2O$ profile concentrations even as high as 2500 $\mu L\ L^{-1}$ (Goodroad and Keeney 1985; Sitaula et al. 1995).

The seasonal variation of $N_2O$ profile concentrations was greatest at lowest sampling depths (Fig. 2.3). The variation within a sampling day among sections was also highest in samples collected at lowest depths. The magnitude of variability observed was consistent with the brief burst of $N_2O$ emission during freeze-thaw and post fertilizer application periods (Christensen and Tiedje 1990). Soil profile $N_2O$ concentrations in the Upper and Middle landscape elements during the post-crop period were relatively low and might be due to increased soil $O_2$ and decreased soil volumetric moisture content in these elements (Fig. 2.5). The higher volumetric moisture content at lower depths (35 cm and 65 cm) in these landscape elements resulted in the highest $N_2O$. In the Lower and Riparian landscape elements the volumetric moisture content was higher which resulted in higher $N_2O$ concentrations at lower depths. Such a relationship between the soil $N_2O$ concentration, volumetric moisture content and $O_2$ content suggested that denitrification was probably the major mechanism for $N_2O$ production (Smith et al. 2003; Yu and Patrick, 2003). Two prominent periods of $N_2O$ production (freeze-thaw and post-fertilization) were observed in all Upper, Middle and Lower landscape elements whereas in the Riparian landscape element only freeze-thaw $N_2O$ was observed. The Riparian element did not receive fertilizer application and was mostly dominated by perennial grasses and aquatic plants. Several authors have also observed higher $N_2O$ production during the freeze-thaw and post-fertilizer application periods (Burton and Beauchamp 1994; Van Bochove et al. 2000; Teepe et al. 2001; Groffman et al. 2006).

$N_2O$ was produced in the outer oxidizing layers (for nitrification) and moderately reducing layers (for denitrification) of soil aggregates (Tiedje et al. 1984). However, $N_2O$ produced at the outer layers probably can move through the oxidizing soil pore space and emit to the atmosphere without significant loss, because $N_2O$ can only be consumed by reduction to $N_2$ under more reducing conditions. When the reducing conditions in the soil of Lower and Riparian landscape elements were sufficiently intense, complete denitrification is likely to occur with $N_2$ being the primary end product. But my results showed the measurements of soil $N_2O$ concentrations at the Lower and Riparian landscape elements were higher than the atmospheric level during the snow-melt period which indicated $N_2O$ was still being produced even under saturated conditions. The higher $N_2O$ accumulations recorded in the Lower and Riparian elements during freeze-thaw periods likely reflect periods of increased denitrification where conditions are such that denitrification does not go to completion and $N_2O$ remains a product (Fig. 2.5).

Several studies indicated that reduced conditions with $O_2$ concentrations of less than 8% were necessary for denitrification to occur (Cey et al. 1999), but many studies have measured denitrification activity in the surface horizon of Riparian soils (Pinay et al. 1993; Clement et al. 2002). Burt et al. (2002) suggested that denitrification occurs mainly during periods of high water table in the Riparian areas and that in summer the water table often declines below the surface organic horizon limiting denitrification, due to lack of organic matter at depth. Denitrification is prominent during the spring-thaw when the soil is saturated as a result of snow melt, whereas aerobic respiration, $NO_3^-$ uptake by vegetation and soil microbial biomass dominates under low soil volumetric moisture content conditions during the summer (Simmons et al. 1992; Correll 1997). The results obtained from the present study confirmed these findings as higher $N_2O$ concentrations were recorded during the freeze-thaw period at shallow depths, mostly 5 and 15 cm, in all the landscape elements.

The accumulation of $N_2O$ in the lower profile suggests $N_2O$ production occurred deeper in the soil profile during the winter months. Although the magnitude of production cannot be determined because of the extent of redistribution is not known, $N_2O$ accumulation indicates the rate of production exceeded the rates of consumption and redistribution. The formation of a frozen layer provides a barrier to the escape of $N_2O$ and thus $N_2O$ production by nitrification and denitrification, in the absence of a sink for $N_2O$ would result in $N_2O$ accumulation (Burton and Beauchamp 1994). Subsurface buildup of $N_2O$ during winter occurred at different depths in all the landscape elements and the redistribution and accumulation were affected by various soil properties. The timing of $N_2O$ buildup and emission to atmosphere as $N_2O$ emission were not consistent. Higher volumetric moisture content (>30%) in the Lower and Riparian landscape elements created a zone of restricted diffusion influencing the upward diffusion of $N_2O$ and resulted in the accumulation of $N_2O$ at lower depths (Fig. 2.5). I hypothesize that following snow-melt, the $N_2O$ retained in the lower depths diffused back to the surface through soil where denitrification was active, resulting in reduction to $N_2$ which then escaped to the atmosphere. This is why higher $N_2O$ concentrations were recorded at 5 and 15 cm depths during snow-melt period in all the landscape elements. Wagner-Riddle et al. (2008) recorded a higher $N_2O$ concentration in the 12-17 cm deep layer when compared to the 0-5 cm shallow layer but they concluded the elevated $N_2O$ emission during snow melt was due to the newly produced $N_2O$ in the shallow layer and not by the release of trapped $N_2O$ from unfrozen deep layers which is contrary to our findings.

The higher amounts of ammoniacal and nitrate nitrogen in the Lower and Riparian landscape elements may influence the rate of nitrification and the extent to which denitrification produced $N_2O$ (Gillam et al. 2008), both resulting in more $N_2O$ production and accumulation at depth in these landscape elements. The lower levels of $N_2O$ in the Lower and Riparian landscape elements are due to the reduction of $N_2O$ to $N_2$ during denitrification that occurred well below the saturated soil surface (Smith et al. 2003). Several ecosystem processes affecting N cycling, including denitrification, have been shown to proceed at a higher rate in foot slope than in shoulder or Upper landscape elements (Pennock et al. 1992). On rolling plains and hummocky landscapes, positions within landscapes can exert a greater influence on C and N dynamics (Pennock et al. 2005).

The $CH_4$ concentrations in soil profiles did not exhibit a regular pattern with depth and among landscape elements (Fig. 2.6 and Table 2.4). The $CH_4$ concentrations tended to be very high in the Lower and Riparian landscape elements at lower depths (35 cm or greater). On each particular date and location, the Lower and Riparian landscape element at lower soil depths generally showed higher concentrations of gas probably because of higher resistance in gas diffusion (and ebullition for the Riparian soils) through the soil/water layer to the atmosphere when the soil gases were saturated (Chareonsilp et al. 2000) or might be due to a closer proximity to the source of $CH_4$ production.

Methane oxidation in aerated soils has been evaluated for its important role in the global $CH_4$ budget (King 1992). Such $CH_4$ consumption activity in soils can substantially abate the amount of $CH_4$ emitted to the atmosphere. In this study, the Lower and Riparian elements represented the only major $CH_4$ sources to the atmosphere. The strength of $CH_4$ source to the atmosphere for the Upper and Middle was probably not strong in the snow-melt period because of $CH_4$ consumption during the drier fall season which might offset the production of $CH_4$ during the thaw period. The Upper and Middle landscape elements act as a net sink for the atmospheric $CH_4$, since the soil $CH_4$ concentrations in the wet season were only slightly higher than the atmospheric $CH_4$ level in these landscape elements. Large amounts of $CH_4$ produced in the anaerobic soils are oxidized when it moved through the outer oxidized layers into the soil air before it emits to the atmosphere (Khalil et al. 1998) which is evident from the present study that high $CH_4$ accumulation was observed in the Lower and Riparian landscape elements at 15 and 35 cm depth, but there was no elevated $CH_4$ emission from these landscape elements. In the Upper and Middle landscape elements during the post-crop period the $CH_4$ concentrations were below ambient levels which indicated mostly they were consumed in the aerobic soils (Fig. 2.6).

Methane consumption is limited by diffusion into the soil, which is inversely related to moisture content. As soil moisture decreases, conditions favor $CH_4$ oxidizers and $CH_4$ consumption can occur, however, there is a point at which microbes become moisture stressed (Gulledge and Schimel 1998). Saturated soil conditions limit aerobic processes and favor $CH_4$

production (Yavitt et al. 2005). Also, for $CH_4$ production to occur, low redox conditions created by prolonged saturated conditions and labile carbon are necessary (Smith et al. 2003). In the Riparian landscape element, during freeze-thaw period $CH_4$ concentration were highest at 5 and 15 cm depth showing a burst of $CH_4$ as a result of anaerobic conditions and higher organic matter accumulation, which presumably supports higher microbial activity. During the cropped period, the soil was dry at shallow depths which allowed an aerobic condition to exist and resulted in less $CH_4$ production at shallow depths. But at the 65 cm depth a higher water content allowed for anaerobic conditions to persist resulting in $CH_4$ production and accumulation (Fig. 2.6). High sulfate content in the Riparian landscape elements provide an alternate terminal electron acceptor and is therefore inhibitory to methane production in the Riparian zone (Mishra et al. 2003). This inhibitory effect is due to the competition between sulfate-reducing bacteria and methanogens for electron donors (such as organic carbon) in sulfate-rich anaerobic environments (Lovely and Klug 1983).

Gas diffusion into the soil is an important factor for the location of $CH_4$ oxidation activity in soil profiles (Striegl 1993). The higher amounts of ammonium in the Lower and Riparian landscape elements inhibited the activity of $CH_4$ oxidizing bacteria and $CH_4$ uptake in the soil profiles (Sitaula et al. 1995). Inhibition of $CH_4$ uptake was detected soon after N fertilization and inhibition persisted for 39 days (Schnell and King 1994). The higher amounts of $CH_4$ in the Lower and Riparian landscape elements suppressed the nitrification and the suppression depends on the concentration gradients and emissions of the substrates $NH_4^+$ and $CH_4$. $CH_4$ suppresses nitrification by competition for $O_2$ and $NH_4^+$ between methanotrophs and nitrifiers (Roy et al. 1996). In contrast to $CH_4$ concentrations, $O_2$ concentrations were higher in the Upper and Middle landscape elements. These results are expected as drier conditions at the Upper and Middle landscape elements create a more aerobic environment, as more soil pores become air-filled. In wet conditions $O_2$ diffusion is restricted, leading to decreased soil $O_2$ concentrations, where $O_2$ is consumed by heterotrophic respiration (Gulledge and Schimel 1998). The $O_2$ concentrations were greater at the shallow depths in all landscape elements except the Riparian element, as $O_2$ was more readily available in the soil at 5 and 15 cm than 35 and 65 cm, as a result of its closer proximity to the source (atmosphere), resulting in conditions becoming more anaerobic with depth (Fig. 2.8 and Table 2.6).

The pattern of $CO_2$ profile concentrations was consistent across landscape elements and depths. The concentrations of $CO_2$ significantly increased with depth in all landscape elements regardless of season. The $CO_2$ concentrations were higher in soil profiles during the early post crop 2005 period. Maximum $CO_2$ concentrations occurred at the beginning of the monitoring period. Higher $CO_2$ concentrations deep in the soil profile, in the earlier part of the sampling period, are likely the result not of high rate of production, but accumulation of soil $CO_2$ as a result of low porosity in wet, compact soil layers near 65 cm. During the wetter summer of 2005, when moderate rates of production were combined with regular rain, the poor diffusivity characteristics of this hardpan became most evident as $CO_2$ accumulated underneath. The increased $CO_2$ concentrations at lower depths during fall 2005 may be due to root turnover following crop senescence and / harvest or by the dissolution of carbonates, which is evident from the highest carbonate content at the lowest depth in the Upper, Middle and Lower landscape elements. The increase in $CO_2$ concentration at increasing depth among all landscape elements was most likely due to the variability in soil characteristics at that depth. The sudden change in soil texture might have caused a soil moisture variation in the soil layer. In the presence of high volumetric moisture content, the water can act as a $CO_2$ sink, thus decreasing

$CO_2$ concentration levels in the soil (Magnusson 1992) which is evident from the lower levels of $CO_2$ concentration in all the landscape element during snow melt in the present study (Fig. 2.7 and Table 2.5).

The subsurface $CO_2$ concentrations measured in the present study were within the range between 350 and 70,000 $\mu L\ L^{-1}$ for the Upper, Middle and Lower landscape elements, which were similar to those results of Sotomayor and Rice (1999) and that of Burton and Beauchamp (1994). But the Riparian element recorded 225,000 $\mu L\ L^{-1}$ at 65 cm depth and 100,000 $\mu L\ L^{-1}$ at 35 cm depth on sample day 218, which were very high and such levels not reported by others. The soil $CO_2$ concentration of welldrained soils generally increased with depth because of the differences in the relative strength of transport and production factors (Magnusson 1992; Oh et al. 2005). The Upper organic material rich soil generally has high porosity that results in the rapid exchange of air with the atmosphere. These finding were corroborated with the similar pattern of $CO_2$ concentrations in the Upper and Middle landscape elements. Below the organic layer the $CO_2$ concentration generally increased because of $CO_2$ accumulation caused by microbial and root respiration with a much slower rate of gas exchange between the subsoil and atmosphere (Jassal et al. 2004). The concentrations of $CO_2$ also increased with depth in poorly drained Lower and Riparian element soils which was in contrast to the findings of Magnusson (1992). It is also interesting to note that the trend of subsurface $CO_2$ concentration show distinct temporal pattern, reflecting the tradeoff between production and storage processes during the year.

Both soil and plant root respirations contribute to $CO_2$ production, resulting in a large amount of $CO_2$ accumulation in the soils (Fig. 2.7). The increased $CO_2$ emission in the cropped 2006 period confirmed that plant root respiration and/or the microbial respiration of root exudates is the primary source of $CO_2$ production in all the landscape elements. Significant $CO_2$ emissions through the soil/water surface to the atmosphere were expected at all the four landscape elements, because the soil $CO_2$ concentrations were two orders of magnitude higher than the atmospheric $CO_2$ levels. Substantial increase of the soil $CO_2$ concentrations when the soil $O_2$ decreased from 12 to 6.5% at the Riparian landscape elements was mainly due to slower release of $CO_2$ to the atmosphere under higher soil moisture conditions (Yu and Patrick 2003).

From the results of the present study, it was observed that among all the three greenhouse gases, $N_2O$ emission occurred immediately during the onset of freeze-thaw and the $CH_4$ emission occurred after thaw following the peak in $N_2O$ emissions. The emissions of $CO_2$ were not prominent during freeze-thaw, but were consistent during the crop growth and crop maturity period.

### 2.5.2 Seasonal and Landscape Effects on Surface Greenhouse Gas Emissions

The emission of $N_2O$, $CH_4$ and $CO_2$ varied temporally throughout the sampling period in all landscape elements. The emissions of $N_2O$, $CH_4$ and $CO_2$ were highest and variable during rainfall, spring-thaw and fertilizer application periods. The spring-thaw emission of $N_2O$ started when the soil temperature rose above $0^0C$ and the soil water-filled porosity was higher. The spring-thaw emissions continued for 5 days and the emissions of $N_2O$ became high again following fertilizer application (UAN solution application in 2006). The application of $NH_4^+$ and $NO_3^-$ nitrogen fertilizers dramatically increased the $N_2O$ emission which is in line with the findings of Tenuta and Beauchamp (2003) and Yates et al. (2006). Soils fertilized with ammonium have also been shown to result in greater $N_2O$ emission than those fertilized with nitrate (Dalal et al. 2003). The $N_2O$ emissions from the present study were within the range of those reported elsewhere (Weller et al. 1994; Groffman et al. 1998; Sozanska et al. 2002). Higher annual emissions have only been measured in specific cases with direct fertilization, for instance on grazed fertilized peaty grasslands (36-42 kg N $ha^{-1}$ $yr^{-1}$; Velthof et al. 2000).

The $N_2O$ emissions are reported to be controlled by the availability of mineral N, soil temperature and soil water content (Skiba et al. 1998). These controlling variables function in different combinations and in different magnitudes of importance both in space and time (Skiba and Smith 2000). In the current study, the difference in $N_2O$ emissions between various landscape elements could mainly be explained by nitrate availability. The nitrate concentrations in the top soil of the Upper and Middle landscape elements were lower than in the Lower and Riparian positions and hence lower $N_2O$ emissions were recorded in the Upper and Middle landscape elements. The lower nitrate levels in the Upper and Middle landscape elements were probably caused by surface runoff of nitrates to the Lower and Riparian buffer zones (Sabater et al. 2003). High soil moisture content also increased the residence time of $N_2O$ in the soil by restricting diffusion and may consequently enhance the reduction of $N_2O$ to $N_2$ (Jacinthe et al. 2000). Due to the microbial preference for the reduction of nitrate over $N_2O$, the further reduction of $N_2O$ would only be prominent in soils that are relatively low in nitrate (Arah et al. 1991). In the present study during post-fertilizer application time, the $N_2O$ emissions were highest in the Lower landscape element, which indicated that high soil moisture content coupled with higher nitrate levels triggered the $N_2O$ emission.

Wagner-Riddle et al. (2008) also observed a burst of $N_2O$ emission during the snow-melt period and they found denitrification was most certainly the major source of $N_2O$ emission from both shallow and deep soil layers by utilizing a $^{15}N$-labeled nitrogen source, tracking the concentration in soil, and measuring the surface emissions. They also noticed that the nitrate added to the shallow layer was the precursor to $N_2O$ production through denitrification. In the present study, even though the three landscape elements Upper, Middle and Lower received the fertilizer application in the form of UAN, only the Lower landscape element and to some extent the Middle landscape element had elevated levels of $N_2O$ emission which indicated besides the nitrogen source, soil moisture and aeration might be responsible for the highest $N_2O$ emission in these landscape elements. The lower denitrification activity in the Upper and Middle landscape elements were closely related to lower soil moisture content in these landscape elements (Fig. 2.9). The very low emissions observed in the Upper and Middle landscape elements in the present study might be due to either low water-filled pore space in the fall preceding the measurement period and/or the low soil nitrate values measured in the fall of 2005.

There was a significant difference in $CH_4$ emission from the Lower element compared to the Upper and Middle landscape elements. The Lower element had higher water-filled pore space and high total carbon, which might be responsible for increased $CH_4$ emission (Reiners et al. 1998). The aerobic condition prevailed in the Upper and Middle element resulting in an environment less conducive to methanogenesis and more conducive for oxidation of methane by methanotrophs (Topp and Pattey 1997). The higher sulfate content in the Riparian landscape element was inhibitory to methane emission in the Riparian zone, as sulfate is known to inhibit the activities of methanogens (Mishra et al. 2003). This inhibitory effect is due to the competition between sulfate-reducing bacteria and methanogens for electron donors (such as organic carbon) in sulfate-rich anaerobic environments (Lovely and Klug 1983).

### 2.5.3 Soil Moisture, Soil Temperature, Aeration and Microbial Activity Effects on Soil Greenhouse Gas Concentrations and Greenhouse Gas Surface Emissions

Frequent fluctuation of soil water content in the Lower and Riparian landscape elements may favor $N_2O$ production and emission to the atmosphere, because $N_2O$ efflux is likely to be greatest at moderately reducing conditions (Smith et al. 2003). A significant positive correlation between $N_2O$ and respiratory gases ($CO_2$ and $O_2$) observed in the present study and those reported by others (Dendooven et al. 1994; Azam et al. 2002) support the contention that enhanced microbial activity is responsible, partially if not entirely, for the observed $N_2O$ emission at shallow depth soils in all the landscape elements during snow melt. However, the increase in $N_2O$ emissions may not be accompanied by a similar increase in $CO_2$ emissions (Williams et al. 1998). The leveling-off of $N_2O$ emissions following an initial burst after snow-melt suggests that easily oxidizable C is exhausted while nitrification could still continue and contribute to $N_2O$ emissions. However, even under conditions promoting rapid nitrification rates, nitrate produced may be lost through denitrification (Wolf and Russow 2000). In the present study, greater accumulation of $N_2O$ and $CO_2$ at lower depths in the Lower and Riparian elements even at relatively higher levels of oxygen corroborate that respiration and denitrification may occur simultaneously even at a relatively high rate of oxygen supply, if a sufficient amount of easily decomposable organic matter is made available or by physical treatment of soil such as freezing/thawing, wetting/drying or disturbances (Reddy 1982; Poth and Focht 1985; Azam et al. 2002).

Nitrous oxide production in peat, loamy sand and clay soils increased drastically with increasing soil moisture content and only a minor amount of $N_2O$ is emitted from dry soils (Velthof and Oenema 1995). Organic soils are generally regarded as potentially greater $N_2O$ sources per land area than mineral soils (Velthof and Oenema 1995). The slightly higher $N_2O$ production rate in moist clay soil (Lower and Riparian soils) than in moist silty clay loam or silty loam (Upper element soil) could be related to a higher denitrification activity as a result of a build-up of anaerobic microsites in the clay soil due to its smaller pore sizes. In the post-crop period of 2005, the soils had a volumetric moisture content of about 10-20% in all the positions. The dry soils soon after wetting during snow-melt period responded to the added moisture and resulted in higher $N_2O$ emissions. Other workers (Scholes et al. 1997; Jorgensen et al. 1998) also observed a steep increase in $N_2O$ emissions within the first one or two days after wetting. This may be caused by a combination of biological production and release of soil absorbed $N_2O$ (Rice and Smith 1982).

The increased $N_2O$ production following thawing in all the landscape elements might also be caused by soil microorganisms that are killed and lysed, releasing substrate into the soil (Schimel and Clein 1996) or detritus that becomes available by the freezing-thawing process, eg. through disintegration of aggregates (Christensen and Christensen 1991). Schimel and Clein (1996) found that thawing of tundra and taiga soils produced an initial pulse in microbial respiration and that the total amount of $CO_2$ respired in each thaw period was largest during the first cycle and declined in successive cycles. Low temperatures in the freeze-thaw period have enhanced $N_2O$ produced by nitrification and/or suppressed the formation of $N_2O$ from denitrification by inhibiting the $NO_2^-$ reductase enzyme (Maag and Vinther 1996).

The soil moisture pattern appears to correlate with the relatively low variability in $CO_2$ concentrations at deeper depths when compared with shallower depths. Kursar (1989) observed less variation in soil respiration during the dry season when the soil volumetric moisture content was uniformly low than the wet season for a lowland moist soil. High variability in soil $CO_2$ concentrations occur as a result of rapid changes in concentration during a rainy season (Certini et al. 2003). The diffusion of $CO_2$ in water is about 10,000 times slower than in air (Hillel 1998). This slow diffusion can maintain high concentration even under low respiration. A gas diffusion coefficient of zero has been reported at an air-filled pore space of less than 10% for soils of contrasting texture (Xu et al. 1992). The phenomenon of gas transport limitation and $CO_2$ accumulation may be more prominent in poorly-drained and fine-textured soil which explained the relatively higher $CO_2$ concentrations at the Lower and Riparian landscape elements. This is in agreement with the findings of Bouma and Bryla (2000) who reported a restricted emission of $CO_2$ from fine-textured soils than sandy soils after wetting.

The positive correlation of subsurface $CO_2$ concentration to soil temperature and volumetric moisture content for each depth was statistically significant (Tables 2.7, 2.8, 2.9, 2.10). The influence of soil volumetric moisture content and soil temperature on soil $CO_2$ production has been shown to be non-linear and site-specific (Borken et al. 2006). As can be seen from my data for Upper, Middle, Lower and Riparian landscape elements, $CO_2$ concentration decreased at both very low and very high soil volumetric moisture contents. Jassal et al. (2004) also observed a similar trend and reported that low soil volumetric moisture content inhibits microbial and root metabolic activity and very high soil volumetric moisture content depletes $O_2$ in the soil air as a result of pore spaces saturated with water.

### 2.5.4 Relationship of Measured Surface Greenhouse Gas Emission to Estimated Profile Greenhouse Gas Emission

At all landscape elements, when theoretical estimates of diffusivity based on soil texture were used, the estimated profile emission values were 15 times higher than the measured static chamber emission values. This variation was due to the influence of fluctuations in soil moisture content at different depths and landscape elements on gas diffusivity. Several studies have indicated the importance of moisture on rates of surface emission (Pinol et al. 1995; Davidson et al. 2000), but in many soils, moisture controls on transport and storage may make it difficult to resolve $N_2O$ and $CH_4$ production/consumption from gaseous transport. In addition, moisture controls on transport/storage and emission may make it difficult to isolate a biological response in many soils. The diffusivity showed a seasonal pattern with soil moisture, low diffusivity in the pre-cropped period accompanying high volumetric moisture content and high diffusivity in the cropped period accompanying lower volumetric moisture content. Maximum diffusivity recorded in the Lower and Riparian landscape element soils due to high porosity/low compaction during dry cropped and post-crop periods resulted in lower diffusivity values when compared to diffusivity values obtained from $CO_2$ through free air (data not shown). The $N_2O$ and $CH_4$ emissions estimated from the profile concentration provided a little understanding of order of magnitude comparison with surface emission. The estimated profile emission and measured static vented chamber emission behaved differently during the freeze-thaw period and the post-fertilizer application periods. The main reason could be the inconsistent diffusivity values calculated with the existing volumetric moisture content and temperature and porosity. Also, the diffusion coefficients were not measured at each location in the field and they were calculated using the binary diffusion coefficients and porosity which might have either over estimated or under estimated. The correction factor, which was arrived by dividing the surface chamber $N_2O$ and $CH_4$ emissions by the corresponding landscape element $CO_2$ emissions, narrowed down the profile emission values to permissible range (±20%). The $CO_2$ concentrations in soil were less susceptible to consumption process when compared to $N_2O$ and $CH_4$. Hence this method of estimating in-situ gas diffusivity based on the $CO_2$ emission data (diffusivity correction factor) will give a best estimate about the emission where the chamber measurements were not possible. Further studies are also necessary to validate this new method of deriving greenhouse gas emissions from concentration gradients at different depths in various ecosystems.

## 2.6. Conclusion

The spatial and temporal variation of $N_2O$, $CH_4$ and $CO_2$ concentrations and greenhouse gas surface emissions were due to varied bulk density, particle density, texture, $NH_4^+$, $NO_3^-$ and organic carbon contents among the sections of the undulating landscape. The greenhouse gas concentrations and emissions were greatly influenced by the volumetric moisture content and $O_2$ concentrations, and the buildup of $N_2O$ and $CH_4$ during winter occurred at different depths. The highest $N_2O$ concentration recorded at the 15 cm depth and the highest $N_2O$ emission in the Lower landscape element during freeze-thaw indicated that the hot spot for $N_2O$ was the Lower landscape element. The higher $N_2O$ concentration and $N_2O$ emission in the Upper, Middle and Lower landscape element during the post-fertilizer application period indicated that UAN fertilizer application had increased the $N_2O$ emission.

The highest $CH_4$ concentration and surface emission were recorded during the freeze-thaw period at the 15 cm depth in the Riparian landscape element, which was rich in organic carbon, high salinity, lower in nitrate and dominated by perennial grasses, indicated that the hot spot for $CH_4$ emissions was the Riparian landscape element. The freeze-thaw period was considered to be optimal for highest $N_2O$ and $CH_4$ emissions. The majority of $N_2O$ and $CH_4$ accumulation occurred at the 5 and 15 cm depths in the Lower and Riparian landscape element. $CO_2$ concentrations were highest at the 65 cm depth in the Riparian landscape element and freeze-thaw period had no effect on $CO_2$ concentrations and $CO_2$ surface emissions and were highest during the cropped period. Therefore, the landscape variation and seasonal variation had a greater influence on subsurface greenhouse gas concentrations and surface emissions. Among all the three greenhouse gases, $N_2O$ emission occurred first with onset of thaw and then followed by $CH_4$ emission after thaw in all the landscape elements. The emissions of $CO_2$ were not increased during freeze-thaw but were consistent throughout the crop growth and crop maturity periods in all the landscape elements. Optimal usage of N fertilizers and avoiding of fall-N application would reduce the buildup of $N_2O$ during winter and reduce the outburst of $N_2O$ during the freeze-thaw period.

The estimated profile greenhouse gas emission of $N_2O$ and $CH_4$ appeared to be strongly controlled by volumetric moisture content as they behaved differently only during the freeze-thaw and post-fertilizer application periods. The calculated or estimated profile greenhouse gas emission agreed well with the measured greenhouse gas surface emission in all landscape elements after normalization. The approach of normalizing profile emission with the $CO_2$ surface emission to obtain estimated profile emission could provide a means of quantifying the contribution of subsurface sources to annual greenhouse gas emission in a variety of ecosystem. Although the surface emission measurements were inevitable for measuring annual greenhouse gas budgets, our results indicated that estimation of emission from profile concentrations would be a powerful tool in assessing the subsurface source and sink as well as the biological activity. Hence, a more comprehensive examination of this approach should be necessary to validate in other ecosystems and should be considered in other studies when quantifying greenhouse gas emission in similar undulating landscapes.

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# CHAPTER 3

# EFFECT OF FREEZE-THAW, SOIL DEPTH AND LANDSCAPE ELEMENT ON NITROUS OXIDE EMISSION

## 3.1 Abstract

To determine how the $N_2O$ emission from soil are influenced by freeze-thaw, soil depth and landscape element and to study the relationship of freeze thaw soil core $N_2O$ emission to freeze-thaw $N_2O$ emission from field and to the soil profile $N_2O$ concentrations, a laboratory incubation study was carried out with frozen and unfrozen soil cores during winter 2006 which were collected from all the Upper, Middle, Lower and Riparian elements at various depths. The $N_2O$ emissions from the unfrozen depths in all the landscape elements were negligible and among the four frozen soil depths the Riparian element at 10-15 cm soil depth recorded the highest $N_2O$ emission of 4.5 $\mu g\ N\ kg^{-1}\ h^{-1}$. In the Upper and Middle landscape elements the frozen 0-5 cm depth soil recorded highest $N_2O$. In all the landscape elements, the $N_2O$ emissions from the soil cores were highest until 24 hours of incubation and after that the emission declined and came to zero after 96 hours of incubation. Higher precedent soil moisture, nitrate concentrations and organic carbon content in the Riparian and Lower landscape position resulted in higher $N_2O$ emission in these landscape elements. The field $N_2O$ profile concentration and freeze-thaw $N_2O$ emissions from incubation study followed a similar trends with highest emissions and concentrations which occurred in Riparian landscape elements. The results from the frozen and unfrozen incubation study revealed that the lower soil depths had lower $N_2O$ emission potential whereas, the surface (0-5 cm) and shallow surface (10-15 cm and 30-35 cm) soils had highest $N_2O$ emission potentials.

### 3.2 Introduction

The concentration of nitrous oxide ($N_2O$) in the atmosphere is approximately 319 ppbv which has increased from the pre-industrial value of 270 ppbv, the most rapid increases having occurred within the past 10 years (IPCC 2007). Nitrous oxide is 296 times more powerful than $CO_2$, in its global warming potential (IPCC 2007). Agricultural activities which add nitrogen to soil (fertilizer application and biological nitrogen fixation) stimulate nitrification and denitrification, which are the main sources of $N_2O$, contributing about 75% of global anthropogenic $N_2O$ emissions (Ruser et al. 2006). Nitrous oxide is produced in soils by bacteria through nitrification in micro-aerobic conditions and through denitrification in anaerobic conditions. The main processes producing $N_2O$ emission namely nitrification and denitrification are strongly influenced by soil moisture content. Ruser et al. (2006) found a strong increase in $N_2O$ emission at moisture contents with 60 and 70% water-filled pore space.

Thawing of soil in spring is a major trigger of $N_2O$ production and contributes significantly to annual $N_2O$ emissions in temperate climates. For example, more than 70% of the total $N_2O$ emission occurred during thawing of frozen soil in spring in a cultivated near Guelph, ON (Wagner-Riddle et al. 1997). Increased $N_2O$ emission during thawing periods may be a result of increased substrate and/or nitrate availability due to killed micro-organisms, destroyed aggregates and dead fine roots (Prieme and Christensen 2001; Teepe et al. 2004).

Freeze-thaw events during winter and spring are known to induce pulses of $N_2O$ emissions occurring shortly after thawing (Dorsch et al. 2004). These events have been attributed in whole or in part to the release of physically trapped $N_2O$ (Burton and Beauchamp 1994), desorption of dissolved $N_2O$ (Goodroad and Keeny 1984) and enhanced biological activity (Oquist et al. 2004). Enhanced oxygen consumption, combined with high water content during freeze-thaw period results in increased anaerobic volume thus enhancing denitrification and increased $N_2O$ emission (Dorsch et al. 2004). Studies by Teepe et al. (2004) and Muller et al. (2002) showed that a combination of high soil moisture, available N, and high C content were favorable for elevated $N_2O$ emission during the freeze-thaw period. Wagner-Riddle et al. (2008) recorded a higher $N_2O$ concentration at the 12-17 cm deep layer when compared to the 0-5 cm shallow layer and they concluded the elevated $N_2O$ emission during snow melt was due to the newly produced $N_2O$ in the shallow layer and not by the release of trapped $N_2O$ from unfrozen deep layers.

The thaw period provides ideal conditions for the release of $N_2O$ produced during the winter through denitrification both below and in the frozen soil layer (Teepe et al. 2001). These emissions are mostly associated with the development of anoxic conditions in soil induced by precipitation and snowmelt water. However, the numerous factors influencing emissions (Dorsch et al. 2004) have not been sufficiently quantified to allow a full understanding of the processes responsible for large emissions after snowmelt. Consequently, there has been a particular interest in winter emissions of $N_2O$ in temperate ecosystems, because much of the annual emission appears to occur during the transition from winter to spring when freeze-thaw events happen. High emissions of $N_2O$ during these periods have been attributed to accumulation and release of $N_2O$ beneath frozen soil layers (Van Bochove et al. 2001) and freezing induced microbial mortality followed by rapid re-growth and high rates of microbial N transformations (Dorsch et al. 2004).

There has been considerable debate on which soil factors are controlling freeze-thaw induced $N_2O$ emissions and overwinter $N_2O$ gaseous losses have been related to management types (Kaiser et al. 1998), previous fall season soil $NO_3^-$ concentrations (Lemke et al. 1998) and position in the landscape (Corre et al. 1996), all of which influence N-cycling processes. The variation in topography also influenced the emission of $N_2O$ from agricultural landscapes as they alter the fundamental hydrologic and pedologic processes within the landscape (Pennock et al. 1992; Florinsky et al., 2004). High freeze-thaw $N_2O$ emissions from Riparian landscape elements soils are associated with high antecedent soil moisture, denitrifying enzyme activity and total organic carbon content. Dunmola (2007) observed that freeze-thaw $N_2O$ emissions under field conditions were not as high as those conducted under laboratory conditions and attributed this to snow cover and perennial vegetation insulating the Riparian soil from freezing during winter as well as the submerged anaerobic condition of the Riparian landscape soil during snow melt leading to reduction of $N_2O$ to $N_2$ and hence lower $N_2O$ emissions.

Laboratory methods used to simulate the effect of freeze-thaw on $N_2O$ emission have included the freezing and thawing of small columns containing either disturbed sieved or undisturbed surface soil cores (Skogland et al. 1988; Wang and Bettany 1993; Wagner et al. 2003; Teepe et al. 2004; Dunmola 2007). Most previous investigations have concentrated on $N_2O$ emission from surface layers in alpine tundra, arctic heath, organic peat and forest soils, grassland ecosystems and agricultural ecosystems (Hugh 2007). Also the laboratory freeze-thaw incubation studies with soil cores did not exactly reflect the field conditions as the frozen cores were set to thaw from all directions. The usage of the uni-directional method of freeze-thaw with water table access allows for the manipulation of freeze thaw in soil columns gradually layer by layer providing the conditions to relate the site of $N_2O$ production in the soil profile with surface $N_2O$fluxes in laboratory studies (Hu et al. 2006).

To my knowledge, no studies have attempted to investigate the effect of freeze-thaw in deeper soil layers and the contribution of soil depth, soil conditions and subsurface soil processes to surface $N_2O$ emissions in an undulating landscape. To obtain a better insight into the dynamics of $N_2O$ emission during the freeze-thaw period, this laboratory study was carried out (i) to determine the effect of freeze-thaw on $N_2O$ emission from different landscape elements, (ii) to determine if soil depth affects the potential of freeze-thaw $N_2O$ emission from different landscape elements, and (iii) to relate $N_2O$ emissions from thawing sub-surface soil to surface $N_2O$ emissions and soil $N_2O$ gas concentration profile results from the field study presented in Chapter 2.

## 3.3 Materials and Methods

### 3.3.1 Soil Core Extraction, Handling and Processing

Soil cores were obtained from the Upper, Middle, Lower and Riparian landscape elements in winter 2006 (March 14, 2006) from the same four sections of the field (Manitoba Zero Tillage Research Association Farm) used in the study presented in Chapter 2. Samples from a landscape element represent four independent replicate sample locations. The predominant soil at the site was mapped as a Newdale Clay Loam series, being a Black Chernozem formed over calcareous glacial tills (Podolsky and Schindler 1993). The soil cores obtained for the incubation study were collected from a location about 50m away from landscape element positions sampled in Chapter 2. This was done to prevent disturbance of sample positions on the transect. All the four replicates of soil cores were collected from the south-eastern side of the pond area of section-2 (Fig. 2.1) which also had the Upper, Middle, Lower and Riparian landscape element as the field study transect. Soil cores up to 100 cm depth were extracted using 100 cm polycarbonate sleeves (6 cm i.d.; Giddings Machine Co., Windsor, CO) fitted with a carbide ice drill bit and inserted and retrieved using a hydraulic tractor mounted auger (Giddings Machine

Co.). The frozen and unfrozen portion of each soil core was determined in the field using a digital thermometer (Traceable; Fisher Scientific Canada, Edmonton, AB) and then cut into frozen (≤ 0°C) and unfrozen (> 0°C) sections and soil cores labeled appropriately with the landscape element and frozen, unfrozen depths. The soil cores were capped with red and black polyurethane caps (to differentiate the up and downside of cores) and then transported to the laboratory separately using a chest freezer filled with snow (for frozen cores) on a pull trailer to minimize the disturbances during transportation and using ice chest with icepacks (for unfrozen cores) transported within vehicles. The unfrozen cores were stored in a walk-in cooler at 4°C, the frozen core section was stored in the same chest freezer kept in an open environment with a temperature of below -5°C. The frozen core sections were sliced into 0-5 cm, 10-15 cm, 30-35 cm, and 55-60 cm sections in the open environment with temperature below -5°C. The unfrozen sections of the cores were sliced into 70-75 cm and 80-85 cm sections inside the walk-in cooler. Slicing of cores was done using a hand operated power saw. The bottom of each 5 cm sliced core section was covered with a muslin cloth and held in place using an elastic band to prevent any loss of soil. The sliced cores, unfrozen and frozen, were labeled and stored separately in the walk-in cooler or a walk-in freezer (-20°C), respectively, until commencement of an incubation study.

A preliminary incubation study with soil cores at different depths was done during September 2005. Soil cores up to 70 cm depth were extracted using 100 cm polycarbonate sleeves (6 cm i.d.; Giddings Machine Co., Windsor, CO) fitted with a metal drill bit and inserted and retrieved using a hydraulic tractor mounted auger (Giddings Machine Co.). The soil cores were collected from all the four replicate sections and from all the four landscape elements. The extracted soil cores were sliced in to 0-5 cm, 10-15 cm, 30-35 cm and 55-60 cm sections and the bottom of each 5 cm soil core covered with a muslin cloth using an elastic band. The soil cores were placed in 1.5L bernardin jars and incubated at $15^0$C and the headspace was replaced with the ambient atmosphere with a 345mL pop can by inserting the pop can 15 times in to the jar and taken out quickly after each gas sampling and then incubated. The headspace was collected every 6 hours for first two days and then every 12 hours for next 3 days. The results from the preliminary fall 2005 soil core incubation study showed a huge variability of $N_2O$ emission among the different sections and replicate sites. Hence, those emission data were not reported in this thesis and also based on those fall 2005 soil core incubation study results it was decided to extract winter soil cores from only one section (Section -2) to minimize the field variability for winter 2006 freeze-thaw incubation study.

### 3.3.2 Incubation Study with Frozen and Unfrozen Soil Cores

The incubation study with the frozen and unfrozen soil cores was carried out in the laboratory under controlled conditions to study the freeze-thaw and soil depth effect on $N_2O$ emission from different landscape elements. The sliced frozen and unfrozen depth soil cores were placed into 1.5L sealer jars. The headspace gas in the jars was replaced with ambient air by flushing the jars 15 times by repeated insertion of a 345mL pop can and then the jars with soil cores closed with lids fitted with a serrated rubber septum (Sigma-Aldrich, Oakville, ON) for easy sampling using a PrecisionGlide® needle 23G fitted to a 10mL Becton-Dickinson disposable syringe (Fisher Scientific Canada, Edmonton, AB). The closed jars were incubated in the dark at $15^0$C for 2 hours before first gas sampling. To mimic the field spring air temperature, an incubation temperature of $15^0$C was chosen. Gas sampling was done by removing 10mL of the headspace gas from each jar, and injecting the samples into 6mL pre-evacuated, helium-flushed (to 500millitorr pressure) Labco Exetainer® gas vials (Labco Limited, Buckinghamshire, UK) with the top of the vials sealed with silicone sealant. The lids of the jars were then removed, the jars covered with Parafilm having five to six holes punctured with a pencil, and the jars returned to the incubator until the next sampling. The Parafilm was punctured to prevent build-up of $N_2O$ over the headspace between samplings, which allow normal emission from the soil cores when the jars were closed and also prevent moisture loss from the soil cores during incubation. The headspace gas of the jars was sampled as previously described at 6 hour intervals for first 2 days and then at 12 hours interval for next 2 days. The results from the previous fall 2005 soil core incubation study showed that peak $N_2O$ emission occurred within the first 24 hours of placement at $15^0$C, necessitating the need to do intensive sampling (every 6 hours) during the first 36 hours of incubation and every 12 hours afterwards until reaching ambient levels.

The gas samples were analyzed for $N_2O$ concentration using a gas chromatograph (Varian 3800; Varian Canada, Mississauga, ON) fitted with an electron-capture detector operated at $300^0$C. The gas chromatograph had a Combi-PAL autosampler (CTC Analytics AG., Zwingen, Switzerland) that injected 2.5mL volume of sample to the gas chromatograph to deliver the sample to the gas chromatograph. The production of $N_2O$ was calculated from the change in headspace $N_2O$ concentration, oven-dried mass of soil, headspace volume of jar, head space $N_2O$ concentration of a blank jar, molecular mass of $N_2O$, incubation temperature, incubation time and universal gas constant using the Ideal Gas Law (PV=nRT). The incubation study was done initially with the first two replicate soil cores and after four days, the remaining two replicate of soil cores were incubated adopting the same procedure. Cumulative $N_2O$ emission from each replicate soil core was calculated by linear interpolation between sampling times for the entire incubation period. Fluxes are expressed as $\mu g\ N_2O - N\ kg^{-1}$ dry soil per hour.

### 3.3.3 Soil Extraction and Analysis

Following 4 days of incubation at 15°C, soil in each core was placed into a polyethylene bag and mixed by hand. Gravimetric moisture contents of soil were determined by drying the soil for 24 hours at $105^0$C. The bulk density of the soil cores were also determined from the mass and volume of the soil cores. The soil cores after the completion of gravimetric moisture content and bulk density determinations were kept accidently at room temperature, and all the soil samples become wet which made the other soil analysis ($NH_4^+$, $NO_3^-$ nitrogen and dissolved organic carbon content) impossible with the wet samples. Hence the fall 2005 soil cores $NH_4^+$, $NO_3^-$ nitrogen and dissolved organic carbon content results were used in this freeze-thaw winter core incubation study. As there was no soil cores collected beyond 70 cm depth in fall 2005, only 4 depths 0- 5 cm, 10-15 cm, 30-35 cm and 55-60 cm soil $NO_3^-$, and $NH_4^+$ nitrogen and extractable dissolved organic carbon contents were presented in Table 3.1.

The $NO_3^-$, and $NH_4^+$ nitrogen and extractable dissolved organic carbon contents of the soil cores were determined by extracting 5g fresh soil with 25mL of 0.5M $K_2SO_4$ solution. The mixtures were shaken for 30 minutes and centrifuged at 3000 rpm (1,560 X *g*) for 1.5 minutes and the clear supernatant (10 mL) was transferred into a labeled scintillation vial. The extracts were kept at $-20^0$C rather than $5^0$C if not analyzed within a week after extraction. The $NO_3^-$, and $NH_4^+$ nitrogen and extractable dissolved organic carbon contents were determined colorimetricaly by the automated cadmium reduction (Method No. 4500-$NO_3$ (F)), phenate (Method No. 4500-$NH_3$ (G)) and persulfate-ultraviolet oxidation (Method No. 5310©) methods, respectively, using separate Technicon™ Autoanalyzer II systems (Pulse Instrumentation Ltd., Saskatoon, SK).

### 3.3.4 Statistical Analysis

Statistical analysis of the $N_2O$ cumulative emission was done using the Statistical Analysis Software package (SAS Institute Inc., Ver 9.1, Cary, NC). A Proc generalized linear model was carried out on the cumulative freeze-thaw $N_2O$ emission. The basic design was a complete randomized design with 'landscape element' and 'depths' as imposed treatments over the entire sampling period. Analysis of variance was performed with the $N_2O$ cumulative emission in order to determine the landscape element and depth effects. Means among different treatments (landscape element and depth) were compared using the least significance difference test at $\alpha = 0.05$.

## 3.4 Results

There was an increase in $N_2O$ emission from soil cores that were frozen and thawed for all the landscape elements (Fig. 3.1). The emissions of $N_2O$ were negligible from unfrozen cores in all the landscape elements. The peak $N_2O$ emission occurred within 40 hours of incubation at 15°C in all the landscape elements. In the Upper and Middle landscape elements the frozen 0-5 cm depth recorded the highest $N_2O$ emission when compared to other depths. In the Lower landscape element the frozen 30-35 cm depth recorded the highest $N_2O$ emissions at 12 hours of incubation which was followed by the frozen 10-15 cm depth. There was a slight emission from the frozen 0-5 cm depth in the Lower landscape element. The highest and earliest $N_2O$ emission occurred in the Riparian element commencing at six hours and peak emission occurred at 24 hours after incubation at 15°C. Furthermore, the results of the incubation study showed that among the four frozen soil depths and two unfrozen depths from four landscape elements, the Riparian element has recorded the highest mean $N_2O$ emission of 4.5 μg N $kg^{-1}$ $h^{-1}$ at the previously frozen 10-15 cm soil depth followed by the 30-35 cm (1.4 μg N $kg^{-1}$ $h^{-1}$) frozen depth (Fig. 3.1).

In the Upper landscape elements the $N_2O$ emissions from the frozen 0-5 cm showed a greater variability among the 4 replications. In the Riparian landscape element the frozen 10-15 cm depth and frozen 30-35 cm depth $N_2O$ emissions showed huge variability (>114% coefficient of variation) among the replications (Fig. 3.1). The coefficients of variation for the Upper 0-5 cm frozen depth $N_2O$ emission at 18, 24 and 30 hours of incubation were 194%, 198% and 194% respectively. The coefficient of variation for the Middle 0-5 cm frozen depth $N_2O$ emission at 18 and 24 hours of incubation were 164% and 170%. The coefficient of variation for the Lower 30-35 cm frozen depth $N_2O$ emission at 24 hours of incubation was 82%. In the Riparian landscape element the coefficient of variation for the 30-35 cm frozen depth $N_2O$ emissions at 18, 24 and 30 hours of incubation were 114%, 120% and 126% respectively.

In the Upper landscape elements the frozen 0-5 cm depth soil recorded the highest $N_2O$ emissions and these emissions were greatest after 24 hours of incubation. In the Middle landscape element the $N_2O$ emissions from the frozen 0-5 cm depth reached a maximum at 12 hours of incubation. In the Upper and Riparian landscape elements the frozen 0-5 cm depth attained the maximum $N_2O$ emission at 24 hours of incubation and started declining until 60 hours of incubation, and again started slightly increasing after 60 hours of incubation, stabilizing after 84 hours of incubation (Fig. 3.1). The highest cumulative freeze-thaw $N_2O$ was from the Riparian and Upper landscape elements, for the previously frozen depths 10-15 cm and 0-5 cm, respectively (Table 3.2). The cumulative freeze-thaw $N_2O$ emission of the Riparian element 10-15 cm depth was approximately three times the cumulative $N_2O$ emission of the 0-5 and 30-35 cm frozen depths, and was more than 50 times higher than other depths. The high cumulative freeze-thaw $N_2O$ emission from the Riparian element was due to consistent very high emissions from replicate one. The Upper 0-5 cm depth replicate core one and four also gave very high $N_2O$ emissions. The cumulative freeze-thaw $N_2O$ emissions were significantly different among the landscape elements and with depths (Table 3.2). The cumulative freeze-thaw $N_2O$ emission from frozen 10-15 cm soil in the Riparian landscape element was 39 times higher than the Upper and Middle landscape elements. The unfrozen depths cumulative $N_2O$ emissions from all the landscape elements were in the range of 0.9 to 4.2 μg $N_2O$-N $kg^{-1}$.

The gravimetric moisture content was lowest in the unfrozen depths in all the landscape elements and in the Riparian and Lower landscape elements at the previously frozen 0-5 and 10-15 cm depths (Table 3.1). Gravimetric moisture content decreased with depth for all landscape elements with surface levels being highest for Riparian and the Lower element. $NH_4^+$- N concentrations were low and decreased with depth with no obvious difference between landscape elements. Nitrate-N concentration was variable with depth and the coefficients of variation of $NO_3^-$- N concentration for the Upper 0-5 cm, 10-15 cm, 30-35 cm and 55-60 cm depths were 153%, 170%, 141% and 93% respectively. The coefficient of variation of $NO_3^-$- N concentration for the Riparian 10-15 cm and 30-35 cm depths were 154% and 164% respectively. The coefficients of variation of $NO_3^-$-N concentration for the Middle 0-5 cm, 10-15 cm, 30-35 cm and 55-60 cm depths were 105%, 121%, 188% and 159% respectively. The extractable dissolved organic carbon concentrations declined with depth for all landscape elements and it was noticeably higher for the previously frozen 0-35 cm depth for the Riparian element (Table 3.1).

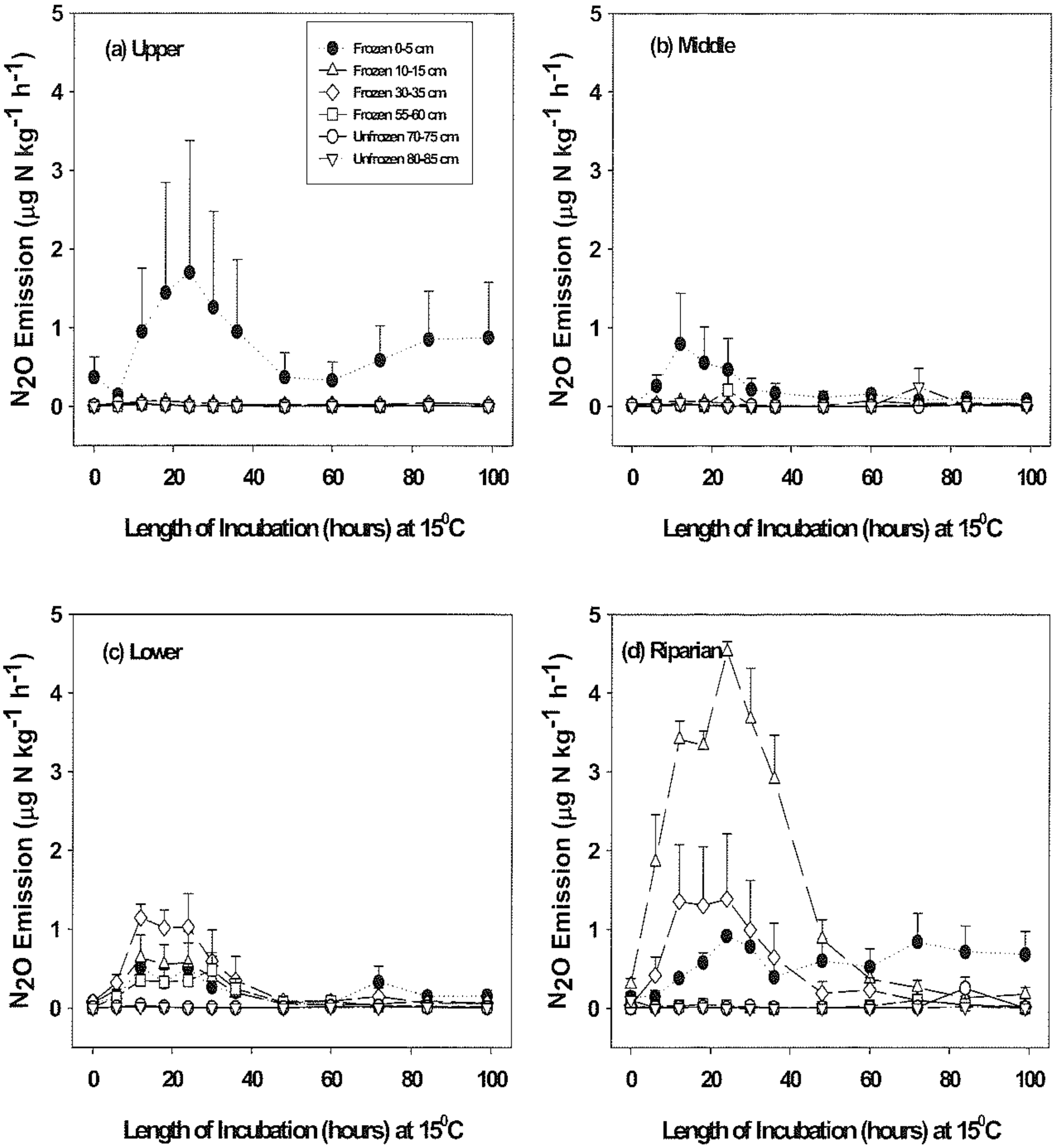


**Figure 3.1** Nitrous oxide ($N_2O$) emission (μg N $kg^{-1}$ $h^{-1}$) from frozen and unfrozen cores taken from various depths and landscape elements; (a) Upper (b) Middle, (c) Lower and (d) Riparian landscape elements. Values shown are the mean plus one standard error of the mean of four replicate soil cores extracted from the section-2.

**Table 3.1** Soil gravimetric moisture content, extractable $NH_4^+$, $NO_3^-$ and dissolved organic carbon of intake cores taken from different depths and landscape elements

| Landscape Element | State | Depth (cm) | Gravimetric Moisture Content (%) | $NH_4^+$-N (mg N $kg^{-1}$) | $NO_3^-$-N (mg N $kg^{-1}$) | Dissolved Organic Carbon (mg C $kg^{-1}$) |
|---|---|---|---|---|---|---|
| Upper | Frozen | 0-5 | 38 (9) | 4.1 (0.3) | 2.7 (0.6) | 258.2 (13.3) |
| | Frozen | 10-15 | 24 (2) | 3.7 (0.5) | 2.3 (0.8) | 226.4 (20.4) |
| | Frozen | 30-35 | 29 (2) | 3.1 (0.2) | 1.7 (0.5) | 142.7 (14.5) |
| | Frozen | 55-60 | 25 (5) | 3.2 (0.3) | 0.6 (0.1) | 106.1 (16.8) |
| | Unfrozen | 70-75 | 18 (1) | N.D. | N.D. | N.D. |
| | Unfrozen | 80-85 | 17 (2) | N.D. | N.D. | N.D. |
| Middle | Frozen | 0-5 | 35 (7) | 4.3 (0.3) | 5.1 (2.7) | 243.6 (13.8) |
| | Frozen | 10-15 | 29 (2) | 3.7 (0.3) | 3.4 (2.1) | 179.6 (18.7) |
| | Frozen | 30-35 | 37 (5) | 2.8 (0.2) | 10.2 (9.6) | 138.5 (12.6) |
| | Frozen | 55-60 | 25 (1) | 2.7 (0.4) | 5.1 (2.7) | 119.6 (7.3) |
| | Unfrozen | 70-75 | 25 (1) | N.D. | N.D. | N.D. |
| | Unfrozen | 80-85 | 23 (2) | N.D. | N.D. | N.D. |
| Lower | Frozen | 0-5 | 64 (3) | 4.6 (0.2) | 7.0 (1.2) | 297.3 (18.5) |
| | Frozen | 10-15 | 47 (2) | 3.8 (0.2) | 7.3 (5.6) | 223.9 (29.9) |
| | Frozen | 30-35 | 50 (1) | 3.0 (0.5) | 4.6 (3.7) | 150.1 (35.5) |
| | Frozen | 55-60 | 36 (4) | 2.7 ( 0.5) | 4.0 (1.8) | 83.2 (10.5) |
| | Unfrozen | 70-75 | 27 (2) | N.D. | N.D. | N.D. |
| | Unfrozen | 80-85 | 26 (2) | N.D. | N.D. | N.D. |
| Riparian | Frozen | 0-5 | 81 (8) | 5.5 (1.3) | 8.1 (6.2) | 434.1 (121.9) |
| | Frozen | 10-15 | 50 (4) | 4.3 (0.7) | 8.8 (7.5) | 347.7 (77.2) |
| | Frozen | 30-35 | 35 (1) | 4.0 (0.5) | 11.1(7.8) | 294.0 (51.4) |
| | Frozen | 55-60 | 25 (1) | 2.9 (0.4) | 2.9 (1.4) | 109.1 (7.4) |
| | Unfrozen | 70-75 | 25 (2) | N.D. | N.D. | N.D. |
| | Unfrozen | 80-85 | 24 (2) | N.D. | N.D. | N.D. |

**Note:** Values are means of four independent replicates of each landscape element and the values in parenthesis are ± one standard error of the mean. Gravimetric moisture content was determined from winter 2006 soil core samples and $NH_4^+$-N, $NO_3^-$-N and extractable dissolved organic carbon were determined from fall 2005 soil samples. N.D. = Not determined.

**Table 3.2** Freeze-thaw cumulative emission of nitrous oxide ($N_2O$) from frozen and unfrozen intact cores taken from various depths and landscape elements

| Position | Frozen 0-5 cm | Frozen 10-15 cm | Frozen 30-35 cm | Frozen 55-60 cm | Unfrozen 70-75 cm | Unfrozen 80-85 cm |
|---|---|---|---|---|---|---|
| | ($\mu g\ N_2O\text{-}N\ kg^{-1}$) | | | | | |
| Upper | 76.4 (64.4) Aa | 3.5 (1.3) Cb | 2.3 (0.9) Cb | 0.8 (0.1) Bb | 1.0 (0.2) Bb | 0.9 (0.2) Bb |
| Middle | 21.8 (14.6) Ca | 3.8 (0.3) Cb | 1.7 (0.4) Cb | 2.5 (1.2) Bb | 1.0 (0.1) Bb | 3.8 (2.8) Ab |
| Lower | 21.0 (7.1) Cb | 19.6 (6.6) Bb | 33.1 (11.8) Ba | 14.7 (6.4) Ab | 1.2 (0.3) Bc | 0.9 (0.2) Bc |
| Riparian | 59.3 (16.9) Bb | 149.3 (18.3) Aa | 45.6 (24.2) Ab | 3.2 (1.0) Bc | 4.2 (2.2) Ac | 1.0 (0.4) Bc |

**Note:** Values are the mean of four independent replicate soil cores per landscape element for freeze-thaw $N_2O$. Values in parentheses are ± one standard error of the mean. Mean values followed by the same lower case letter (within the rows - landscape elements) and the same upper case letter (within the columns - soil core depths) are not significantly different using least significant difference ($P > 0.05$).

## 3.5 Discussion

Nitrous oxide emission from thawing soil varied with landscape element and with depth. The emission of $N_2O$ from the frozen cores of different landscape elements peaked after about 24 hours of incubation (Fig. 3.1). Other workers (Scholes et al. 1997; Jorgensen et al. 1998) also observed a steep increase in the $N_2O$ emission rate within the first few hours of thawing. This might be caused by a combination of biological production and release of water dissolved and trapped $N_2O$. The soil cores were thawed at $15^0C$ and the frozen cores attained the incubation temperature after 24 hours, by that time the steep increase in $N_2O$ emission was prominent. When the soil cores were exposed to such a high incubation temperature, the activity of the microbes might be enhanced, which would have resulted in the steep increase in $N_2O$ emission.

$N_2O$ emissions are reported to be controlled by the availability of mineral N, soil temperature and soil water content (Skiba et al. 1998). From the results of the present study, the difference in $N_2O$ emissions among four landscape elements might be due to variation in soil nitrate availability and soil water content. Lower nitrate concentrations in the Upper and Middle landscape element were probably caused by crop uptake and leaching into the Riparian wetlands (Sabater et al. 2003). The high $NO_3^-$ content in the Riparian and Lower landscape element resulted in elevated $N_2O$ emissions from these elements. The highest freeze-thaw cumulative $N_2O$ emission observed from the Riparian landscape element at the 10-15 cm depth (Table 3.2) were related to higher soil volumetric moisture content and $NO_3^-$ determined in the fall.

For most soils, soil water content (through its effect on aeration) together with N supply has been shown to be a dominant variable controlling $N_2O$ emission (Hutsch et al. 1999). Ruser et al. (1998) indicated that the highest $N_2O$ emissions resulted from the loss of macro-pores due to compaction which increased the water-filled pore space to 85%. In the present study it is evident that high soil moisture in combination with high available N for microbial transformations ($NO_3^-$, $NH_4^+$) and high extractable dissolved organic carbon are responsible for increased $N_2O$ emissions in Lower and Riparian elements during freeze-thaw events (Fig. 3.1, Table 3.1).

In the Riparian and Lower landscape elements, the prevalence of high soil moisture content might enhance the $N_2O$ emissions. High soil moisture contents with increasingly anoxic conditions stimulate denitrification activity and thus facilitate $N_2O$ production. The high soil moisture content also increases the residence time of $N_2O$ in the soil by restricting diffusion and may consequently enhance the reduction of $N_2O$ to $N_2$ gas (Jacinthe et al. 2000). Denitrification was one of the major sources of $N_2O$ emission from the soil cores in the Riparian and Lower landscape elements (previous fall 2005 incubation study with soil cores from different depths; unpublished data. Results of $N_2O$ emission not presented here as there was a huge variability among the replicate sections). The lower $N_2O$ emissions from the deeper soils (10-15 cm, 30-35 cm and 50-55 cm) in the Upper and Middle landscape element were due to a lower soil moisture content.

In the Upper and Middle landscape elements, I found higher $N_2O$ emissions at 0-5 cm depths which corresponds to the rich organic layers. Also the gravimetric moisture content of the frozen soil depths was higher when compared to the unfrozen soil depths (Table 3.1). The gravimetric moisture contents reflected the antecedent moisture status of the soils used in the present study. 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).

Several processes explaining the burst in $N_2O$ emission during freeze-thaw have been proposed (Christensen and Tiedje, 1990; van Bochove et al. 2000; Teepe et al. 2001; Lemke et al. 1998). All these studies believed that the increased emissions triggered by thawing are either due to stored $N_2O$ that is released during melting and or/due to new $N_2O$ produced as the soil layers thaw. The results from this study also partly support these findings as the surface 0-5 cm depth of frozen soil in the Upper and Middle landscape element recorded the highest $N_2O$ emission when compared to other depths. But the highest $N_2O$ emission from the frozen cores occurred from cores collected from the 10-15 cm and 30-35 cm depths soils located in the Riparian and Lower landscape elements. Thus it would appear that the zone of highest $N_2O$ production potential is not a simple function of depth, but rather reflects other factors that are a complex function of depth and landscape position. Cores collected from below the frozen layer, which remained unfrozen, did not produce any $N_2O$ emissions which clearly indicated the role of soil freezing and suggest that soils below the depth of freezing did not contribute to thaw-induced $N_2O$ emissions.

The Riparian landscape element had the highest potential for freeze-thaw emission of $N_2O$, which is related to its high soil moisture content, organic carbon content and nitrate content. This is consistent with the reported potential of Riparian soils for denitrification resulting from its high moisture and organic matter content (Groffman 1994). The release of $N_2O$ during thawing occurred within a short span of time (less than 40 hours) and was similar to the field $N_2O$ emissions (Chapter 2).

Stadler (1996) reported that a thin water layer would be present around the frozen soil core and this thin water layer is favorable for the denitrification process to occur. Moreover, the availability of labile carbon may be high in this water film as a consequence of microbial lysis. Coupled with these favorable conditions for denitrification, $N_2O$ emission from the frozen soil cores of Riparian and Lower landscape elements were higher because of the suppression of $N_2O$ reductase at low temperature resulting in $N_2O$ being the dominant product of the denitrification process (Stahli and Stadler, 1997).

The freeze-thaw $N_2O$ emissions from the core incubation study were similar to that of the freeze-thaw $N_2O$ emissions from the field (Chapter 2 results, Fig. 2.9) with the highest $N_2O$ emission being from the Lower landscape element. The length of freeze-thaw emission from the field study and the soil core incubation study were also similar indicating the emission occurred within a short span of time (less than 40 hours). Wagner-Riddle et al. (2008) also recorded a higher $N_2O$ concentration in a 12-17 cm deep layer when compared to the 0-5 cm shallow layer and they concluded the elevated $N_2O$ emission during snow melt was due to the newly produced $N_2O$ in the shallow layer and not by the release of trapped $N_2O$ from unfrozen deep layers, which is similar to our findings. A distinct pattern of freeze-thaw $N_2O$ emission with the landscape was observed both in the soil core incubation study at the laboratory and from the field. The potential for thaw-induced $N_2O$ emissions is low at the unfrozen depths. The $N_2O$ profile concentrations from the field study were in line with the freeze-thaw $N_2O$ emission from the soil core incubation study. The $N_2O$ concentrations in the Upper element were highest at 5 and 15 cm depths (Fig. 2.5) and similar higher freeze-thaw $N_2O$ emissions were observed in the Upper element at 0-5 cm frozen soil (Fig. 3.1). The $N_2O$ concentration profile and freeze-thaw $N_2O$ emission from the incubation study followed a similar trend with highest emission and concentration both occurring in the Riparian landscape element.

### 3.6 Conclusion

The freeze-thaw $N_2O$ emission potential was significantly affected by landscape position and soil depth. The Riparian landscape element gave the highest $N_2O$ emission potential from the frozen 10-15 cm depth. Cores collected from depths that experience freezing had the highest freeze-thaw $N_2O$ emission potential for all the landscape elements. When incubated at 15 $^{o}$C, the $N_2O$ emissions from the frozen cores were brief and lasted up to 40 hours with the peak emission observed between 12 and 24 hours for different depths in various landscape elements. This exhibited similar patterns to the $N_2O$ emissions observed in the field freeze-thaw study (Chapter 2). The soil moisture content, nitrate concentration and organic carbon content in the Lower and Riparian landscape element soil was associated with high cumulative freeze-thaw $N_2O$ emissions. The freeze-thaw $N_2O$ emission potential from the soil core incubation study was highest in the Riparian landscape element, whereas the $N_2O$ emission from the field study was highest in the Lower landscape element. From the present study it was concluded that deeper soils that remain unfrozen did not have a greater $N_2O$ emission potential and the shallow depths, which do undergo freezing, had the highest $N_2O$ emission potential. Further research work is needed to elucidate the processes occurring in the frozen layers at the 10-15 cm and 30-35 cm depths in the Lower and Riparian landscape soils during thawing to better understand the underlying processes leading to highest $N_2O$ emission during freeze-thaw periods.

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# CHAPTER 4

# OVERALL SYNTHESIS

## 4.1 General Findings, Discussion and Conclusion

Greenhouse gas emission studies from prairie pothole landscapes have shown that these landscapes have a varying potential for GHG emissions. Some of the GHG emission studies in these landscapes have found that Lower and Riparian elements had greater emission potential than the Upper and Middle landscape elements and suggested that the hotspots for $N_2O$ and $CH_4$ emission within the landscape are localized and driven by varying soil conditions (Pennock and Corre 2001; Pennock et al. 2005; Dunmola et al. 2010). Though there were few studies conducted in these prairie pothole landscapes, they didn't explore the subsurface GHG concentrations, processes governing their production, consumption, transport and their relation to surface emissions. Without this understanding, we will not have a clear idea of how these subsurface GHG concentrations contribute to surface emissions. Therefore, the present research was done to have a better understanding of the subsurface GHG processes, their relation to surface emission and to determine the hot spots and the pattern of GHG emission in various landscape elements in these prairie pothole landscapes.

The objective of this thesis was to study the dynamics of profiles of GHGs in a topographically variable landscape in western Canada. The thesis included a field study and a laboratory study. The field study addressed the pattern of GHG concentration profiles and surface GHG emission from various landscape elements and explored the relationship between subsurface profile GHG accumulation, surface emissions and soil conditions. The study also aimed at determining the relationship between estimated and measured GHG emissions. The laboratory study determined the effect of freeze-thaw, soil depth and landscape element on $N_2O$ production and their relation to field $N_2O$ emissions.

Results from the field study (Chapter -2) indicated that the landscape elements had an influence on the GHG profile concentrations and surface emissions. The landscape elements Upper, Middle, Lower and Riparian had varying soil conditions (soil moisture, soil temperature, bulk density, particle density, air-filled porosity and nutrient content) which affected the GHG accumulation and surface emissions. There are two distinct periods where the $N_2O$ profile concentrations and $N_2O$ surface emissions were prominent, one during freeze-thaw and the other during fertilizer application. The hot spots of $N_2O$ were found in Lower and Riparian landscape elements which had higher volumetric moisture content and lower $O_2$ content. The elevated $N_2O$ concentrations at 15 and 35 cm depths in these landscape elements during the freeze-thaw period observed in the present study were either due to the release of trapped $N_2O$ (Burton and Beauchamp 1994) during winter or by newly produced $N_2O$ at the shallow depth soils (Wagner-Riddle et al. 2008). In both cases, the higher $N_2O$ accumulation during freeze-thaw periods likely reflects periods of increased denitrification where conditions are such that denitrification does not go to completion and $N_2O$ remains a major product. The elevated $N_2O$ concentrations and surface emissions during fertilizer application were due to increased denitrification activity. The spring-thaw $N_2O$ emission started when the soil temperature rose above $0^0$C and continued for 5 days and again the emission became high during fertilizer application. From the present study it was concluded that during freeze-thaw and post-fertilizer application the $N_2O$ surface emission and $N_2O$ concentrations at the 15 and 35 cm depths were highest in the Lower landscape. We hypothesize that the high soil moisture content coupled with higher nitrate levels triggered the $N_2O$ emission.

The $CH_4$ concentrations were highest at lower soil depths (35 cm or greater) in the Lower and Riparian landscape elements because of higher resistance to gas diffusion (and ebullition for the Riparian soils) through the soil/water layer to the atmosphere when the soil gases were saturated (Chareonsilp et al. 2000) or might be due to a closer proximity to the source of $CH_4$ production. The Upper and Middle landscape elements act as a net sink for the atmospheric $CH_4$. In the Upper and Middle landscape elements large amounts of $CH_4$ produced at lower depths (anaerobic soils) are oxidized when it moved through the outer oxidized shallow layers before it emits to the atmosphere. High variability in soil $SO_4^{2-}$ concentrations persisted among different sections of Riparian element resulting in varying $CH_4$ levels because of the inhibitory effect due to the competition between sulfate-reducing bacteria and methanogens for electron donors (such as organic carbon) in sulfate-rich anaerobic environments (Lovely and Klug 1983). From the present study it is obvious that the higher sulfate content in the Riparian landscape element was inhibitory to methane emission though the $CH_4$ concentrations were very high.

The concentrations of $CO_2$ increased with depth in all the landscape elements and neither the freeze-thaw nor the fertilization period had influenced the $CO_2$ concentrations and surface emissions but were highest during the crop growth and maturity. The highest $CO_2$ concentrations in the lower depths were likely the result not of high $CO_2$ production but accumulation as a result of low porosity and high compactness near 65 cm. Furthermore, the increased $CO_2$ accumulation at lower depths in poorly drained Lower and Riparian element soils contradicted the findings of Magnusson (1992) who found lower $CO_2$ concentrations in saturated soils. This increasing $CO_2$ concentration in saturated soil conditions from the present study needs to be further explored. The increased $CO_2$ emission during the cropped 2006 period from the present study revealed that the plant root respiration and microbial respiration of root exudates are the primary source of $CO_2$ production in all the landscape elements. The results from the field study (Chapter -2) clearly indicated that among all the three greenhouse gases, the occurrence of $N_2O$ emission was immediately during the onset of freeze-thaw and continued for 5 days. The occurrence of $CH_4$ emission was after thaw following the peak in $N_2O$ emission and the $CO_2$ emissions were not affected by freeze-thaw but consistent during crop growth and maturity periods.

Several factors could explain the increased subsurface accumulation of $N_2O$, $CH_4$ and $CO_2$ in soil and their subsequent surface emissions, but soil moisture, temperature, aeration and microbial activity were reported to have greater influence on GHG emissions (Kursar 1989; Hutsch et al. 1999; Burt et al. 2002; Smith et al. 2003). In the present study, higher accumulation of $N_2O$ and $CO_2$ at lower depths in Lower and Riparian elements even at a relatively higher $O_2$ levels corroborate that respiration and denitrification occur simultaneously even at higher rates of $O_2$ supply, provided easily decomposable organic matter is available or there is physical treatment of soils such as freezing/thawing or wetting/drying (Azam et al. 2002). Low temperatures during the freeze-thaw period have enhanced $N_2O$ production by nitrification and/or suppressed the $N_2$ formation by inhibiting nitrous oxide reductase. Subsurface $CO_2$ concentrations were positively correlated with soil temperature and volumetric moisture content and shown to be non-linear and site specific. This can be seen from my data that for all the landscape elements the $CO_2$ concentrations decreased at both very low and very high soil moisture.

Greenhouse gas emissions from various ecosystems have been determined by several researchers and most of those studies utilized the static vented chamber technique to quantify the surface emissions (Mosier et al. 1996; Maljanen et al. 2003; Dunmola et al. 2010). Only a few studies have attempted to utilize the subsurface GHG concentrations to estimate the surface emissions (Risk et al. 2002; Jassal et al. 2005) because of the difficulty in estimating the *in situ* diffusion coefficient and huge variability in soil physical, chemical and biological characteristics within the soil profiles. Risk et al. (2002) used the relationship of $CO_2$ emission to $CO_2$ concentrations to derive the *in situ* diffusivity for estimating the emission from concentration gradients. A similar approach was used in the present study to derive the *in situ* estimate of diffusivity using the $CO_2$ surface emission and concentration, as $CO_2$ is considered as a more conservative tracer than $CH_4$ or $N_2O$ which is less dramatically influenced by consumption processes in soil. In the present study after normalizing the estimated profile emissions with the *in situ* diffusion coefficient, the estimated profile $N_2O$ and $CH_4$ emissions were closer to the measured $N_2O$ and $CH_4$ emissions. But the scatter plots of the measured and estimated surface emissions of $N_2O$ and $CH_4$ from all the landscape elements showed no consistent relationship between these values. A more comprehensive study is required to examine the individual depth site diffusivity as the *in situ* diffusion coefficient arrived by this approach using binary diffusion coefficient did not give an accurate estimation.

The laboratory incubation with the frozen and unfrozen soil core study (Chapter-3) results revealed that the $N_2O$ emission potential was higher for the frozen soil than the unfrozen soil. The pattern of $N_2O$ emission from frozen soil cores was similar to the $N_2O$ emission observed in the field study (Chapter-2) with the highest emission in Lower and Riparian landscape element frozen soils and the emission occurred within 40 hours of thawing. This clearly indicated that the freeze-thaw period is the most important period where the majority of the $N_2O$ emission occurred in the undulating landscape soils and the frozen depth soils have greater potential for $N_2O$ emission.

In conclusion, the buildup of $N_2O$ and $CH_4$ during winter occurred at different depths and there was two prominent periods of $N_2O$ emission, one during freeze-thaw and the other during fertilizer application. $CH_4$ emission was prominent after thawing. The Lower landscape elements were 'hot spots' for $N_2O$ and the Riparian landscape elements were 'hot spots' for $CH_4$. The highest $N_2O$ and $CH_4$ concentrations occurred at 5 and 15 cm depths in the Lower and Riparian landscape elements. $CO_2$ concentrations were highest at 65 cm depth in the Riparian landscape element and freeze-thaw period had no effect on $CO_2$ concentrations. $CO_2$ surface emissions were highest during the cropped period. The estimated profile greenhouse gas emissions of $N_2O$ and $CH_4$ behaved differently during the freeze-thaw and post-fertilizer application periods. The approach of normalizing profile emission with the $CO_2$ surface emission to obtain estimated profile emission could provide a means of quantifying the contribution of subsurface sources to annual greenhouse gas emission in a variety of ecosystems. A more comprehensive examination of this approach should be necessary to validate in other ecosystems and should be considered in other studies when quantifying greenhouse gas emission in similar undulating landscapes. Frozen soils had greater $N_2O$ emission potential than the unfrozen soils and the pattern of $N_2O$ emission from frozen soil cores was similar to the $N_2O$ emission from the field. Further research work is needed to elucidate the processes occurring in frozen soil at the 10-15 cm and 30-35 cm depths in Lower and Riparian landscape soil during thawing to better understand the underlying processes leading to higher $N_2O$ emission.

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