GREENHOUSE GAS FLUXES AND BUDGET FOR AN ANNUAL CROPPING SYSTEM IN THE RED RIVER VALLEY, MANITOBA, CANADA

BY

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ABSTRACT

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Rising atmospheric greenhouse gas (GHG) concentrations from industrial activities during the past two centuries are influencing climate and will contribute to significant global climate change in the coming decades. The quantification and estimation of GHG sources and sinks has become a priority for those engaged in various aspects of Earth science, engineering, economics and social policy. Agriculture contributes significantly to national and global GHG inventories, but there is considerable control over management decisions. Changes in production methods could lead to a significant reduction and possible mitigation of emissions from the sector. For example, conservation tillage practices have been suggested as a method of sequestering atmospheric carbon dioxide (CO_2), however, many questions remain unanswered regarding the short-term efficacy of this production method and knowledge gaps exist regarding possible interactions with essential nutrient cycles, and the production of non-CO_2 GHGs, such as nitrous oxide (N_2O).

Between autumn 2005 and 2009, a micrometeorological flux system was used to determine net CO_2 and N_2O exchange from an annual cropping system situated on clay soil in the Red River Valley of southern Manitoba. Four plots (4-ha each) were independently evaluated and planted to corn in 2006 and faba bean in 2007; in 2008, two spring wheat plots were monitored. As well, during the non-growing season in 2006-2007 following corn harvest, a second micrometeorological flux system capable of simultaneously measuring stable C isotopologue ($^{12}CO_2$ and $^{13}CO_2$) fluxes was operated

at the site. Tillage intensity and crop management practices were examined for their influence on GHG emissions. Significant inter-annual variability in CO_2 and N_2O fluxes as a function of crop and related management activities was observed. Tillage intensity did not affect GHG emissions from the site. Considerable variation in fluxes among plots each year added to the uncertainty of GHG budget estimates.

The annual cumulative net ecosystem exchange of CO_2 was -720, 70 and -2400 kg C ha^{-1} y^{-1} for the corn, faba and spring-wheat crop years, respectively. Enhanced respiration during the faba year was largely responsible for the loss, whereas the large gain in the spring-wheat year was a combination of high photosynthetic activity and reduced respiration. After accounting for harvest removals, the net ecosystem C budgets were 510 (source), 3140 (source) and -480 (sink) kg C ha^{-1} y^{-1} for the three respective crop years, summing to a three-year loss of 3170 kg C ha^{-1}. Stable C isotope flux measurements during the non-growing season following corn harvest indicated that approximately 70 % and 20 – 30 % of the total respiration originated from crop residue C during the fall of 2006 and spring of 2007, respectively. Annual gap-filled N_2O budgets were 5.5, 1.4, and 4.3 kg N ha^{-1} in the corn, faba and spring wheat crop years, respectively. Emissions from fertilizer nitrogen addition and soil thaw the following spring were responsible for the greater cumulative flux in the corn and spring wheat years. The N_2O emissions at the site exacerbated the net global warming potential of this annual agroecosystem.

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FOREWORD

This thesis has been prepared in the manuscript format in adherence with the guidelines established by the Department of Soil Science at the University of Manitoba.

A version of Chapter 2 has been published:

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A version of Chapter 3 will be submitted for publication in the near future.

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1. INTRODUCTION

Agricultural soils can act as a significant sink or source of carbon dioxide (CO_2), and can be a substantial source of nitrous oxide (N_2O). Much previous research has focused on soil CO_2 fluxes, which are the result of autotrophic and heterotrophic respiration, and mechanisms of organic matter decomposition. In recent years, work has increasingly focused on N_2O emissions, as the agricultural sector is estimated to be the greatest anthropogenic source of N_2O to the atmosphere and N_2O has approximately 300 times the greenhouse warming potential of CO_2 (Forster et al., 2007; Smith et al., 2007; Davidson, 2009). Although some agricultural soils have been shown to accumulate CO_2-C, the C and N cycling dynamics in soils are inherently linked, and it is unclear how farm management practices devised to increase the C sink strength of soils may affect N_2O emissions. The production of N_2O in agricultural soils is the result of the microbial processes of nitrification and denitrification, and is regulated by a myriad of complex, interacting factors, such as moisture and oxygen availability, C substrate availability and quality, and annual freeze/thaw cycles (Beauchamp, 1997). Greater understanding of the regulating controls of N_2O fluxes from agricultural soils and the coupling to organic C cycling processes is required for more complete elucidation of net greenhouse gas (GHG) budgets.

1.1 Carbon Dioxide Balance of Cropland Ecosystems

Agricultural soils utilized for crop production in Canada have been depleted of organic C over the years compared to the natural grassland and forest ecosystems they

replaced (Smith et al., 1997; Janzen et al., 1998). They have acted as a significant source of CO_2 as a result of the harvest of biomass produced and the subsequent consumption of crops, as well as, intensive annual cropping practices involving soil tillage resulting in rapid oxidation of soil C pools due to the establishment of conditions conducive to decomposition. The extensive use of summer-fallow in many parts of the Prairies has also accelerated this decline in soil organic C pools. Initial cultivation of landscapes in Canada resulted in rapid loss of soil organic C in the first few decades (Janzen et al., 1998). However, according to results from Century model analysis (Smith et al., 1997), currently the soil organic C levels throughout most of the land under agricultural production in western Canada have reached a steady-state in terms of change. Inputs of residues approximately match outputs, and total emissions of CO_2 from agricultural soils in Canada are thought to be relatively small as the soil has become increasingly depleted in organic stores. The Century model study estimates of average soil C emissions for 1990 of approximately 40 kg ha^{-1} for Canadian agricultural soils (Smith et al., 1997) were smaller than detectable with measurement precision (Janzen et al., 1998).

The practice of conservation tillage is increasing in agricultural production, in part due to its potential to sequester and stabilize C in soil organic matter (SOM) (Schlesinger, 1999; Desjardins et al., 2001; Garnier et al., 2003; Li et al., 2005). The challenge of obtaining C sequestration in agricultural soils requires understanding both the inputs and outputs and how they interact within the ecosystem. In the case of inputs, understanding of both the quantity (amount of biomass) and quality (biochemical composition) of aboveground and belowground plant litter remaining post-harvest is desirable. On the output side of the ecosystem balance, the goal of conservation tillage techniques for example, is to create biophysical conditions that slow the rate of organic matter

decomposition, and provide biochemical conditions that eventually stabilize and protect soil C in aggregates.

Common assessments of net C transformations in agricultural ecosystems have been based on inventories conducted by quantifying temporal changes in biomass (accounting for crop removal and litter-fall) and soil organic carbon (SOC) content. Although these investigations are useful for the characterization of agricultural soils and can be a valuable indirect measure of historic ecosystem metabolism, they provide little specific temporal or spatial information as to the amount of CO_2 taken up by crops via photosynthesis or released to the atmosphere by plant and microbial respiration. Experimental work is required to examine the short-term (days to months to years) influence of agricultural management decisions on gross primary production and ecosystem respiration to complement research documenting longer temporal (years to decades to centuries) processes regulating organic C stabilization into soil aggregates. Direct, *in situ* measurements are required to quantify rates of canopy-atmosphere CO_2 flux under contemporary agronomic and global change forcing and these in turn may be linked or correlated to the long-term processes dictating SOM turnover rates, and used to calibrate and validate process-based models. Due to the interacting dynamics of crop and weed photosynthesis, plant respiration, soil respiration and SOM decomposition, micrometeorological measurements of the net ecosystem CO_2 exchange (NEE) from crop systems with a high degree of temporal resolution are an important contribution to understanding the C balance of agricultural soils. Measurements of NEE combined with harvested biomass accounting give a net C balance for crop ecosystems at seasonal and annual time scales, helping close the temporal gap between snapshot assessments of soil C inventories and when alternative management strategies were implemented.

In Chapter 2 of this thesis, NEE measurements were made for three years over a corn-faba-spring wheat rotation in the Red River Valley of southern Manitoba and used to estimate cumulative C budgets for the site over the triennium. This measurement campaign is a Canadian complement to the small but growing body of international literature reporting multi-year cropland NEE studies examining the inter-annual patterns of the C balances of these important managed ecosystems.

1.2 Partitioning Sources of Heterotrophic Soil Respiration

All C input to agricultural soils, whether originating from plant residues, root exudates, or manure, undergoes the process of decomposition. Decomposition releases CO_2 into the atmosphere and mineral inorganic nutrients into the soil, while leaving behind a remnant pool of complex organic molecules that are more resistant to further decay (Chapin III et al., 2002). Plant litter and other organic inputs are acted upon by forces such as physical fragmentation, biological interactions between and within soil food web trophic levels, mineralization and eventual humus formation (Schlesinger, 1977; Batjes, 1996). The main driving force behind decomposition is the biochemical alteration of litter and detritus, mainly accomplished by the activity of soil fungi and bacteria (Norton and Firestone, 1991). In agricultural systems, the factors that have the greatest influence on decomposition rates that are controlled by humans are the introduction of organic matter into soils (quantity and quality of litter), fertilizer rates, and tillage intensity (Schnürer et al., 1985; Neely et al., 1991; Beare et al., 1992; Garnier et al., 2003). Physical mixing from tillage operations can alter decomposition and decay rates by varying the distribution of litter incorporation in the soil profile in ploughed agricultural operations or by placement on or near the surface with conservation tillage

techniques (Aulakh et al., 1991; Garnier et al., 2003). Buried plant residue can have decay rates that are 2 to 3 times greater than that of surface litters due to the influence on the decomposer community and associated microclimatic (temperature and moisture) conditions (Schnürer et al., 1985; Beare et al., 1992).

There are many ways of characterizing SOM pools, and they are often conceptualized or modelled in terms of the different organic C fractions. In a simple characterization, SOM consists of three compartments in soil: fresh litter, incompletely decomposed, and humus (Schlesinger, 1977). Due to differences in the turnover rate of the various organic fractions, residency times are often used to classify C pools in soils (Schnürer et al., 1985; Parton et al., 1988; Davidson et al., 2000; Knorr et al., 2005). These residency times can vary from < 1 to > 1000 years, and reflect the degree of decay and decomposition in the different organic C compartments. In agroecosystems, often a distinction in SOM is made between recently fixed C by photosynthesis or crop residue carbon (CRC) and resident SOC that is the pooled remnants of ecosystems past and previous production regimes. When studying the effect of conservation tillage on the soil C balance, this simple dichotomy is often used to assess the efficacy of the management decision due to expected effects resulting from contrasting placement of litter and degrees of mechanical disturbance of top-soil between different tillage systems.

Chapter 3 uses stable C isotope techniques combined with recently developed micrometeorological instrumentation and theory to partition substrate sources of soil respiration between that derived from recently fixed CRC and older SOM following corn harvest at the southern Manitoba site in 2006. The study reports on measurements made over recently implemented reduced tillage plots and continued intensive tillage plots at the site.

1.3 Nitrous Oxide Emissions and Cumulative Cropland GHG Budgets

Nitrous oxide (N_2O) is a 300X more potent GHG than CO_2 in the troposphere, contributes to the destruction of ozone in the stratosphere, and is commonly emitted from agricultural soils, making its production a concern. The microbial biochemical processes of nitrification and denitrification contribute to N_2O emissions from soils (Focht and Verstraete, 1977).

Nitrification is the aerobic oxidation of ammonium (NH_4^+) to nitrite (NO_2^-) and NO_2^- to nitrate (NO_3^-). Most nitrifiers derive their energy from the oxidation of NH_4^+ or NO_2^- and belong to the family Nitrobacteraceae (Focht and Verstraete, 1977; Prosser, 1989). The two groups of nitrifying bacteria are often closely associated in soil, therefore NO_2^- rarely accumulates, with successive progression to the nitrate end product (Chapin III et al., 2002). Nitrifying bacteria have also been shown to produce NO and N_2O, as gaseous "losses" or side products from the nitrification process (Prosser, 1989; Davidson, 1992).

Denitrification is the sequential reduction of nitrogen oxides (NO_3^-, NO_2^-, and NO) to nitrous oxide (N_2O) and diatomic nitrogen (N_2). Therefore, denitrification is intrinsically linked with nitrification rates in soils (which produces NO_3^-), despite the spatial and temporal separation between the two processes (Focht and Verstraete, 1977; Prosser, 1989). The majority of denitrification believed to take place in agricultural soils is the result of facultative anaerobic metabolism and is carried out by many genera of bacteria. This type of denitrification is a form of dissimalatory respiratory reduction where NO_3^- is used as an electron acceptor to derive energy in oxygen deprived environments, rather than being assimilated and reduced to biochemical cell constituents,

such as amino acids or enzymes (Focht and Verstraete, 1977). As most denitrification in agricultural soils is carried out by organotrophs, the reaction is highly dependent on quantities and quality of SOC pools (Aulakh et al., 1991; Beauchamp, 1997). Therefore, biological denitrification rates in agricultural soils are coupled to the decomposition processes discussed and evaluated in Chapter 2 and Chapter 3.

Most measurements of N_2O exchange between agricultural ecosystems and the atmosphere have been conducted with soil chamber or cover (enclosure) techniques. However, there is significant spatial-temporal variability in the highly episodic N_2O fluxes measured under field conditions (Rover et al., 1999) that is difficult to capture with chambers due to limited replication and logistical (time and human labour) constraints. As well, chambers can alter the soil environment and microclimate, potentially introducing biases and artifacts to N_2O flux studies. Tower-based micrometeorological methods enable the continuous quantification of net cropland-atmosphere N_2O exchange integrated over the landscape scale, and provide a non-invasive alternative to chambers, that captures spatial and temporal heterogeneity.

Chapter 4 reports findings from continuous micrometeorological N_2O flux time series and budgets over the three-year annual crop rotation (corn-faba-spring wheat) studied and compares results obtained from recently established reduced tillage plots to continued intensive tillage at the site. Combining annual N_2O budgets from the study with those for CO_2 discussed in Chapter 2 allowed for an innovative assessment of the net GHG balance of the annual cropping system, at seasonal, annual and multi-year time scales.

1.4 Thesis Organization

Following this general introduction are three chapters prepared in a stand-alone, manuscript format. The first data chapter (Chapter 2) reports on three-years of continuous net CO_2 flux measurements made over land in annual crop production in the Red River Valley of southern Manitoba. The following chapter (Chapter 3) builds on the work from Chapter 2, and focuses specifically on non-growing season CO_2 fluxes using stable C isotope micrometeorological techniques to partition the respiration flux into that derived from recent crop residues compared to indigenous SOM at the cropland site. The final data chapter (Chapter 4) reports on three-years of continuous N_2O fluxes measured at the site simultaneously with net CO_2 exchange, enabling an estimation of the net GHG balance of the land-use. The dissertation concludes with a synthesis chapter that: highlights and integrates the three data chapters, discusses important findings, implications, and limitations of the work, and outlines future research initiatives and challenges.

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2. NET CARBON DIOXIDE FLUX AND BUDGETS FOR AN ANNUAL CROPPING SYSTEM IN THE RED RIVER VALLEY, MANITOBA, CANADA

2.1 Abstract

Net carbon dioxide ecosystem exchange (NEE) was measured over three years (2006-2008) in an annual crop rotation in the Red River Valley of southern Manitoba, Canada using the flux-gradient method. The turbulent transfer coefficients were obtained using a similarity-theory, eddy-covariance based aerodynamic method and the carbon dioxide vertical gradient was measured with a tunable diode laser analyzer. The system measured 30-min-average fluxes sequentially over two reduced tillage plots and two intensive tillage plots at the site. Annual cumulative NEE was -720, 70 and -2400 kg C ha^{-1} $year^{-1}$ for corn, faba and spring-wheat crop years, respectively. Enhanced respiration during the faba year was largely responsible for the loss, whereas the large gain in the spring-wheat year was a combination of high photosynthetic activity and reduced respiration. The three years experienced sequentially cooler and wetter years that likely affected crop performance. After accounting for harvest removals, the net ecosystem C budgets were 510 (source), 3140 (source) and -480 (sink) kg C ha^{-1} y^{-1} for the three respective crop years, summing to a three-year loss of 3170 kg C ha^{-1}. The recent conversion from intensive tillage to a reduced tillage practice showed no difference because of relatively large variability in NEE among the plots at the site.

2.2 Introduction

Decomposition of organic matter following land clearing, drainage and the cultivation of soils for agricultural production increased atmospheric carbon dioxide (CO_2) concentrations and influenced climate over thousands of years during the pre-industrial Holocene (Ruddiman, 2003; Salinger, 2007). Human-induced mineralization and oxidation of soil organic matter (SOM) was accelerated during the industrial era and has significantly contributed to rising CO_2 concentrations and climate change (IPCC, 2001; Lal, 2004).

In the past century, significant decomposition of SOM from agricultural fields was detected on the Prairies of western Canada, where up to 30 – 50 % of the large pools of native soil organic carbon (SOC) was returned to the atmosphere within decades following clearing, plowing, summer fallowing, and cropping of former grasslands and forests (Janzen, 2001; 2005 *and references therein*). The Prairies account for an estimated 90 % of the SOC lost from agricultural soils in Canada over the past century (Smith et al., 1997). The present SOC balance of agricultural soils in western Canada is considered to be approximately neutral, with inputs matching losses (Janzen et al., 1998), but optimism exists to replenish a portion of the pool of organic matter that once existed in the soils of current cropland.

Growing interest in offsetting anthropogenic greenhouse gas emissions has led to the promotion of conservation tillage (reducing tillage intensity and frequency) techniques on intensively cultivated cropland to sequester and stabilize atmospheric CO_2 in SOM (Lal, 2004; Hutchinson et al., 2007; Smith et al., 2007; Lal, 2008; MAFRI, 2008; Spargo et at., 2008; CCX, 2009). From the studies conducted, there is considerable

variability in reported rates of C sequestration by soils in North America resulting from the interaction of regional climatic and edaphic conditions, the influence of applying various conservation tillage techniques, and the sampling approaches used by investigators. Estimated rates of SOC accumulation following the reduction of soil tillage range from 0 to 1000 kg C ha^{-1} yr^{-1} for different climate regions in North America (West and Post, 2002; VandenBygaart et al., 2003; Campbell et al., 2005; Hutchinson et al., 2007; Lal, 2008). Within Canada there is a reported difference in C sequestration potential between humid eastern agricultural regions and the drier, western Prairies (VandenBygaart et al., 2003). Studies from eastern Canada indicate no net C sequestration with adoption of conservation tillage, just redistribution of where SOC accumulates in the subsurface profile (Angers et al., 1997; Gregorich et al., 2005). In western Canada, estimates of contemporary soil C sequestration rates by no-till systems range from 100 to 700 kg C ha^{-1} yr^{-1} (VandenBygaart et al., 2003; Campbell et al., 2005). Studies from the Canadian Prairies have most often been limited to the semi-arid regions of Saskatchewan and Alberta while data from the sub-humid, eastern Prairies of Manitoba are lacking.

Virtually all introduction of organic C to agricultural ecosystems originates from the photosynthetic reduction of atmospheric CO_2 by crop plants (in some management systems the addition of animal manure contributes an additional organic source of C). Carbon dioxide is fixed through the process of photosynthesis into carbohydrates, giving plants energy to build tissues and reproduce. During the growing season, much of the CO_2 fixed through photosynthesis is released back to the atmosphere as a result of plant respiration due to metabolic growth and maintenance requirements *(*Amthor, 1989; 2000). Some C is introduced to the rhizosphere during the growing season via root exudation

(secretions), where it stimulates the growth and activity of heterotrophic fungi and bacteria (Lynch and Panting, 1980; Chapin et al., 2002). However, the principal introduction of C from agricultural crops into soils is the residual amount of plant biomass remaining following harvest, including shoot and root litter, which contributes to the dynamic soil C pool (Batjes, 1996). As a result, increasing inputs via greater biomass production is often suggested to increase C sequestration. The use of nitrogen (N) fertilizer to improve yields is commonly believed to increase C sequestration (Harapiak et al., 1993; Liebig et al., 2005), especially when combined with increasing cropping frequency and decreasing tillage intensity (Campbell et al., 2005). However, it remains unclear whether increasing crop biomass production with intensive industrial inputs such as fertilizers and herbicides can actually result in net atmospheric CO_2-C sequestration. This can be considered in terms of energy dependence on non-renewable, fossil-fuel C inputs (Schlesinger, 1999; Izaurralde, 2000; Hoeppner, 2001; Zentner et al., 2004; Khakbazan et al., 2009) but is also questionable from an ecophysiological perspective, with recent studies reporting both no detectable change (Hofmann et al., 2009) and often increases in SOC decay rates (Khalil et al., 2007; Khan et al., 2007; Zhu et al., 2007; Russell et al., 2009) with applied N fertilization and increased crop yields over time. Nitrogen fertilizer changes the C:N ratio of plant tissue and the soil solution, and influences crop physiology and anatomy, such as the shoot:root ratio, which generally increases with greater rates of application. Although the contribution of plant organic C from aboveground biomass is substantial in some instances, the largest SOC input from crops is usually the root systems and exudates (Lynch and Panting, 1980; Paustian et al., 1990), and recent studies imply that C sequestration may be organ dependent and variable with ecosystem (Crow et al., 2009), with C from roots being stabilized preferentially to

that derived from shoots in grassland and agricultural soils (Gale and Cambardella, 2000; Matamala et al., 2008; Russell et al., 2009).

Due to the interacting dynamics of crop and weed photosynthesis, plant respiration, soil respiration and SOM decomposition, micrometeorological measurements of the net ecosystem CO_2 exchange (NEE) from crop systems with a high degree of temporal resolution are an important contribution to understanding the C balance of agricultural soils. Such techniques enable the continuous quantification of surface-atmosphere CO_2 exchange, integrated over the landscape scale (Baldocchi et al., 1988; Kaimal and Finnigan, 1994). Earlier micrometeorological studies from agricultural fields have addressed seasonal and diurnal variations of NEE for sugar beets (Monteith and Szeicz, 1960), wheat (Denmead, 1969); barley (Biscoe et al., 1975), soybeans (Baldocchi et al., 1981a; Anderson et al., 1984), alfalfa (Baldocchi et al., 1981b; Held et al., 1990; McGinn and King, 1990), corn (Lemon, 1960; Dejardins et al., 1984; Dejardins, 1985; Held et al., 1990; McGinn and King, 1990), sunflower (Held et al., 1990), cotton (Held et al., 1990) and sorghum (Anderson and Verma, 1986). With advancements in instrumentation and data acquisition systems, the scope of the studies were soon expanded to include comparative or simultaneous growing season measurements of neighboring C_3 and C_4 crop canopies (McGinn and King, 1990; Baldocchi, 1994); cropped vs. fallow fields (McGinn and Akinremi, 2001); irrigated vs. rainfed agroecosystems (Suyker et al., 2004); and different N fertilization treatments (Pattey et al., 2001). Examples from the past decade include the use of eddy covariance measurements to estimate the annual CO_2-C balance for a winter wheat crop in Germany (Anthoni et al., 2004), and multi-year studies that have examined the influence of agricultural management decisions, such as the inclusion of cover crops (Baker and

Griffis, 2005), use of irrigation water (Verma et al., 2005), and conservation tillage techniques (Baker and Griffis, 2005; Verma et al., 2005; Hollinger et al., 2005), on the annual C budgets of the ubiquitous corn-soybean agroecosystem of the U.S. Mid-west.

Much micrometeorological theory and principles has origins in agricultural settings because of research questions about crop physiology, and also because developing theory and instrumentation was easier at flat, uniform sites that could be controlled by investigators. However, in the recent decade, the majority of micrometeorological studies of NEE have been conducted in natural systems with a much lower proportion conducted at agricultural sites compared to the past. Ironically, this is mainly due to advancements made in theory, instrumentation and data processing capabilities largely based on earlier work in agricultural fields. Although we now have the ability to measure more complex and challenging terrain than in the past, and natural ecosystems are very important to the global C cycle and climate system, there is a resurged need to pose ecological questions at agricultural sites to assist policy-makers in making socio-economic and political decisions in response to climate change scenarios and to assess the potential impact of various possible anthropogenic mitigation strategies, such as biological C sequestration.

In the present study, NEE was measured using an aerodynamic flux gradient technique for three years from plots of an agricultural field located in the Red River Valley of southern Manitoba, Canada. The Red River Valley is a predominately agricultural region (majority of land base and economy is dedicated to crop and livestock production) of southern Manitoba, eastern North Dakota and western Minnesota. Most of the arable land base has been in production since the late 19th century. The valley's location as the paleogeographic center of glacial Lake Agassiz, is a very level landscape

(typical relief is < 1 m km^{-1}) with fine textured soils formed by glaciolacustrine deposits that aggraded over time. Due to a high smectitic clay and associated moisture content, and the historical existence of tall-grass prairies and wetlands, the soils in the Red River Valley have a notably high organic matter content and fertility that has marveled scientists for over a century (Lawes and Gilbert, 1885; Ellis and Shafer, 1928). Periodic flooding, excessive moisture and inadequate drainage are the greatest agronomic production challenges in the region.

The objectives of the study were to: (1) compare the carbon balance of annual crops in the Red River Valley of southern Manitoba, Canada to other agricultural regions; (2) examine the short-term influence of conservation tillage techniques on net CO_2 fluxes and carbon sequestration in the cropping system; and (3), identify some of the controls driving seasonal and inter-annual variability of net CO_2 exchange at the site.

2.3 Materials and Methods

2.3.1 Site Description

The experimental field (49.64°N, 97.16°W; 235 m a.s.l.) where CO_2 flux measurements were performed was located at the University of Manitoba Glenlea Research Station, approximately 16 km south of Winnipeg, Manitoba, Canada. The research site was situated in the Red River Valley, a near-level to very gently sloping (0 to < 2 % slope, typically < 1 m km^{-1}), glaciolacustrine clay floodplain. The soils at the site were of the Red River association, consisting of a combination of Osborne clay and Red River clay soil series depending on local drainage characteristics and the micro-relief

of the landscape (Ehrlich et al., 1953; Michalyna et al., 1971). The hydrology ranges from poorly (micro-lows, Osborne clay series) to imperfectly (micro-highs, Red River clay series) drained soils. The Red River clay soil series is classified as a Gleyed Humic Vertisol (Canadian system) or a fine smectitic frigid Typic Epiaquert (USDA system), while the Osborne clay series is classified as a Gleysolic Humic Vertisol (Canadian system) or a fine smectitic frigid Typic Endoaquert (USDA system). The texture of the 0-20 cm soil surface layer at the site was approximately 60 % clay, 35 % silt and 5 % sand. The dominant clay mineral group found in the Red River soil association are 2:1 smectites. The average bulk density and organic C content of the 0 – 0.2 m layer of soil at the site when the study was initiated were approximately 1.2 Mg m^{-3} and 3.2 %, respectively.

2.3.2 Agronomic History

Following a summer-fallow[1] year in 2005, different soil management treatments were initiated in the spring of 2006 with the establishment of four 200 m by 200 m (4 ha each, or 16 ha total) experimental treatment plots inside of a larger 30 ha field. Two plots were managed as intensive tillage (IT) treatments and two plots were managed as reduced tillage (RT) treatments. The IT plots were cultivated[2] to a depth of approximately 0.20 m on April 27, 2006, while the RT plots received a light (single-pass) harrowing as seed bed preparation on April 28, 2006.

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[1] No crops planted, no fertilizer applied; weeds controlled by chemical and mechanical means (Brady and Weil, 2008).

[2] The tillage implement used on the intensive tillage (IT) plots during the study consisted of a field cultivator with three rows of shanks with 0.20 m sweeps spaced 0.30 m apart followed by three rows of spring-tine harrows spaced 0.10 m apart. One pass over the surface of the IT plots was made with the implement every cultivation date.

On May 16, 2006 all four plots and the surrounding field were sown to corn (*Zea mays* L. cv 'DKC27-12 (Roundup Ready®)', DEKALB®) in north-south oriented rows spaced 0.9 m apart, at a rate of 74,130 seeds ha^{-1}. A granular fertilizer blend (32-25-10-10; Viterra Inc.) was side-banded with the seed at planting at a rate of 180 kg ha^{-1}. Granular urea (46-0-0) was broadcast applied at 112 kg ha^{-1} on May 17 and lightly tine-harrowed to incorporate into the soil on the plots. Roundup® (a.i. glyphosate, Monsanto Company Inc.) was applied on June 13, 2006 to all plots at a rate of 1.7 L ha^{-1}. Grain was harvested from all plots on October 6, 2006, yielding an average of 3,200 kg ha^{-1} for the field. On October 25, 2006, standing aboveground corn biomass (stalks and leaves) on all plots was shredded with a flail-mower. The IT plots were double-disced once on October 27, 2006 and cultivated[2] once on October 28, 2006, while the RT plots were undisturbed with all flailed corn stover remaining on the surface.

On May 9, 2007, the IT plots were cultivated[2] once and harrowed once; the RT plots were harrowed once. Faba bean (*Vicea faba minor* L. cv 'CDC Blitz', Crop Development Centre, University of Saskatchewan) was planted to all plots on May 11, 2007 at a rate of 202 kg ha^{-1}. A self-adhering peat-powder inoculant (Becker Underwood Canada Ltd., Saskatoon, Saskatchewan) was hand applied as the faba bean was being augered into the seeder. A buffer of 100 to 200 m of faba was sown beyond the four 4 ha^{-1} experimental treatment plots, with the rest of larger surrounding field left fallow. No fertilizer or herbicide was applied to the faba bean crop for the duration of the growing season. The faba bean crop was harvested on August 27, 2007, yielding 8,970 kg ha^{-1} of silage. Post-harvest herbicides were applied to all plots on September 6, 2007, consisting of a mixture of Roundup Ultra® (a.i. glyphosate, Monsanto Company Inc.) at 1.7 L ha^{-1}

and 2,4-D Amine 600 (a.i. 2,4-Dichlorophenoxyacetic acid, Interprovincial Cooperative Ltd.) at 0.8 L ha^{-1}. The IT plots were double-disced on October 25, 2007.

In spring 2008, the tillage treatment comparison was discontinued at the site. The IT plots remained in annual crop production for 2008 while the former RT plots were converted to a perennial forage crop. Only the two IT plots remaining in annual crop production during 2008 were considered for the purposes of this study. On May 16, 2008 the plots were cultivated[2] and tine-harrowed once. Wheat *(Triticum aestivum* L. cv '5602 RS - Hard Red Spring', Viterra (Proven® seed) Inc.) was sown to the experimental plots and surrounding field on May 21, 2008 at a rate of 135 kg ha^{-1}. A granular fertilizer blend (60-10-0) was banded with the seed at planting at a rate of 163 kg ha^{-1}. Herbicide was applied on June 23, 2008, consisting of a mixture of Axial™ (a.i. pinoxaden, Syngenta AG) at 0.6 L ha^{-1}, Curtail® M (a.i. clopyralid (50 g L^{-1}) and MCPA ester (280 g L^{-1}), Nufarm Agriculture Inc.) at 2.0 L ha^{-1}, and the surfactant, Merge™ (BASF Canada Inc.) at 0.5 L 100 L $water^{-1}$. Grain was harvested on September 16, 2008, yielding 3,070 kg ha^{-1}. Straw from the crop was subsequently round-baled, yielding approximately 2,200 kg ha^{-1}. The plots were cultivated[2] on November 3, 2008.

2.3.3 Carbon Dioxide Flux Measurements

Micrometeorological equipment to measure net CO_2 fluxes from the four plots was deployed at the site beginning August 2005. A tunable-diode-laser based trace gas analyzer (Model TGA100A, Campbell Scientific Inc., Logan, Utah, USA) was installed in a line-powered (AC), temperature-controlled instrumentation trailer located in the centre of the four experimental plots. The laser and associated optical hardware and electronics for the trace gas analyzer (TGA) were further housed within an insulated,

temperature-controlled enclosure. The lead-salt tunable-diode-laser of the TGA (Model IR-N2O/CO2, Laser Components GmbH., Olching, Germany) was operated at a temperature of 84 K in a dual-ramp, jump-scanning mode (eg. Fried et al., 1993) and parameterized for the concurrent measurements of atmospheric concentrations of CO_2 and N_2O at 10 Hz. The TGA system contained two detectors (Model MCT-5-TE3-1.0, InfraRed Associates Inc., Stuart, Florida, USA); one located in a reference cell and one located in a sample cell, a splitter in the optical path of the single, non-reflecting laser beam deflected energy on to both detectors (for a more detailed description of the TGA100 see Edwards et al., 2003). Reference gas with concentrations of approximately 300,000 ppm CO_2 and 2000 ppm N_2O was continuously passed through the reference cell of the TGA at a rate of 10 mL min^{-1}. Unknown (eg. atmospheric, zero or calibration) gas samples were drawn through the sample cell and mapped to the reference cell gas spectral template based on HITRAN atlas data and software parameterization of the TGA to calculate CO_2 and N_2O concentrations. At system operating temperature and pressure, the first ramp of the TGA laser was parameterized to scan a N_2O absorption line peak located at a wavenumber of 2243.110 cm^{-1} by applying a DC current of ~567 mA, while the second ramp was tuned to scan a $^{13}CO_2$ absorption line peak located at a wavenumber of 2243.585 cm^{-1} by applying a DC current of ~589 mA. The tunable-diode-laser in the TGA was calibrated by the manufacturer for the use of the $^{13}CO_2$ absorption line as a proxy to calculate total CO_2 concentrations.

The flux gradient (FG) micrometeorological technique was used to determine the net exchange of CO_2 between the soil-crop system and the lower atmosphere. The FG technique applies the extension of simple laws, analogous to those which govern molecular diffusion in laminar flow, to the turbulent exchange of mass and energy in the

atmosphere (Kaimal and Finnegan, 1994). Using the FG method, the flux of CO_2 between a crop system and the lower atmosphere ($F_{C\text{-}NEE}$) can be represented as:

$$F_{C\text{-}NEE} = - K \frac{\Delta[CO_2]}{\Delta z} \quad (1)$$

where K is the turbulent transfer coefficient or "eddy diffusivity" for CO_2, $\Delta[CO_2]$ is the vertical concentration gradient of CO_2 in the surface layer, and Δz is the vertical distance between CO_2 concentration observation heights. The sign notation adopted implies negative flux into the ecosystem, and positive flux out of the ecosystem.

The eddy diffusivity (K) term was estimated using a similarity theory, eddy covariance based aerodynamic method (eg. Pattey et al., 2006; Phillips et al., 2007; Denmead, 2008; Monteith and Unsworth, 2008). A sonic anemometer-thermometer (CSAT-3, Campbell Scientific Inc., Logan, Utah, USA) was mounted within the surface layer to an instrumentation tower in each tillage treatment and used to calculate the covariances required to estimate K (friction velocity (u_*) and the sensible heat flux). Integrated similarity functions for momentum were applied to correct K calculations for dynamically stable (as given by Businger et al. 1971) and unstable (as given by Paulson, 1970) atmospheric conditions based on the Obukhov length. Linear regressions between the sonic anemometer-thermometer from each management treatment indicated no significant difference (slope = 1 ± 10 %) in 30-minute K values over the course of the study (Appendix A), so the average value was used for flux calculations. The classic micrometeorological assumption of equality between the turbulent transport of momentum, energy and mass was applied for the purpose of the analyses reported. Snow depth, stubble and crop height (h_c) were measured manually with a ruler or a tape twice-

weekly to weekly during the course of the study. These surface parameter records were used to estimate the zero-plane displacement height (d) and calculate the effective observation heights (z - d) to be used in the evaluation of stability corrections and determination of K. For periods of snow cover, d was assumed to be equal to the depth of snow, during the rest of the year it was assumed to be $0.66h_c$ (Garratt, 1992; Denmead, 2008) and interpolated between periods when manual surface observations were made.

For the calculation of $\Delta[CO_2]$, two stainless steel gas sample intakes (12.5 mm internal diameter (i.d.)) were mounted at different heights within the atmospheric surface layer to a triangular, aluminum instrumentation tower located at the approximate centre of each experimental plot. The upper and lower sample intakes were generally maintained with a vertical separation distance (Δz) of 0.65 m, with some exceptions, such as when gradient tests were performed. Each sample intake had a cover with a screen to prevent insects and debris from entering the line.

Care was taken to ensure a balance between measuring gradients far enough above the surface to minimize roughness sub-layer effects but low enough to contain the flux footprint to each experimental plot of interest. During the winter, the bottom intakes were located approximately 0.5 m above the snow-pack, for the spring and fall non-cropping seasons the bottom intakes were kept approximately 0.5 m to 0.75 m above the stubble, residue or bare soil except during serious weed infestations where they were raised according to plant heights in the individual experimental plots. During the growing season, the intake assembly was raised periodically according to the h_c. The lower and upper intakes during the corn year (2006) were maintained between approximately $1.2h_c$ to $2h_c$ during the growing season, with the shortest distance between the crop surface and

bottom intakes ($\approx 1.2h_c$) occurring at peak crop height (July 27, 2006 to harvest in October, 2006). During the faba bean (2007) and spring wheat (2008) years the upper and lower intakes were maintained between approximately $1.6h_c$ to $2.2h_c$ when there was a crop present in the field. Because of the large size of the experimental plots (4 ha each) and location of the FG towers in the centre, fetch to effective observation height ratios of approximately 90:1 to 100:1 were generally maintained for all plots, in all cardinal directions throughout the study.

The two atmospheric CO_2 sample intakes mounted on each flux tower were connected separately with Dekaron tubing (6.4 mm i.d., Model 1300, Synflex, St-Gobain Performance Plastics, Wayne, New Jersey, USA) to a gradient-valve assembly. The gradient-valve assembly consisted of two 1-way solenoid valves (Model 8020, Red Hat II, ASCO valve, Brantford, Ontario, Canada) controlled to bypass flow from either of the sample heights through an in-line air-filter (Model F-Series, Swagelok®, Sonolon, Ohio, USA) containing a sintered 7 μm filter-element, followed by an in-line 50-tube Nafion® (Perma Pure Inc., New Jersey, USA) air dryer (Model PD625, Campbell Scientific Inc., Logan, Utah, USA). Gas samples were drawn from the air dryers at each site to a second solenoid-valve manifold assembly located in the instrumentation trailer with a rotary vacuum pump (Model RB0021, Busch Vacuum Technics, Boisbriand, Quebec, Canada) through LDPE tubing (4.3 mm i.d., Model P, Synflex, St-Gobain Performance Plastics, Wayne, New Jersey, USA) at a rate of 20 L min^{-1} (or 5 L min^{-1} from each site). The manifold inside the instrumentation trailer consisted of four 3-way, high-flow solenoid valves (Model A5-13257 Red Hat II, ASCO valve, Brantford, Ontario, Canada) connected with Dekaron tubing (6.4 mm i.d., Synflex 1300, St-Gobain Performance

Plastics, Wayne, New Jersey, USA) that directed sample line flow from any of the four sites selected through a 200-tube Nafion® (Perma Pure Inc., New Jersey, USA) air dryer (Model PD1000, Campbell Scientific Inc., Logan, Utah, USA) and on to the TGA. The length of sample tubing was approximately 200 m from each site gradient assembly to the site-selection manifold in the instrumentation hut. As atmospheric samples passed through two air dryers and were brought to a constant temperature before being analyzed, density corrections were not required for calculated CO_2 concentrations. Switching between the upper and lower intake heights at each site, and switching between the four site-selection valves was conducted with a 16-channel AC/DC control module (Model SDM-CD16AC, Campbell Scientific Inc., Logan, Utah, USA) driving diodes connected to the solenoid valves with relay switches. Activation signals for the sampling system were controlled by datalogger (Model CR1000, Campbell Scientific Inc., Logan, Utah, USA) software.

Switching between the upper and lower intakes occurred every 12 s for the calculation of average [CO_2] gradients. As one sample line was used for both intakes, samples immediately following valve switching between the upper and lower intakes were discarded from the calculation of gradients to allow for equilibration, and a lag due to the length of the sample line between the observation tower and TGA was accounted for with processing software (Wagner-Riddle et al., 2005). Half-hourly atmospheric surface-layer gradients of [CO_2] were calculated over the four experimental plots sequentially, obtaining approximately one average 30-minute gradient every two hours per plot. Control was introduced with the logger software to address potential time-of-day bias by measuring the plot sampled from 12:00 am to 12:30 am local time each day for a

second 30-minute period from 12:30 am to 1:00 am to advance the site-selection time-series by 30 minutes each day. This sampling sequence scenario resulted in 13 possible 30-minute gradients per day for the site sampled over entire the midnight hour, 12 possible 30-minute gradients per day for two of the remaining three plots, and 11 possible 30-minute gradients per day for the remaining site (which would be sampled for two 30-minute periods over the midnight hour the following day). Over four days the experimental design employed could obtain 48 average half-hour [CO_2] gradients per experimental plot. All raw high-frequency and processed TGA and sonic data used to calculate aerodynamic CO_2 fluxes were recorded to flash-memory cards by dataloggers (Model CR1000, Campbell Scientific Inc., Logan, Utah, USA) located at each sonic tower for the turbulence data, and inside the instrumentation trailer in the case of the TGA.

2.3.4 Supporting Environmental Measurements

A weather station was installed at the site in August 2005 and was located near the centre of the four plots in the experimental field on an undisturbed, grassed area. Air temperature and relative humidity were measured with a combined probe (Model HMP45C, Vaisala Inc., Woburn, Massachusetts, USA) mounted within a naturally-ventillated radiation shield (Model 41003-5 10-Plate Gill Radiation Shield, R.M. Young Company, Traverse City, Michigan, USA) 2 m above the ground surface. Incoming solar radiation was measured with a pyranometer (Model SP-LITE Silicon Pyranometer, Kipp & Zonen, Delft, the Netherlands), and photosynthetically-active photon flux density (PPFD) was measured with a optically-filtered quantum sensor (Model PAR LITE, Kipp & Zonen, Delft, the Netherlands), mounted at heights of 2.25 m and 2.5 m above the

ground respectively. Wind speed and wind direction were measured 3 m above the surface with a propeller anemometer (Model 05103-10 Wind Monitor, R.M. Young Company, Traverse City, Michigan, USA). The aforementioned weather station instruments were attached to a tripod stand (Model CM110 Tripod and Grounding Kit, Campbell Scientific Inc., Logan, Utah, USA). A precipitation gauge (Model T-200B Series Precipitation Gauge, Geonor Inc., Milford, Pennsylvania, USA), was installed approximately 3 m away from the main weather station tripod on an independent pedestal. A soil temperature profile with measurements at 0.02 m, 0.05 m, 0.1 m, 0.2 m, 0.5 m and 1 m beneath the surface consisting of 6 thermistors (Model 107B Soil/Water Temperature Probe, Campbell Scientific Inc., Logan, Utah, USA) was installed beneath the tripod stand of the weather station. Station pressure was measured with a barometric pressure sensor (Model 61205, R.M. Young Company, Traverse City, Michigan, USA) that was mounted within a fibreglass enclosure housing a datalogger, with the pressure port vented to the outside environment with a piece of PVC tubing. Weather station data were recorded by a programmed datalogger (Model CR1000, Campbell Scientific Inc., Logan, Utah, USA) with a scan rate of 10 s (0.1 Hz) and output in 30-minute, 60-minute and daily intervals.

2.3.5 Data Analysis

2.3.5.1 Gap-filling and Flux Partitioning Missing TGA and sonic data during periods of fieldwork (tillage, seeding, and harvest), system maintenance or mechanical malfunction, power disruptions, and low-quality calculated half-hour CO_2 fluxes needed to be gap-filled (Falge et al., 2001) to estimate seasonal and annual CO_2 budgets. The sampling layout used in the study allowed for the monitoring of the net CO_2 flux from

four plots but measurement sequencing only allowed returning to observe the same plot every 2 to 2.5 hours causing gaps in the individual CO_2 flux time series for each plot. Other significant ongoing systematic gaps that caused data removal were system maintenance and a turbulence threshold (u_* filter). A liquid nitrogen dewar cooled the laser and required re-filling twice per week. The data recorded during re-filling episodes and for the following hour were discarded from further analysis due to the influence of resulting vibrations and temperature perturbations inside the enclosure on gas concentration calculations. Other less frequent examples of system maintenance introducing gaps to the flux time series included: changing pump oil and parts, replacing the reference gas cylinder; raising sample intakes; performing gradient and timing tests; and changing air filters. After discarding data due to system maintenance and mechanical malfunctions, [CO_2] data coverage from the TGA was approximately 72 % for the duration of the three-year study. When including quality turbulence data from the sonics, data available for the calculation of net CO_2 fluxes was approximately 66 % of possible half-hours.

Initially, a minimum u_* threshold of 0.1 m s^{-1} was applied to all data based on visual inspection of the fluxes and gradients, and was similar to that imposed by other contemporary authors using the flux gradient (Griffis et al., 2004; Drewitt et al., 2009) and eddy covariance (Anthoni et al., 2004; Baker and Griffis, 2005) micrometeorological techniques in agricultural fields. In the case of our FG measurements, we observed unrealistically high positive fluxes as a result of not being able to compensate for the large measured [CO_2] gradients with an appropriate aerodynamic K value from the sonics during times of low turbulent mixing and stratification of the surface layer during both night and day periods. The overestimation of ecosystem respiration during periods of low

u_* values from our FG measurements is the opposite situation of the commonly observed underestimation of nocturnal ecosystem respiration by eddy covariance during times of inadequate turbulent mixing. An algorithm was used to determine u_* thresholds for the non-growing season and growing season separately for each of the three crop years based on nocturnal $F_{C\text{-}NEE}$ measurements. Outliers were removed (0.5 % highest and lowest values) and nighttime $F_{C\text{-}NEE}$ data were aggregated into u_* classes, consisting of bins with an equal number of points that were averaged. The u_* threshold was taken as a $F_{C\text{-}NEE}$ value that was 20 % greater than the average value from the u_* bins that were higher than 0.10 m s^{-1} for each period, and rounded to the closest 0.01 m s^{-1}. This approach resulted in u_* thresholds of: 0.15 m s^{-1} and 0.12 m s^{-1} for the corn growing season and non-growing season respectively; 0.18 and 0.12 m s^{-1} for the faba bean growing and non-growing seasons respectively; and 0.15 and 0.12 m s^{-1} for the wheat growing and non-growing seasons respectively. After application of the u_* filters, the total data coverage of acceptable measured net CO_2 fluxes utilized in this study was 48 % of possible 30-minute periods. The acceptable measured $F_{C\text{-}NEE}$ data coverage for the four individual experimental plots was approximately 12 % of possible 30-minutes periods each.

The gap-filling procedure used in this study was based on the Fluxnet-Canada Research Network (FCRN) standard protocol, which utilizes a 100-point, moving-window technique to estimate empirical relationships between temperature and respiration, and light and photosynthesis over time (Barr et al., 2004). In a recent review of gap-filling techniques, the FCRN method performed similarly to other methods utilized by the international flux community, and was among the top techniques for both daytime and nighttime gap-filling, when performance was ranked according to root mean square error (Moffat et al., 2007). Exceptions to the standard FCRN methodology made for the

present study were that air temperature was used to model respiration, no storage term was applied to net aerodynamic CO_2 fluxes (it was negligible after applying the u_* filters), and the u_* filters were applied to both daytime and nighttime data, not just nocturnal. First, small gaps in the flux time series of two hours (four 30-minute periods) or less (for example between two observations at an individual plot in this study) were filled by linear interpolation. Larger gaps were then filled by photosynthesis (Michaelis-Menton type rectangular hyperbole, dependent on PPFD) and respiration (logistic, dependent on temperature) regression parameters, whose relationships were adjusted via the moving window and time-varying parameters to account for changing environmental and phenological conditions. Gaps in the meteorological data used to fill fluxes occurred during approximately 0.5 % of possible 30-minute periods over the three years and were filled by linear interpolation for gaps of a day or less and by the mean diurnal variation of before and after neighboring periods for larger gaps.

Seasonal and annual micrometeorological CO_2-C flux budgets were estimated from summing the 30-minute gap-filled $F_{C\text{-}NEE}$ data. Crop years were defined as the period from May 1 of the year the crop was planted to April 30 the following calendar year: the corn year was May 1, 2006 to April 30, 2007, the faba bean year was May 1, 2007 to April 30, 2008, and the wheat year considered for annual C budgets was May 1, 2008 to April 30, 2009. Crops were seeded within the first three weeks of the respective year (the specific dates were aforementioned in Section 2.2). The gap-filled sums of $F_{C\text{-}NEE}$ ($\Sigma F_{C\text{-}NEE}$) were used to estimate total annual C balances of the agricultural field ($F_{C\text{-}ECOSYSTEM}$) using a system rate of change, conservation of mass (C input – C output / ∂time) approach (Olson, 1963). Considering the influence of directional forcing and

episodic disturbances concurrently (Randerson et al., 2002), $F_{C\text{-}ECOSYSTEM}$ was calculated as: $\Sigma F_{C\text{-}NEE} + F_{C\text{-}HARVEST}$ where, $F_{C\text{-}HARVEST}$ is the amount of biomass C taken from the ecosystem during harvest episodes, calculated from scale-weight, corrected for moisture content and converted to mass C content. Other C mass flux contributions from the ecosystem (eg. soil erosion, leaching of dissolved or particulate organic or inorganic C, hydrocarbons (VOCs, CH_4, CO), herbivory, fire, etc.) were not measured or estimated and are neglected from the C budgets reported but were most likely insignificant compared to the magnitudes and errors associated with $\Sigma F_{C\text{-}NEE}$ and $F_{C\text{-}HARVEST}$.

2.3.5.2 Error Analysis The relative error of the seasonal and annual $\Sigma F_{C\text{-}NEE}$ determined from this study was estimated by combining the random error of the FG measurements (δ_{random}) and an estimate of the systematic uncertainty ($\delta_{systematic}$) or biases associated with our chosen u_* filters and gap-filling procedures. The δ_{random} term was derived from estimating the relative error of the individual variables from Eq. 1 (K, $\Delta[CO_2]$, and Δz) used to calculate $F_{C\text{-}NEE}$ in a manner similar to the approach of Laubach and Kelliher (2004) for CH_4 fluxes or Phillips et al. (2007) for N_2O fluxes. The relative error in our aerodynamic K (δ_K) term was evaluated using a simultaneous two-tower, differencing approach (Hollinger and Richardson, 2005) to assess the random measurement error of the instrumentation, and uncertainty resulting from footprint heterogeneities and the stochastic nature of the turbulent transport of entities. The random error of K was estimated as the standard deviation of the absolute differences between simultaneous estimates of K from two sonic anemometer-thermometers measuring different plots and footprints. This standard deviation term was then expressed as a fractional error relative

to the mean K for specific periods of time (monthly and annually) to estimate δ_K. The random measurement error of our ability to resolve vertical [CO_2] gradients at the site ($\delta_{\Delta[CO2]}$) was estimated from the standard deviation of $\Delta[CO_2]$ during tests where the intakes were mounted at the same height (zero vertical gradient or Δz = 0 m) divided by the mean $\Delta[CO_2]$ (when Δz = 0.65 m) measured over specific periods of time (monthly and annually). The relative error of the Δz term was estimated to be approximately 0.01 m (1 cm) for each intake height measured, or 0.02 m / Δz (0.03 for the vertical separation distance of 0.65 m used in the study).

The systematic uncertainty ($\delta_{systematic}$) or bias of $\Sigma F_{C\text{-}NEE}$ associated with the u_* filters and gap-filling procedures was evaluated by performing a u_* threshold (u_{*th}) sensitivity assessment akin to that of Barford et al. (2001), Anthoni et al. (2004) or Morgenstern et al. (2004). Measured $F_{C\text{-}NEE}$ was filtered varying u_{*th} from 0 m s^{-1} to 0.45 m s^{-1} (in increments of 0.05 m s^{-1}) and used to construct separate gap-filled annual $\Sigma F_{C\text{-}NEE}$ budgets based on the accepted data. The standard deviation of the 6 CO_2-C budgets determined for each year with increasing u_{*th} from 0.1 m s^{-1} to 0.35 m s^{-1} was expressed as a fractional error relative to the annual balances calculated with a threshold of 0.1 m s^{-1} to estimate the $\delta_{systematic}$ term.

The uncertainty in $F_{C\text{-}HARVEST}$ ($\delta F_{C\text{-}HARVEST}$) was estimated from hand-clipped aboveground biomass samples taken prior to mechanical harvesting each year. Samples were taken from 6 random locations in each of the 4 experimental plot tower footprints (24 total for the site) and air-dried at 40°C. The standard error of the dry-weight of the appropriate organ(s) that were removed by mechanical harvest was determined from the hand-clipped plots and used to estimate the landscape-scale $\delta F_{C\text{-}HARVEST}$.

2.3.5.3 Relationships between Carbon Dioxide Flux and Environmental Variables

Empirical non-linear functions were used to derive relationships between $F_{C\text{-}NEE}$ and measured meteorological variables during specific periods of interest during the triennium. The common Michaelis-Menton type function, a non-linear rectangular hyperbole (Landsberg, 1977; Ruimy et al., 1995) was used for calculating light-response curve regressions, while nocturnal and non-growing season $F_{C\text{-}NEE}$ data (= ecosystem respiration) were fit to exponential regressions (Lloyd and Taylor, 1994; Fang and Moncrieff, 2001; Tjoelker et al., 2001) with air temperature (T_{air}). The regressions were initially performed using the 30-minute flux and meteorological data, but due to the noise and variation inherent to the micrometeorological measurements and environmental conditions, stronger regressions (as indicated by higher r^2 and lower root mean square values) with statistically similar parameter estimates were obtained by aggregating and averaging the $F_{C\text{-}NEE}$ and the driving meteorological (PPFD and T_{air}) data in bins. Mean diurnal trends (bin-averages by time of day) of $F_{C\text{-}NEE}$ and PPFD were fitted during the monthly periods of peak CO_2 uptake each growing season. Inclusion of T_{air} in the model function to address temperature dependency of the light-response curves did not significantly improve the fitted relationships (according to the r^2 and root mean square values), so the simpler model (dependence on PPFD only) where the y-intercept of the regression represents the average ecosystem respiration rate for the period (Ruimy et al., 1995), was retained and is reported. Nighttime respiration was fit in 2°C bins of air-temperature with an exponential Q_{10} function during the monthly periods of peak daytime CO_2 uptake each crop year. During the non-growing season, post-harvest autumn $F_{C\text{-}NEE}$ data from each year was fit in 2°C bins of air-temperature with an exponential Q_{10} function while the soil temperature at the 0.2 m depth remained > 0°C and before the

onset of snow cover. Spring $F_{C\text{-}NEE}$ data from each year was fit in 2°C bins of air-temperature with an exponential Q_{10} function after the soil temperature at 0.02 m surpassed > 0°C. The exponential respiration-temperature relationships were also fit to the Lloyd and Taylor (1994) regression model, with both the temperature sensitivity parameter (E_0) fixed at 308.56 K and allowed to float. While a parameterized E_0 provided stronger regressions with the $F_{C\text{-}NEE}$ data than using the universal value (as previously found by Ruppert et al., 2006 *and references therein*) the fitted parameter values varied substantially between periods and years, with no clear pattern and broad confidence intervals. Furthermore, the Lloyd and Taylor model with fitted E_0 did not improve the strength of the regressions compared to the use of the Q_{10} model, so the latter was utilized and is reported for conceptual simplicity. All non-linear regressions for the $F_{C\text{-}NEE}$-light and temperature response relationships were performed with the *nlinfit* function from MATLAB® (Verson 7.6.0, Statistics Toolbox 6.2 (R2008a), The Mathworks Inc., Natick, Massachusetts, USA) with no bounds placed on the ordinary least-squares (Gauss-Newton with the Levenberg-Marquardt modification) parameter (P_{max}, α, R; R_{10} and Q_{10}) estimates. The 95 % confidence intervals for the parameter estimates were calculated from the residuals and estimated coefficient covariance matrix using the *nlparci* function.

2.4 Results

2.4.1 Environmental Conditions

The average air temperature at the site during 2006 was higher than the 30-year normal for the area, while the air temperature in 2007 was lower and closer to normal and 2008 was a cooler year than the long-term average (Table 2.1). The growing-degree-days (GDD) above 10°C followed the same decreasing trend as the average air temperatures for 2006, 2007 and 2008. The GDD in 2006 was above average, 2007 was near average and 2008 was lower than normal (Table 2.1). The average air temperatures during June through the end of August were 19.6°C, 18.7°C, and 17.7°C, for 2006, 2007, and 2008, respectively. Total precipitation was 57 % of the normal annual amount in 2006, close to normal in 2007, and above average during 2008 (Table 2.1). During the 2006 corn growing season (seeding to harvest), the site only received 150 mm of precipitation, less than half as much as either the 2007 faba or 2008 spring wheat crops, which received 390 mm and 365 mm, over growing season periods that were approximately 6 and 3 weeks shorter in duration, respectively.

Table 2.1 Climatic conditions during the three study years measured by the onsite weather station. The 30-year (1971 - 2000) climate normals and standard deviations are for Winnipeg, Manitoba (Environment Canada, 2010).

	2006	2007	2008	30 year normal
Mean Air Temperature (°C)	4.7	2.9	1.4	2.6 ± 1.3°C (S.D.)
Growing Degree Days > 10°C	1103	978	798	1006
Precipitation (mm)	292	559	727	514

2.4.2 Seasonal and Annual Net CO_2 Exchange

The cumulative CO_2 flux ($\Sigma F_{C\text{-}NEE}$) at the site over the triennium shows both considerable intra- and inter-annual variability (Figure 2.1). While the four experimental plots in the field had similar $\Sigma F_{C\text{-}NEE}$ during late spring and early summer 2006, they began to diverge as the corn year progressed, exhibiting from 60 % to 90 % variability mid-summer through autumn. Plot to plot variability was the greatest during the faba bean year (May 1, 2007 to April 30, 2008), where individual plots at the site differed in gap-filled annual $\Sigma F_{C\text{-}NEE}$ by over 100 %. The four plots varied from C neutral to being significant atmospheric CO_2 sinks (≅ -2600 kg C ha^{-1}) at the end of the second year of the tillage intensity comparison study (April 30, 2008; Figure 2.1). Variability in $\Sigma F_{C\text{-}NEE}$ was much lower during the spring wheat crop year (May 1, 2008 to May 1, 2009) with individual plots at the site differing by about 30 to 40 % (Figure 2.1).

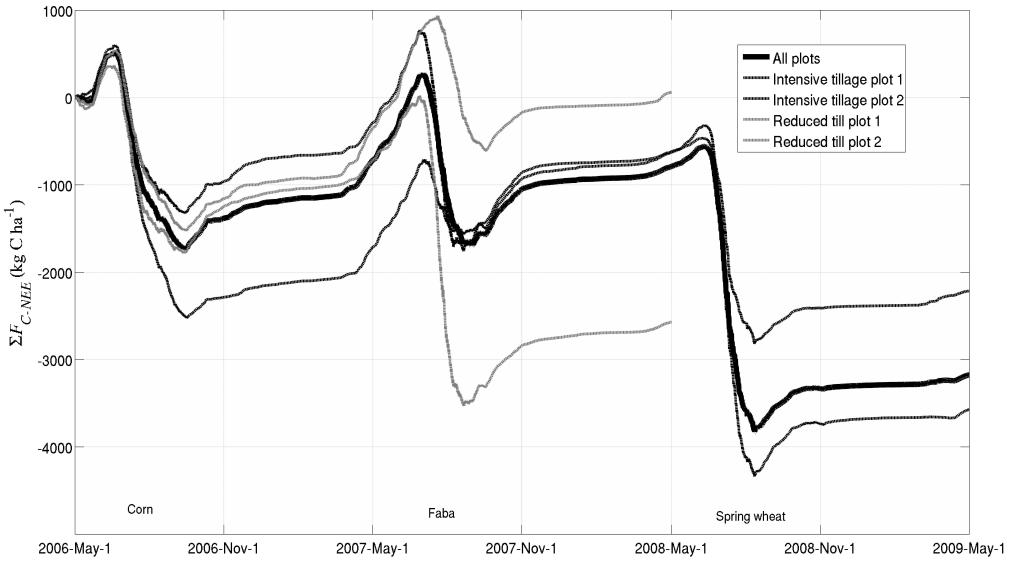

Figure 2.1 Time series of the cumulative, gap-filled net CO_2 flux ($\Sigma F_{C\text{-}NEE}$) at the site. The solid black line is the cumulative net CO_2 flux resulting from combining all observations at the site. Dotted grey lines represent gap-filling of measurements from individual reduced tillage (RT) plots at the site; dotted black lines represent gap-filling of measurements from individual intensive tillage (IT) plots at the site.

A clear distinction in $\Sigma F_{C\text{-}NEE}$ between the intensive tillage (IT) and reduced tillage (RT) treatments could not be made over the two year transition period. Greater variability was observed between the two IT plots than between the two RT plots for the corn year (2006), and the opposite situation happened during the faba bean year in 2007 (Figure 2.1). When combining all IT and all RT observations into two separate classes and gap-filling, the two treatments vary by approximately 60 % for both 2006 and 2007, but the trend in $\Sigma F_{C\text{-}NEE}$ is opposite between the years. When measurements from the two IT plots and the two RT plots were combined in two separate classes and gap-filled accordingly, the IT plots were calculated to be a more significant sink ($\Sigma F_{C\text{-}NEE}$ = -1180 ± 280 kg C ha^{-1} yr^{-1}) than the RT plots ($\Sigma F_{C\text{-}NEE}$ = -400 ± 100 kg C ha^{-1} yr^{-1}) in 2006; while the RT plots were a sink for atmospheric CO_2 ($\Sigma F_{C\text{-}NEE}$ = -570 ± 300 kg C ha^{-1} yr^{-1}) and the IT plots a source ($\Sigma F_{C\text{-}NEE}$ = 380 ± 130 kg C ha^{-1} yr^{-1}) in 2007. Over the two-year corn-faba bean rotation, the treatments had similar cumulative NEE values (IT $\Sigma F_{C\text{-}NEE}$ = -700 ± 290 kg C ha^{-1}; RT $\Sigma F_{C\text{-}NEE}$ = -970 ± 410 kg C ha^{-1}).

For the entire triennium considered and gap-filling all available, high-quality measured fluxes from the plots under annual production, the crop-soil system at the site was a net biological CO_2 sink of approximately 3,100 kg C ha^{-1} (Figure 2.1; Table 2.2). The estimated C sink of the site was largely driven by the 2008 growing-season, as net CO_2 uptake was approximately twice as great during the spring wheat crop year compared to the corn or faba bean years (Figure 2.1; Table 2.2).

Table 2.2 Carbon balance components for the three crop years (May 1 to April 30) of the study: gap-filled cumulative net CO_2 ecosystem exchange ($\Sigma F_{C\text{-}NEE}$), C removed by harvest ($F_{C\text{-}HARVEST}$), and C balance ($F_{C\text{-}ECOSYSTEM} = \Sigma F_{C\text{-}NEE} + F_{C\text{-}HARVEST}$). Negative fluxes represent ecosystem C gain, positive fluxes are loss. Error values given are ± 1 S.E.

	2006	2007	2008	Three years
$\Sigma F_{C\text{-}NEE}$, kg C ha^{-1}	-720 ± 170	70 ± 30	-2,400 ± 430	-3,050 ± 1400
$F_{C\text{-}HARVEST}$, kg C ha^{-1}	1,230 ± 90	3,070 ± 90	1920 ± 250	6,220 ± 930
$F_{C\text{-}ECOSYSTEM}$, kg C ha^{-1}	510 ± 130	3140 ± 1100	-480 ± 110	3,170 ± 1520

The time series was split into growing season (= seeding to harvest) and non-growing season (= harvest to subsequent seeding) periods. Although 30-minute rates of $F_{C\text{-}NEE}$ were much lower during the non-growing seasons, because it is such an extended period of time relative to the respective growing seasons, $\Sigma F_{C\text{-}NEE}$ values integrated over the non-cropped period were substantial components of the annual C budgets. For example following corn harvest in 2006 and faba bean harvest in 2007, the estimated net CO_2 released by respiration back to the atmosphere over the following fall, winter and spring offset the net uptake during the growing season by approximately 50 % and 80 %, respectively. Following harvest in 2008, a much smaller fraction (< 10 %) of the equivalent CO_2 taken up by the spring wheat crop was respired prior to seeding in 2009.

The corn crop yielded 1,230 kg C ha^{-1} of grain in 2006; 3,070 kg C ha^{-1} of faba bean was harvested for silage in 2007; and 1,180 kg C of grain and 740 kg C ha^{-1} of straw bales from the spring wheat in 2008. This resulted in the corn and faba bean years losing 510 kg and 3,140 kg of C ha^{-1} from the ecosystem respectively, while the spring wheat year gained 480 kg C ha^{-1} (Table 2.2). Therefore, over the three-year study, this agroecosystem was a net C source of approximately 3,200 kg ha^{-1}.

2.4.3 Error Analysis

On an annual basis, the random error of the FG measurements (δ_{random}) made during the course of the experiment was 14 %, 17 % and 17 % for the corn, faba bean, and spring wheat crop years, respectively. The largest source of δ_{random} over a year was from δ_K (average for three years ≈ 12 %) compared to $\delta_{\Delta[CO2]}$ (average for three years ≈ 10 %), while $\delta_{\Delta z}$ was negligible by comparison (constant 3 %). When δ_{random} was assessed by month, both δ_K and $\delta_{\Delta[CO2]}$ exhibited a seasonal pattern of larger uncertainty during the winter non-growing-season than for the growing-season (Figure 2.2). During the winter months, $\delta_{\Delta[CO2]}$ was often the largest contributor to the δ_{random} term, and was as high as 45 % in February 2008, while the largest monthly δ_K calculated was 22 % for February 2007 (Figure 2.2).

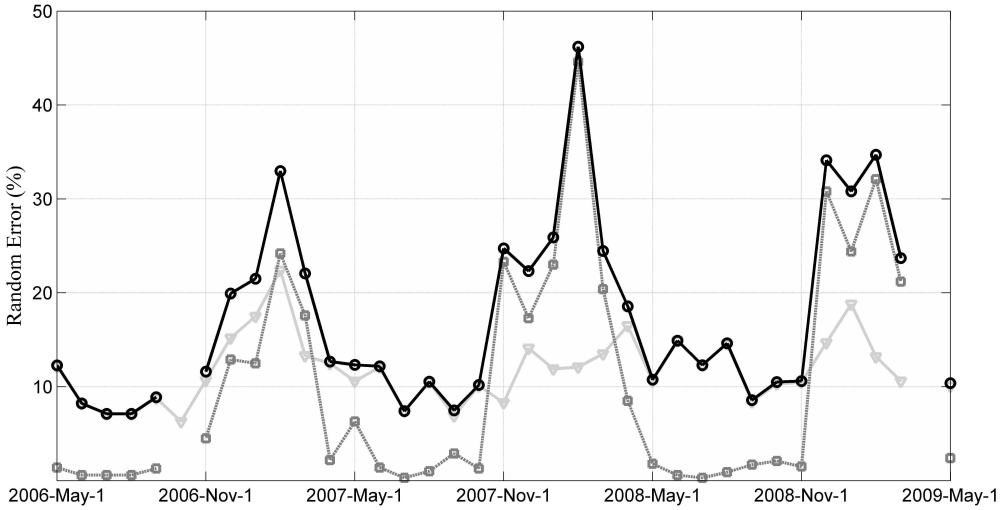

Figure 2.2 Monthly estimates of the random error (δ_{random}) of flux gradient measurements made during the study. The composite random error is represented by open, black circles, the random error of K (δ_K) by open, light-gray triangles, and random error of $\Delta[CO_2]$ ($\delta_{\Delta[CO2]}$) by open, dark-gray squares.

The systematic error of our annual ecosystem C budgets that was related to our data filtering, flux partitioning and gap-filling scheme ($\delta_{systematic}$) was estimated to be 20 %, 30 % and 5 % for the corn, faba bean, and spring wheat crop years, respectively. The standard deviations of the separate annual C balances constructed from the six u_{*th} classes each year to estimate $\delta_{systematic}$ were approximately 150, 70 and 100 kg C ha^{-1} for the corn, faba bean, and spring wheat years respectively.

By combining δ_{random} and $\delta_{systematic}$ in quadrature, the relative composite error of $\Sigma F_{C\text{-}NEE}$ was estimated to be 24 %, 35 %, and 18 % for the three respective annual C budgets. The standard error of $F_{C\text{-}HARVEST}$ was estimated to be 7 % for the grain corn harvested in 2006, 3 % for the faba bean silage in 2007, and 13 % for the spring wheat grain and bales in 2008. Thus, the estimated relative error in the $F_{C\text{-}ECOSYSTEM}$ values reported herein is 25 %, 35 %, and 22 % for the three respective crop years, or 48 % for the entire triennium C balance (Table 2.2).

2.4.4 Relationships between Carbon Dioxide Flux and Environmental Variables

At peak growing season crop CO_2 uptake, the spring wheat had a greater photosynthetic capacity (P_{max} = 67 ± 20 µmol m^{-2} s^{-1} (± 95% C.I.); r^2 = 0.98) than the corn (P_{max} = 31 ± 3 µmol m^{-2} s^{-1} (± 95% C.I.); r^2 = 0.99) or faba bean (P_{max} = 37 ± 8 µmol m^{-2} s^{-1} (± 95% C.I.); r^2 = 0.96) crops (Figure 2.3). The apparent quantum yield (α, the initial slope of light response curve) of the crops during periods of peak photosynthetic CO_2 uptake was similar during the three years, varying from 0.034 to 0.041 mol CO_2 mol photon^{-1}. The average dark respiration rate (the y-intercept of the light-response curve) during peak growing season was significantly higher for the faba bean (R = 6.5 ± 0.9

µmol m^{-2} s^{-1}) than for the corn (R = 4.5 ± 0.5 µmol m^{-2} s^{-1}) crop, and statistically similar to the spring wheat (R = 5.0 ± 0.9 µmol m^{-2} s^{-1}) year (Figure 2.3).

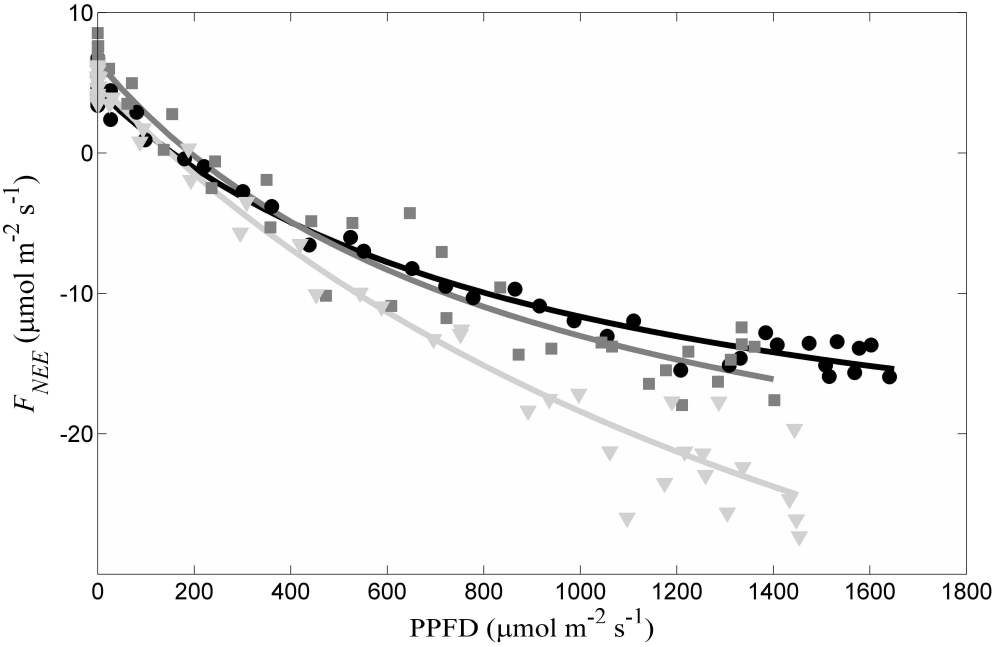

Figure 2.3 Mean diurnal light-response curves of net CO_2 flux during the periods of peak uptake for each of the three study years. Each point represents an ensemble of 30-minute mean values binned by time of day ($8 \leq n \leq 30$). Corn (from June 25 to July 25, 2006) is represented by black circles, faba bean (from July 1 to August 1, 2007) by dark-grey squares and spring wheat (from June 23 to July 23, 2008) by light-grey triangles. Solid-lines (black for corn, dark-grey for faba bean and light-grey for spring wheat) are fitted non-linear regression curves.

The relationships between nocturnal respiration rates and air temperature during peak growing season were statistically similar for the corn (R_{10} = 3.7 ± 1.1 µmol m^{-2} s^{-1}; Q_{10} = 1.3 ± 0.4 (± 95% C.I.); r^2 = 0.27), faba bean (R_{10} = 4.1 ± 2.2 µmol m^{-2} s^{-1}; Q_{10} = 1.8 ± 0.6 (± 95% C.I.); r^2 = 0.52), and spring wheat (R_{10} = 3.5 ± 1.4 µmol m^{-2} s^{-1}; Q_{10} = 1.7 ± 1.0 (± 95% C.I.); r^2 = 0.59) crops (Figure 2.4). Although it was not possible to significantly distinguish between the R_{10} and Q_{10} parameter estimates for the different crops for the 10°C to 20°C temperature range, a general trend of the faba bean canopy

and soil system having greater thermal sensitivity and higher respiration rates at a given temperature than the corn crop appears to be present in the data, particularly during warm summer nights that occurred in 2006 and 2007. Using a higher reference temperature in the Q_{10} model that is perhaps better suited to the range of air temperature bins being compared, such as 20°C instead of 10°C (Figure 2.4), yields a statistically higher respiration rate for the faba bean (R_{20} = 7.5 ± 1.5 µmol m^{-2} s^{-1}) than corn (R_{20} = 4.8 ± 0.7 µmol m^{-2} s^{-1}) crop. For the three 2°C air temperature bins greater than 20°C, the faba bean year had higher respiration rates (according to the standard errors) than the corn crop at peak growing season. For the 25°C air-temperature bin, the mean nocturnal respiration rate was approximately 7 µmol m^{-2} s^{-1} greater during the faba bean (12.0 ± 3.0 (S.E.) µmol m^{-2} s^{-1}) year than the corn (4.7 ± 0.4 (S.E.) µmol m^{-2} s^{-1}) during peak season. There was a much lower range of nocturnal temperatures observed in 2008 (five 2°C air-temperature bins between 10°C and 20°C) making direct comparison at higher temperatures between the spring wheat crop system and the previous two growing seasons impossible.

Regressions between $F_{C\text{-}NEE}$ and air temperature during the non-growing season indicated greater thermal sensitivity and higher respiration rates at the 10°C reference temperature for the fallow period following faba bean harvest (R_{10} = 1.2 ± 0.1 µmol m^{-2} s^{-1}; Q_{10} = 2.9 ± 0.5 (± 95% C.I.); r^2 = 0.96), than for the autumn and early winter period subsequent to corn (R_{10} = 0.9 ± 0.2 µmol m^{-2} s^{-1}; Q_{10} = 1.8 ± 0.6 (± 95% C.I.); r^2 = 0.59) and spring wheat (R_{10} = 0.7 ± 0.2 µmol m^{-2} s^{-1}; Q_{10} = 1.3 ± 0.3 (± 95% C.I.); r^2 = 0.36) harvest (Figure 2.5). However, respiration rates were higher during the non-growing season of spring 2007, following the corn harvest in fall 2006 and prior to the seeding of

faba bean (R_{10} = 1.5 ± 0.2 µmol m^{-2} s^{-1}, Q_{10} = 1.3 ± 0.3 (± 95% C.I.), r^2 = 0.45), than for spring 2008 following faba bean harvest in fall 2007 and prior to planting spring wheat (R_{10} = 0.5 ± 0.1 µmol m^{-2} s^{-1}, Q_{10} = 1.8 ± 0.3 (± 95% C.I.), r^2 = 0.91; Figure 2.6). Unfortunately, due to local flooding of the Red River, the site was temporarily decommissioned for emergency preparations for the majority of April 2009, which drastically limited the amount of data available for analysis for the spring non-growing season fallow period following the wheat harvest in 2008 and prior to seeding in 2009.

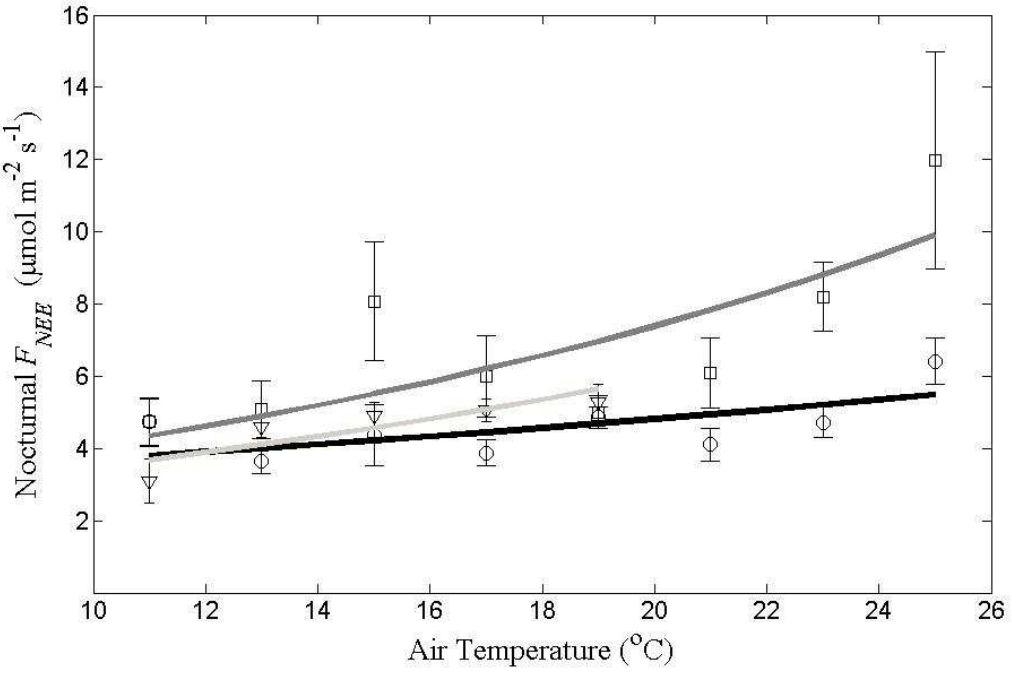

Figure 2.4 Bin-averaged (2°C bins) temperature-response curves for nocturnal net CO_2 flux during the periods of peak uptake for each of the three study years. Corn (from June 25 to July 25, 2006) is represented by black circles, faba bean (from July 1 to August 1, 2007) by dark-grey squares and spring wheat (from June 23 to July 23, 2008) by light-grey triangles. Error bars represent standard error for each bin average ($3 \leq n \leq 112$). Solid-lines (black for corn, dark-grey for faba bean and light-grey for spring wheat) are fitted non-linear regression curves (Q10 model).

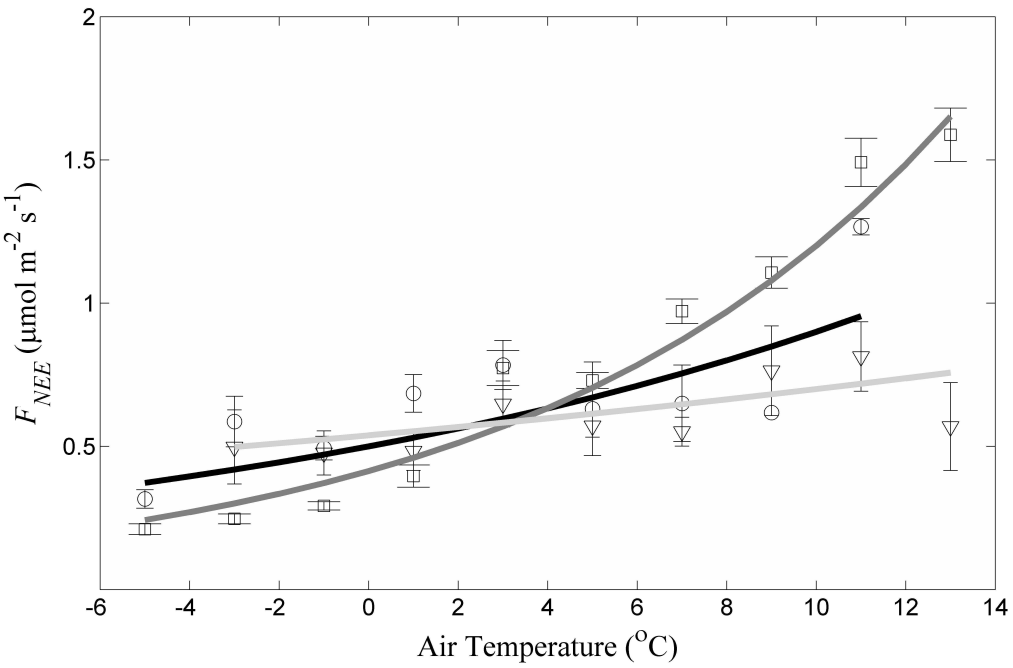

Figure 2.5 Bin-averaged (2°C bins) temperature-response curves for net CO_2 flux during the fall non-growing season periods following harvest (while T_{soil} at 0.2 m remained > 0°C) for each of the three study years. Post corn harvest is represented by black circles, post faba bean by dark-grey squares and post spring wheat harvest by light-grey triangles. Error bars represent standard error for each binned average ($10 \leq n \leq 291$). Solid-lines (black for corn, dark-grey for faba bean and light-grey for spring wheat) are fitted non-linear regression curves (Q10 model).

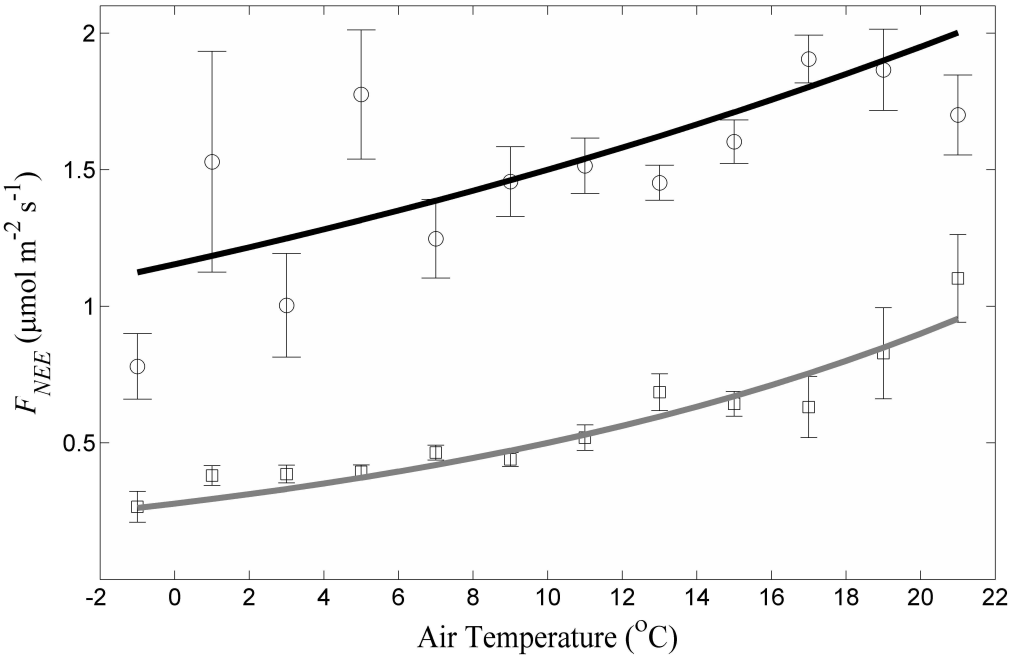

Figure 2.6 Bin-averaged (2°C bins) temperature-response curves for net CO_2 flux during the spring non-growing season periods following harvest and prior to subsequent planting (when T_{soil} at 0.02 m was > 0°C). Post-corn is represented by black circles and post-faba bean by dark-grey squares. There was a lack of available data with an adequate temperature range in the spring period post-wheat harvest and no relationship with temperature could be found (data not shown). Error bars represent standard error for each binned average ($7 \leq n \leq 151$). Solid-lines (black for corn and dark-grey for faba bean) are fitted non-linear regression curves (Q10 model).

2.5 Discussion

2.5.1 Tillage Comparison

In this southern Manitoba study, no difference in the cumulative NEE of intensively tilled (IT) vs. reduced tillage (RT) agricultural plots was detectable over a two-year management transition period, and neither ecosystem was a net C sink when accounting for biomass removal at harvest, similar to previous micrometeorological

studies at agricultural sites conducted in Minnesota (Baker and Griffis, 2005) and Nebraska (Verma et al., 2005; Grant et al., 2007). Over the two-year corn-faba bean rotation in the present study, the treatments had similar cumulative NEE values (IT $\Sigma F_{C\text{-}NEE}$ = -700 ± 290 kg C ha^{-1}; RT $\Sigma F_{C\text{-}NEE}$ = -970 ± 410 kg C ha^{-1}). On a silt loam soil in southern Minnesota, the two-year cumulative NEE for a corn-soybean rotation was approximately –3760 and –3500 kg C ha^{-1}, for a conventional (tilled) field and an alternative management (strip-tillage and inclusion of cover crop) field, respectively (Baker and Griffis, 2005). The amount of C removed from the ecosystems during harvest episodes in Baker and Griffis (2005) was approximately 1500 kg ha^{-1} of soybeans and 3000 kg ha^{-1} of corn grain or ≈4500 kg C ha^{-1} total, resulting in both management treatments being net sources of C of approximately 900 kg C ha^{-1} for the two years. The corn in our study yielded approximately 1200 kg ha^{-1}, about 1/3 of the yield in the southern Minnesota study, which is similar to the difference in cumulative NEE between the two studies when considering the maize years alone. However, we harvested the majority of the aboveground biomass of the faba bean grown (≈ 3100 kg C ha^{-1}) for animal feed silage, causing our IT and RT management plots to be net C sources of approximately 3500 kg C ha^{-1} over the two-year comparison. Although the total biological C removed in harvests was similar between the Manitoba and Minnesota studies, the lower cumulative NEE (less negative) in the former resulted in the agroecosystem being a C source that was approximately three times greater than the latter.

Perhaps the tillage comparison and soil characteristics of the two treatments in the present study had not diverged to the extent they would have in a more mature no-till

ecosystem. Measurements of NEE and grain C accounting from a mature (>15 years) no-till corn-soybean rotation in Illinois indicate the system may be a small net C sink (300 kg C ha^{-1}) when calculated over several years (Hollinger et al., 2006). In contrast, during the first three years of transitioning to no-till and best management practices, Verma et al. (2005) reported that a rainfed corn-soybean rotation was C neutral, irrigated continuous maize was somewhere between being C neutral to a small source, and that an irrigated corn-soybean rotation was a source of 700 to 1000 kg C ha^{-1} yr^{-1} on a silty clay loam in eastern Nebraska. However, there was no comparative tilled or control plots utilized in the studies from Illinois and Nebraska. Although one must recognize that the short-term effects during the transition to conservation tillage management are more subtle than for a mature no-till system, the inability to detect a tillage treatment effect appears to be the result of inter-annual and within-treatment variability being greater than between-treatment variability, most likely caused by landscape heterogeneity and differential crop performance.

2.5.2 Variability and Uncertainty

The large inter-plot or landscape-scale variability of net CO_2 fluxes within a common, seemingly flat and uniform agricultural field was a surprising finding from this study. For example, the cumulative difference between our two reduced-tillage plots by the end of the two years was greater than that between any other treatments compared (gray dotted lines, Figure 2.1), which was amplified during the faba bean year (2007). When combining all IT and all RT observations into two separate classes and gap-filling, the two treatments varied by approximately 60 % in $\Sigma F_{C\text{-}NEE}$ for both 2006 and 2007, but

the trend in the magnitude and relative direction of the flux comparison was opposite between the years (results presented in Section 2.4.2).

The observed variation in $\Sigma F_{C\text{-}NEE}$ among individual plots or within the two different tillage treatments at the site may have been partially due to higher uncertainty because of the lower number of actual flux measurements (n ≈ 25 % of total when gap-filling the individual plots and ≈ 50 % of total when gap-filling the two tillage treatment classes, compared to utilizing all observations at the site) used to derive annual C budgets. Previous work indicates that the uncertainty in gap-filled annual C budgets based on eddy covariance measurements increases with decreasing amounts of actual flux data coverage used in deriving budgets (Falge et al., 2001; Moffat et al., 2007). While the total percentage of gaps in the individual plot or tillage treatment annual time series is high, the gaps are small (many are filled by linear interpolation) and relatively uniform. Comparing running means from the individual plots for various durations (from single days, 4-day, up to a week) and summation of the actual, filtered FG measurements with no gap-filling revealed similar trends of between plot or within-treatment variability (*data not shown*), so a bias due to low data coverage was not the sole contributor to the large observed variation between the individual plots that is apparent in Figure 2.1.

The variation between the individual plot time series relative to the combination of all observations (Figure 2.1) was reflected in the independent estimations of random error for the three years, with the faba bean crop having the greatest uncertainty, and the spring wheat year having the lowest. The greater inter-plot variability and estimation of relative error during the faba bean year was likely the result of a wet spring and early summer in 2007, which lead to saturation of the soil at the site, causing delay and

suppression of plant germination and emergence on the poorly drained areas of the field. Certain weeds (such as *Rumex* sp.) were able to grow in the anoxic conditions of the poorly performing areas of the landscape. Although such weeds competed with the crop, they also fix C through photosynthesis which is reflected in $\Sigma F_{C\text{-}NEE}$. The lower variation in 2008 may be due to the spring wheat plots being more uniform in emergence and growth that year, and a larger cumulative CO_2 uptake than the previous two years.

Over annual cycles of $\Sigma F_{C\text{-}NEE}$, the systematic uncertainty ($\delta_{systematic}$) related to applying the u_* threshold and gap-filling missing or low-quality data was higher than measurement δ_{random} during the corn and faba years, but lower than the estimated δ_{random} during the spring wheat year. The difference in estimated $\delta_{systematic}$ between the faba bean and spring wheat years for example, reflects the overall magnitudes of the calculated annual $F_{C\text{-}NEE}$ budgets, with the faba bean year being essentially C neutral ($\Sigma F_{C\text{-}NEE} \approx 0$) and the spring wheat being a significant C sink (Table 2.2), resulting in higher and lower relative fractional errors, respectively.

The magnitude of the random error of the FG measurements made during this study show a seasonal trend (Figure 2.2). The mean K and $\Delta[CO_2]$ values were very low during the winter months and this made robust measurements more challenging. Our ability to estimate K in the Manitoba winter was likely hampered by cold temperatures, snow-pack that can be smooth or drifting, and low u_* values when the surface is smooth. Our ability to resolve vertical CO_2 gradients during winter months was challenged by very low air and soil temperatures and the resultant influence on ecosystem respiration, making low average $\Delta[CO_2]$ values more difficult to resolve.

2.5.3 Crop Photosynthesis and Ecosystem Respiration

The light-response parameters (P_{max}, α, R) estimated from the fitted non-linear regressions for the crops grown in this study were within the range reported for other C_3 and C_4 canopies (e.g. Ruimy et al., 1995). At peak growing season, the spring wheat had a significantly higher photosynthetic capacity, but similar respiration rates as the two previous crops grown (Section 2.4.4; Figure 2.3; Figure 2.4). However, cooler temperatures and moist conditions during the summer of 2008 likely caused a lower cumulative ecosystem respiration for the spring wheat crop compared to the previous two years. Interestingly, the spring wheat performed significantly better and the faba bean crop performed statistically similar to the corn canopy according to the light-response relationships at peak growing season. In the broad sense this may be a reflection of the difference between the relative adaptation and growth of C_3 vs. C_4 plants in Manitoba's climate and short summers. In the context of the present study, however, it is clear that the corn was likely moisture limited as well, as the crop received less than half the amount of precipitation as either of the subsequent growing seasons, which periodically had excessive soil moisture. Although leaf area index was not monitored in the present study, the wide spacing of the corn rows (0.9 m) and low biomass production relative to the spring wheat crop, would indicate that the wheat canopy had a much higher density of photosynthetically-active tissue per unit ground area which could also lead to higher exchange rates of CO_2 per hectare (Baldocchi, 1994).

While $\Sigma F_{C\text{-}NEE}$ for the corn and wheat years in the present study indicated net CO_2 uptake, the faba bean crop year was nearly C neutral to being a slight source of CO_2 to the atmosphere (Table 2.2). This was mainly the result of higher respiration rates and

cumulative CO_2 release during both the growing and fall non-growing season compared to the previous or subsequent years. Although the faba bean crop exhibited the highest amount of apparent landscape scale variability, the photosynthetic parameter estimates during the peak growing stage were comparable to the corn canopy the previous summer. However, the apparent dark respiration rate from the light-response function was about 2 µmol CO_2 m^{-2} s^{-1} higher for the faba bean than for the corn canopy (Section 2.4.4), and nocturnal respiration rates were from 4 to 7 µmol m^{-2} s^{-1} higher when air temperatures were greater than 20°C (Figure 2.4). The greater rates of ecosystem respiration during the 2007 growing season (faba bean) relative to the 2006 (corn) growing season may be partially attributable to both legume physiology and soil biochemical conditions. There is a biological C cost associated with symbiotic N fixation, nodule growth, and maintenance (Amthor, 1989; 2001) that could cause higher rates of respiration from legume crop canopies compared to non-leguminous counterparts, which may have contributed to the difference observed in the present study. As well, there was a greater availability of recent plant-derived C within the soil matrix and on the surface in 2007 from the previous corn growing season, a crop that had been preceded by a summerfallow[1] year in 2005. Lastly, inadequate moisture may have limited growth and associated plant and soil respiration during 2006, whereas in 2007 it was not a limiting factor, although excessive wetness may have been at times.

During the fall non-growing season period following faba bean harvest, the agroecosystem had greater respiration rates (Figure 2.5), and significantly higher R_{10} and Q_{10} values (Section 2.4.4) than the autumn periods following corn and wheat harvest. However, during the spring non-growing seasons, the period following corn harvest and prior to the seeding of the faba bean crop in 2007 had a higher basal ecosystem

respiration rate (R_{10}) than the spring 2008 period preceding the seeding of spring wheat (Figure 2.6). Interestingly, the cumulative net CO_2 emissions during the non-growing seasons following the corn and faba bean harvests were similar despite the former being harvested as grain (≈ 1,200 kg C ha^{-1}), and the latter being harvested for silage (≈ 3,100 kg C ha^{-1}) leaving a substantially different amount of aboveground litter behind each year. It is likely that the large amount of corn residue left behind in fall 2006 carried over and influenced respiration rates during the 2007 faba bean year, both during the growing season and the non-cropping season. Furthermore, the faba bean residue (belowground autotrophic and heterotrophic components, and aboveground short stubble and harvest waste), would have a C:N ratio in the range of 15 to 30, about 1/3 of what would be expected of the corn stover, which may have lead to higher rates of decomposition in the ecosystem in the fall of 2007. As well, a post-harvest herbicide application occurred 10 days following the faba bean cutting (details in Section 2.3.2) to deal with a fairly substantial weed infestation and crop re-growth in the fall (weed and volunteer biomass C ≈ 400 kg ha^{-1}) which ceased photosynthesis and may have increased ecosystem respiration rates by providing a labile C source following plant senescence and decomposition. Both glyphosate alone and commercial formulations have been shown to increase soil respiration, although the mechanism is not completely clear, the herbicide may provide an additional C and/or other nutrient (eg. N or P) source(s) to soil microorganism communities (Carlisle and Trevors, 1986). Another factor contributing to the difference in $\Sigma F_{C\text{-}NEE}$ between the autumn post-corn and post-faba respiration rates is the length of integration, with the faba being harvested approximately 6 weeks earlier than the corn crop in 2006, extending the fallow period considered by that much. As well,

the average air temperature during the non-growing season following the faba bean crop (6.9°C) was greater than that for the period following corn (4.5°C) and spring wheat harvest (3.5°C). The length of integration for $\Sigma F_{C\text{-}NEE}$ during the non-growing season after the spring wheat crop was intermediate between the faba (approximately 3 weeks shorter) and corn (approximately 3 weeks longer). Rates of respiration were lower than following faba bean (Figure 2.5) and cumulative respiration was low due to low air temperatures during the spring wheat non-growing season compared to the previous two. The wheat crop was both combined for grain and baled for straw, leaving very little aboveground residue or stubble behind. The spring wheat litter left behind in the system (mostly belowground biomass) would be expected to have a much higher C:N ratio than the corn stover or faba bean residue, which may have further retarded decomposition and soil respiration.

2.5.4 Carbon Sequestration Potential

For the entire triennium considered and gap-filling all available, high-quality measured fluxes from the plots under annual production, the crop canopy-soil system at the site was a net CO_2 sink of -3,100 ± 1400 kg C ha^{-1} ($\Sigma F_{C\text{-}NEE}$: Figure 2.1; Table 2.2). The magnitude and direction of $\Sigma F_{C\text{-}NEE}$ was largely driven by the 2008 C balance, as net uptake was twice as great during the spring wheat crop year compared to the corn (2006), while the faba bean year (2007) was a small net source of CO_2 to the atmosphere according to $\Sigma F_{C\text{-}NEE}$. When grain and other standing biomass taken from the field ($F_{C\text{-}HARVEST}$) is accounted for in the ecosystem C balance ($F_{C\text{-}ECOSYSTEM} = \Sigma F_{C\text{-}NEE} + F_{C\text{-}HARVEST}$), the corn and faba bean crops were net C sources of approximately 500 and 3,100

kg ha^{-1} respectively, while the spring wheat crop year was a small net C sink (Table 2.2). The agroecosystem was a net source of CO_2 of approximately 3,200 kg C ha^{-1} for the three years reported (Table 2.2), corresponding to an annualized rate of loss of approximately 1 Mg C ha^{-1} yr^{-1}.

The annual magnitudes of $\Sigma F_{C\text{-}NEE}$ and $F_{C\text{-}HARVEST}$ in the present study are comparable to other annual micrometeorological CO_2 flux studies conducted at agricultural systems in the mid-western USA and Germany. Studies investigating the annual C balance of corn-soybean rotations showed rates of both $\Sigma F_{C\text{-}NEE}$ and $F_{C\text{-}HARVEST}$ during corn years that were approximately three times greater in southern Minnesota (Baker and Griffis, 2005), and four to five times greater in eastern Nebraska (Verma et al., 2005) and Illinois (Hollinger et al., 2006) than in the present study. The most significant reason for the differences in annual corn $\Sigma F_{C\text{-}NEE}$ and $F_{C\text{-}HARVEST}$ is regional climatic, with the Manitoba site being approximately 5° of latitude north of the Minnesota site and 9° north of the Illinois and Nebraska sites, with an average air temperature that is 4°C and 7°C cooler respectively, and a significantly lower accumulation of growing degree days or heat units and incident solar radiation. However, during the soybean phase of the rotation, all three U.S. studies had years where $\Sigma F_{C\text{-}NEE}$ was positive, indicating the system was a net CO_2 source before accounting for harvest during those legume years. Verma et al. (2005) partially attributed the net C loss during soybean years to litter from the previous maize crop, a situation analogous to what likely happened in the present study during the faba bean crop year. An estimate of the annual $\Sigma F_{C\text{-}NEE}$ for a winter wheat crop grown near Gebesee, Thuringia, Germany (≈ -1900 to -2500 kg C ha^{-1}, Anthoni et al., 2004) is similar to that of the spring wheat crop reported herein.

After accounting for grain biomass harvested from the ecosystem, Baker and Griffis (2005) reported an annualized rate of C loss on a silt loam soil in southern Minnesota that is one-half to a third less than the $F_{C\text{-}ECOSYSTEM}$ estimated from our study in southern Manitoba. The rate of annual C loss in the present study is greater than that for a rain-fed corn-soybean rotation and an irrigated continuous maize system, but similar to an irrigated corn-soybean rotation on a silty clay loam in eastern Nebraska (Verma et al. 2005). Conversely, a mature no-till corn-soybean rotation in Illinois may be a small net C sink after accounting for harvest when calculated over several years (Hollinger et al. 2006). The winter wheat crop ecosystem studied by Anthoni et al. (2004), grown on a silty clay loam in Germany, was estimated to be a C source of approximately 450 to 1,050 kg ha^{-1} yr^{-1} after grain harvest, similar to the rate reported in the present study.

Obviously, making comparisons between the limited number of year-round micrometeorological CO_2 flux studies conducted in contrasting agroecosystems is complicated by regional climatic and edaphic (such as texture and associated organic matter content) factors, and differences in the specific agricultural management strategies employed. However, the common observation from majority of these recent studies (this study included) that the amount of C harvested by humans most often exceeds the cumulative NEE measured on annual and multi-year scales indicates that many annual cropping systems are likely significant biological C sources, suggesting that SOC sequestration will prove quite challenging and require much more radical shifts in agronomic and land-use management practices than previously believed and promoted. Another contributing factor to the often reported $F_{C\text{-}HARVEST} > \Sigma F_{C\text{-}NEE}$ may be widespread, systematic underestimation of net CO_2 flux measurements by micrometeorological

methods. Indeed, Baker and Griffis (2005) discussed the influence that a lack of energy balance closure may have had on their eddy covariance measurements of NEE, reporting that $F_{C\text{-}HARVEST} \approx \Sigma F_{C\text{-}NEE}$ after applying a theoretical closure factor to the CO_2 fluxes.

In the present study utilizing the aerodynamic flux gradient technique, two factors that may have caused an underestimation of the net CO_2 flux were possible roughness sublayer effects when the corn canopy was at peak height, and the assumption of similarity in K values for momentum, energy and mass (Denmead, 2008). Micrometeorological theory indicates that the flux-gradient and stability correction equations are only strictly valid at twice the plant canopy height ($2h_c$) or greater (Kaimal and Finnegan, 1994), as the concentration gradient can become decoupled from the scalar flux density due to near-field effects at lower observation heights, so-called roughness sublayer effects. Comparisons of flux-gradient and eddy covariance measurements of net CO_2 flux within and over the tall canopies of a forest (Simpson et al., 1998) and a corn crop (Griffis et al., 2007) indicate that similarity theory may hold better at lower observation heights than previously suspected, but that an 'enhancement factor' of approximately 2X (ratio of eddy covariance flux to flux-gradient flux) occurs around $1.2h_c$. During peak corn canopy height (July 28, 2006 to harvest in October 2006) in the present study, the lowest [CO_2] intake was approximately $1.2h_c$ which may have lead to an underestimation of $F_{C\text{-}NEE}$ by our system during that period. The second mechanism by which $F_{C\text{-}NEE}$ may have been underestimated in the present study is the assumption made that K is equal for momentum and mass when research conducted by Flesch and co-workers (2002) indicates that the ratio of the two eddy diffusivities (momentum:mass a.k.a. the turbulent Schmidt number) is approximately 0.6. To investigate the influence

these two factors may have had on our annual and multi-year cumulative C balances, an enhancement factor of 2X was applied to $F_{C\text{-}NEE}$ for the period during the corn crop in 2006 when the lower [CO_2] intake was mounted at $1.2h_c$, and all eddy diffusivity (K) values for the three years were increased by a factor of 1.4X to account for possible difference between the turbulent transfer of momentum and mass. Applying these factors to the flux time series resulted in the corn crop year becoming a slight sink for CO_2 ($F_{C\text{-}ECOSYSTEM} \approx$ -150 kg C ha^{-1}) whereas it was a slight source $F_{C\text{-}ECOSYSTEM} \approx$ 500 kg C ha^{-1}, Table 2) according to the original calculations. For the entire three-year period, applying the corrections to calculated $\Sigma F_{C\text{-}NEE}$ resulted in the agroecosystem being a net C source ($F_{C\text{-}ECOSYSTEM} \approx$ 2700 kg C ha^{-1} for three years, or annualized rate $\approx$ 900 kg C ha^{-1} yr^{-1}) that was not significantly different according to error estimations, from the original calculation reported (Table 2.2).

Application of theoretical correction factors for the underestimation of net CO_2 flux with our flux-gradient measurements results in the southern Manitoba annual cropping system remaining a significant biological C source. The size of this source indicates that assuming the ecosystem is in equilibrium or is C neutral is a mistake, as this estimation of biological C source strength is approximately twice as great as the CO_2 emissions attributed to non-renewable energy-use and manufactured inputs on farms (West and Marland, 2002; 2003). Clearly, studies on GHG emissions of agricultural land and practices focused on non-renewable energy-use, that either ignore or estimate photosynthesis based on rough empirical relationships with yield data and that neglect plant and soil respiration (eg. West and Marland, 2002; Khakbazan et al., 2009) could be erroneous in the constructed budgets and conclusions. More multi-year

micrometeorological CO_2 flux studies in different agricultural systems could shed light on both the true net ecosystem exchange of CO_2 and potentially identify and address weaknesses of the measurement techniques employed.

2.6 Conclusions

The NEE of CO_2 for a recently established reduced tillage treatment was not different from a more intensive tillage treatment at the Red River Valley site, and likely would require more time to express detectable effects on the net C flux. Variation in NEE among the four plots at the site was large, and caused by landscape variations in crop growth. The three-year crop rotation of corn-faba-spring wheat in southern Manitoba was a net C sink to the crop-soil system of 3050 kg C ha^{-1}, but taking harvested biomass into account meant the rotation was a significant source of 3170 kg C ha^{-1}. Differences among years were most likely due to characteristics of the different crops, including the length of the fallow season and amount of biomass harvested. Inter-annual variability in weather is imposed on these characteristics and interacts with crop growth and ecosystem respiration. Additional multi-year micrometeorological CO_2 flux studies in different agricultural systems could help identify practices that result in C gains by the ecosystem and perhaps optimize crop rotations to achieve co-benefits.

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3. CONTRIBUTION OF CROP RESIDUE CARBON TO THE TOTAL SOIL RESPIRATION OF AN ANNUAL CROPPING SYSTEM DURING THE NON-GROWING SEASON IN MANITOBA, CANADA

3.1 Abstract

Heterotrophic respiration from agricultural soils may be differentiated as originating from microbial decomposition of recent litter inputs or crop residue carbon (CRC) and resident soil organic carbon (SOC) pools of varying age and stages of decomposition. In the present study, a tunable diode laser trace gas analyzer was used to determine atmospheric stable C isotope ratio ($\delta^{13}C$) values and $^{12}CO_2$ and $^{13}CO_2$ fluxes over an agricultural field in the Red River Valley of southern Manitoba, Canada. Measurement campaigns were conducted in the fall of 2006 and spring of 2007 following harvest of a corn (C_4) crop from soil having SOC derived from C_3 photosynthesis. Stable CO_2 isotopologue gradients were measured from the center of four 200 by 200 m experimental plots, and fluxes were calculated using the aerodynamic flux gradient method. The soil in two of the experimental plots underwent intensive tillage, while the other two plots were managed using a form of reduced tillage. Approximately 70 % and 20 – 30 % of the total respiration flux originated from the corn C_4-CRC during the fall of 2006 and spring of 2007, respectively. No difference in the partitioning of heterotrophic respiration into that derived from CRC and SOC was detected between the intensive tillage and recently established reduced tillage treatments at the site.

3.2 Introduction

Carbon dioxide (CO_2) emissions from agricultural soils originate from living plant roots and associated rhizomicrobial heterotrophic respiration, and from heterotrophic microbial decomposition of necromass and various resident soil organic matter (SOM) pools. The SOM substrate-derived component can comprise 40 – 70 % of the total soil respiration during the growing season in the presence of an actively growing crop stand (Rochette and Flanagan, 1997; Buchmann and Ehleringer, 1998; Rochette et al., 1999; Griffis et al., 2005; Werth and Kuzyakov, 2009), and up to 100 % during the non-growing season, defined herein as harvest to seeding. The non-growing season can be greater than 6 months in many agricultural regions of North America, such as the upper U.S. Midwest and the Canadian Prairies. Climate change during the non-growing season in these regions is predicted to result in warmer air temperatures with less depth and duration of snow cover (Christensen et al., 2007), which could lead to larger amounts of CO_2 released to the atmosphere from soils under annual crop production. Although rates of soil respiration are much lower during the non-growing season, because it is such an extended period of time relative to the active growing season, values of the net CO_2 flux integrated over this period are a substantial component of annual C budgets (e.g. 10 % to 80 % of the net CO_2 uptake during the growing season, Chapter 2). Growing interest in offsetting anthropogenic greenhouse gas emissions has led to the promotion of conservation tillage (reducing tillage intensity and frequency) techniques on intensively cultivated cropland to sequester and stabilize atmospheric CO_2 in SOM (Smith et al., 2007). The goal of conservation tillage techniques is to create biophysical conditions that slow the rate of organic matter decomposition, and provide bio-physical-chemical conditions that

eventually stabilize and protect soil C in aggregates. Intensive CO_2 flux studies during the non-growing season aid in the assessment of conservation tillage techniques without the confounding effects of photosynthesis and plant respiration.

Heterotrophic CO_2 sources from agricultural soils during the non-growing season may be differentiated between those originating from the decomposition of recent plant litter inputs or crop residue carbon (CRC) and resident soil organic carbon (SOC) pools of varying age and stages of structural decay through the use of stable C isotope methods (Conen et al., 2006; Vanhala et al., 2007; Drewitt et al., 2009). This area of atmospheric and ecological research allows partitioning of CO_2 fluxes into source components, which furthers understanding of underlying mechanisms contributing to emissions, and the refinement of global C cycling hypotheses and models of turnover rates. Much scientific debate in recent years has focused on the temperature sensitivity of decomposition for different pools of soil C in the context of climate change (Davidson et al., 2000; Knorr et al., 2005; Davidson and Janssens, 2006; Hartley and Ineson, 2008), with stable C isotope methods playing an important role in elucidating such kinetics (Conen et al., 2006; Vanhala et al., 2007).

The relative concentrations of the two stable C isotopes, ^{12}C and ^{13}C, are used as tracers in ecosystem CO_2 flux research to constrain the origins of ecosystem respiration (R). The heavier isotope is much less abundant, with ^{13}C comprising approximately 1.1 % of all C on Earth (Farquhar et al., 1989; Ehleringer et al., 2000). Soil, plant tissue, chamber headspace and atmospheric gas samples are commonly analyzed for $^{13}C/^{12}C$ content relative to a known standard using isotope-ratio mass spectrometry (IRMS) and the stable C isotope ratio ($\delta^{13}C$) is calculated as:

$$\delta^{13}C = \left(\frac{[^{13}C] / [^{12}C]}{R_{VPDB}} - 1 \right) x\, 1000 \quad (1)$$

where R_{VPDB} refers to the ratio of the current isotopic reference material (NBS-19) expressed according to the Vienna PeeDee Belemite standard scale (Griffis et al., 2004). The ratio, $\delta^{13}C$, is expressed in parts per thousand as the dimensionless unit per mille (‰).

Most stable C isotope techniques are based on the fractionation of CO_2 during photosynthesis, with plants fixing a proportionally larger amount of $^{12}CO_2$ and discriminating against the heavier isotopologue, $^{13}CO_2$ (Farquhar et al., 1989; Flanagan and Ehleringer, 1998; Ehleringer et al., 2000). This results in relative atmospheric enrichment of $^{13}CO_2$ during the daytime in the presence of photosynthesis (Yakir and Wang, 1996; Griffis et al., 2004; Zhang et al., 2006). The subsequent release of plant fixed C into the atmosphere as a result of autotrophic respiration, and heterotrophic oxidation of root exudates and SOM influences the concentrations of $^{12}CO_2$ and $^{13}CO_2$ relative to the background troposphere, and is observed as depletion in the relative abundance of atmospheric $^{13}CO_2$ during nighttime or non-growing season measurements. Work by Keeling in the late 1950s showed that there was a strong linear relationship between the atmospheric $\delta^{13}C$ and the reciprocal of the total CO_2 mixing ratio (Keeling, 1958). As CO_2 is added to the atmosphere from respiration, increasing the total CO_2 mixing ratio, this CO_2 has a different isotopic signature than background tropospheric values, and is depleted in ^{13}C relative to ^{12}C. The y-intercept of these "Keeling plots" is often used to quantify the $\delta^{13}C$ signature of the respired CO_2 (Yakir and Wang, 1996; Griffis et al., 2004). Besides ecosystem photosynthesis and respiration, the other major

influence on mixing ratios and the $\delta^{13}C$ value of CO_2 encountered in terrestrial settings is due to the anthropogenic combustion of fossil fuels. As fossil fuel C was originally fixed by photosynthesis, the $\delta^{13}C$ values of commonly combusted energy products by humans (petroleum, coal and natural gas) are depleted in magnitude similar to contemporary natural biogenic CO_2 sources to the atmosphere (Clark-Thorne and Yapp, 2003; Zimnoch et al., 2004; Pataki et al., 2007).

For plants with C_3 metabolism, the two primary mechanisms contributing to stable C isotope discrimination during photosynthesis are diffusional fractionation (the slower diffusion of $^{13}CO_2$ relative to $^{12}CO_2$) and enzymatic fractionation associated with Rubisco activity (Farquhar et al., 1989). The $\delta^{13}C$ value for C_3 tissues varies between -21 ‰ and -30 ‰, (Ehleringer et al., 2000; Diels et al., 2001) compared to the background tropospheric value of approximately -8 ‰ at present. Plants with the C_4 photosynthetic pathway exert less influence on stable C abundances in the atmosphere, as the initial enzyme involved in CO_2 fixation, phosphoenolpyruvate carboxylase, exerts a smaller fractionation effect than Rubisco and reported $\delta^{13}C$ values for C_4 tissues vary from -10 ‰ to -15 ‰ (Farquhar et al., 1989; Diels et al., 2001). The difference in preferential isotope discrimination between C_3 and C_4 metabolic pathways has applications for studying C substrate sources contributing to respiratory CO_2 fluxes in natural ecosystems that have undergone ecological succession where there are shifts in dominant vegetation (Flanagan and Elheringer, 1998; Diels et al., 2001) or in agricultural systems with abrupt and deliberate shifts in crop species grown (Schönwitz et al., 1986; Rochette and Flanagan, 1997; Drewitt et al., 2009). Observed $\delta^{13}C$ values in CO_2 emissions from respiration (Schönwitz et al., 1986; Rochette and Flanagan, 1997; Drewitt et al., 2009) or changes in

the isotopic signature of soils over time (Arrouays et al., 1995; Gregorich et al., 1995) represent the substrate sources contributing to the cycling process. Natural stable C isotope labeling of SOM pools is possible by growing C_4 crop species on C_3 derived top-soil or *vice versa*. A two-source end member ($\delta^{13}C_3$ and $\delta^{13}C_4$) linear mixing-model can be used to estimate the fractional contributions of recently fixed C and native SOC to soil respiration (Robinson and Scrimgeour, 1995).

The results from studies relating the $\delta^{13}C$ signature of CO_2 effluxes to substrates must be interpreted with caution as there has been ongoing debate regarding "isotopic disequilibrium" between soil respiration and that of SOM, most often reported for forest ecosystems (Ehleringer et al., 2000; Boström et al., 2007). Hypotheses invoked to explain the observed disequilibrium include: changing atmospheric chemistry ($\delta^{13}[CO_2]$ decreasing over time due to combustion of fossil fuels) causing older C in deeper soil layers to be more enriched in ^{13}C relative to recently fixed C, microbial fractionation during litter decomposition, preferential decomposition of litter and SOM by microbes, and the mixing of older soil C and recent C pools, such as plant, microbial and fungal residues (Ehleringer et al., 2000). Considering pre-industrial tropospheric $\delta^{13}C$ values of approximately -6.5 ‰ compared to present background values of -8 ‰ or slightly more negative, the potential error or bias associated with isotopic disequilibrium between older and younger SOM caused by changes in the composition of atmospheric CO_2 over time is less than 2 ‰. This is similar in magnitude to recently reported values for microbial biomass enrichment in ^{13}C relative to bulk SOM, or to potential fractionation during respiration (Werth and Kuzyakov, 2010). These potential biases are considerably less than the difference in $\delta^{13}C$ values between SOC and CRC (> 10 ‰) found in most C_3-C_4

natural labeling experiments, but are not negligible, and could introduce additional uncertainty during partitioning exercises.

The majority of stable C isotope ecosystem respiration studies to date have been based on chamber gas or atmospheric flask sample collection in the field, followed by IRMS analysis in the laboratory (Bowling et al., 2003). While these gas sample isotope-ratio studies have been important for developing standard stable C isotope methodology (such as the use of Keeling plots and $\delta^{13}C$ notation) and determining environmental influences on observed fluctuations, they have limitations from a long-term monitoring perspective (Bowling et al., 2003). Flask sampling techniques require a significant amount of labour in the field and the lab, IRMS analyses can be expensive, and there is often significant spatial and temporal separation between sample collection and sample analyses. The development of tunable diode laser (TDL) based micrometeorological systems for concurrent measurement of $^{12}CO_2$ and $^{13}CO_2$ exchange between the surface and atmosphere allows unprecedented temporal resolution and duration of stable isotope-ratio measurements (Bowling et al., 2003; Griffis et al., 2004). In addition to giving investigators an alternative method to IRMS for applying Eq. 1 and Keeling plots to determine ecosystem respiration $\delta^{13}C$ values, the simultaneous measurement of $^{12}CO_2$ and $^{13}CO_2$ fluxes by TDL absorption spectroscopy allows an additional tool for quantifying the $\delta^{13}C$ signal of respiration. The "flux ratio" technique (Griffis et al., 2004) for determining the $\delta^{13}C$ signal of ecosystem respiration is given by:

$$\delta^{13}C_R = \left(\frac{F^{13}CO_2 / F^{12}CO_2}{R_{VPDB}} - 1 \right) x\,1000 \qquad (2)$$

where $F^{13}CO_2$ and $F^{12}CO_2$ are the independently measured fluxes of $^{13}CO_2$ and $^{12}CO_2$ using the TDL and micrometeorological methods such as eddy covariance or the flux-gradient technique. For flux-gradient measurements the relationship is simplified to the ratio of vertical mixing ratio gradients ($\Delta[^{13}CO_2]/\Delta[^{12}CO_2]$) as the turbulent "eddy diffusivity" (K), vertical gradient distance (Δz) terms, and associated stability corrections cancel out in the calculation of the ratio of fluxes (Eq. 2) over sufficient surface-layer averaging intervals (e.g. 15 to 60 minutes). A clear advantage of applying the flux ratio technique over using single-point atmospheric concentration measurements and Keeling plots to discern $\delta^{13}C_R$ values is realized when considering fetch limitations from spatially finite experimental plots or ecosystems, as the concentration footprint is an order of magnitude greater than flux footprints (Griffis et al., 2007). The use of the flux ratio method affords the investigator more control over constraining micrometeorological observations to the upwind surface of interest.

In the present study, micrometeorological stable C isotope techniques were applied to CO_2 flux measurements made over an agricultural field in the Red River Valley of southern Manitoba, Canada. A C_4 crop, corn (*Zea mays* L.), was grown during the 2006 season on soil that had historically been under C_3 crop production. The addition of crop residues with a different $\delta^{13}C$ signature than resident SOC facilitated determining the contribution of CRC to emissions of CO_2 and the identification of SOC derived emissions from recently established reduced and intensive tillage treatments. This investigation builds on research from a previous study conducted in southern Ontario, Canada, under a contrasting climate and soil type (Drewitt et al., 2009), investigating the influence of soil tillage on C sequestration, as evaluated from the non-growing season respiratory C loss

from CRC and SOC sources. The objectives of the study were to: (1) determine the relative contribution of recently derived CRC *vs.* resident SOC to total CO_2 fluxes under reduced and intensive tillage treatments; and (2) examine the sensitivity of the two C pools to physical disturbance and the environmental conditions at the site.

3.3 Materials and Methods

3.3.1 Site Description

The experimental field (49.64°N, 97.16°W; 235 m a.s.l.) where vertical $^{12}CO_2$ and $^{13}CO_2$ mixing ratio gradient measurements were performed was located at the University of Manitoba Glenlea Research Station, approximately 16 km south of Winnipeg, Manitoba, Canada. The research site was situated in the Red River Valley, a near-level to very gently sloping (0 to < 2 % slope, typically < 1 m km^{-1}), glaciolacustrine clay floodplain. The soils at the site were of the Red River association, consisting of a combination of Osborne clay and Red River clay soil series depending on local drainage characteristics and the micro-relief of the landscape (Ehrlich et al., 1953; Michalyna et al., 1971). The hydrology ranges from poorly (micro-lows, Osborne clay series) to imperfectly (micro-highs, Red River clay series) drained soils. The Red River clay soil series is classified as a Gleyed Humic Vertisol (Canadian system) or a fine smectitic frigid Typic Epiaquert (USDA system), while the Osborne clay series is classified as a Gleysolic Humic Vertisol (Canadian system) or a fine smectitic frigid Typic Endoaquert (USDA system). The average bulk density and particle size distribution of the surface

layer (0 – 0.2 m) soil at the site when the study was initiated were approximately 1.2 Mg m^{-3}, and 60 % clay, 35 % silt and 5 % sand, respectively. The pH was 6.2 and there was an absence of carbonate minerals in the surface layer. The average organic carbon and total nitrogen content of the surface layer were 3.2 % and 0.4 %, respectively.

3.3.2 Agronomic History

Prior to 2005, the experimental field was exclusively under C_3 crop production, primarily cereals and oilseeds. After a fallow year that included weed management by tillage and chemical means in 2005, different soil management treatments were initiated in the spring of 2006 with the establishment of four 200 m by 200 m (4 ha each) experimental treatment plots inside of a larger 30 ha field. Two plots were managed as intensive tillage (IT) treatments and two plots were managed as reduced tillage (RT) treatments. The IT plots were tilled to a depth of 0.2 m on April 27, 2006 with a field cultivator consisting of three rows of shanks with 0.20 m sweeps spaced 0.30 m apart followed by three rows of spring-tine harrows spaced 0.10 m apart. The RT plots received a light (single-pass) harrowing as seed bed preparation on April 28, 2006. All plots were sown to corn (*Zea mays* L. cv 'DKC27-12 (Roundup Ready®)', DEKALB®) on May 16. A granular fertilizer blend (32-25-10-10; Viterra Inc.) was side-banded with the seed at planting at a rate of 185 kg ha^{-1}. Granular urea (46-0-0) was broadcast applied at 110 kg ha^{-1} on May 17 and lightly tine-harrowed to incorporate into the soil on IT and RT plots. Herbicide (Roundup®, a.i. glyphosate, Monsanto Company Inc.) was applied on June 13, 2006 to all plots at a rate of 1.7 L ha^{-1}. Grain was harvested from all plots on October 6, and on October 25, 2006 standing aboveground corn biomass (stalks and leaves) on all

plots was shredded with a flail-mower. The IT plots were tandem-disced on October 27, and tilled once to a depth of 0.2 m with the field cultivator previously described on October 28, 2006. The top-soils of the RT plots were undisturbed post-harvest, with all flailed corn stover remaining on the surface. Field operations (tillage, seed-bed preparation, and seeding) for the following growing season began on May 9, 2007.

3.3.3 Measurements of Vertical $^{12}CO_2$ and $^{13}CO_2$ Mixing Ratio Gradients

A tunable-diode-laser (TDL) based trace gas analyzer (Model TGA100A, Campbell Scientific Inc., Logan, Utah, USA) was installed at the site in late August 2006 inside a grid-powered instrumentation trailer located in the centre of the four experimental plots. The air temperature inside the trailer was kept at approximately 20°C for the duration of monitoring with electric heat and air-conditioning as required. The TDL was parameterized for the concurrent measurement of atmospheric mixing ratios of $^{12}CO_2$ and $^{13}CO_2$ at a frequency of 10 Hz. See Drewitt et al. (2009) for specific details on the TDL configuration, calibration routines, plumbing, sampling sequence and control system employed.

For the calculation of the vertical mixing ratio gradients, $\Delta[^{12}CO_2]$ and $\Delta[^{13}CO_2]$, two gas sample intakes were mounted at different heights (Δz = 0.65 m) within the atmospheric surface layer to a triangular, aluminum instrumentation tower located at the approximate centre of each experimental plot, beside existing intakes for another TDL ($[N_2O]$ and $[CO_2]$ analyzer) at the site. As one atmospheric sampling tube was used for both intakes at each tower, samples immediately following valve switching between the upper and lower intakes were discarded from the calculation of gradients to allow for

equilibration, and a lag due to the length of the sample tube between the observation tower and TDL was accounted for with processing software (Wagner-Riddle et al., 2005). Half-hourly gradients were calculated over the four experimental plots sequentially, obtaining one 30-minute average $\Delta[^{12}CO_2]$ and $\Delta[^{13}CO_2]$ every two hours per plot or 12 possible stable C isotopologue mixing ratio gradients per plot each day. Care was taken to ensure a balance between measuring gradients far enough above the surface to minimize roughness sub-layer effects but low enough to contain the flux footprint within each plot. Because of the large size of the experimental plots (4 ha) and location of the micrometeorological towers in the centre, fetch to effective observation height ratios of approximately 90:1 to 100:1 were maintained for all plots, in all directions, during the monitoring campaigns.

Three distinct campaigns of vertical $\Delta[^{12}CO_2]$ and $\Delta[^{13}CO_2]$ measurements conducted at the site were utilized in the present study. The first period consisted of nocturnal measurements made over the corn crop canopy between September 3 and September 16, 2006 (Corn Crop 2006) and was primarily used for testing and evaluating the performance of the system. The second period considered are measurements made over the post-harvest soil surface for 30-days prior to thorough freezing of the 0 – 0.5 m depth and the onset of significant snow cover, from November 10 to December 10, 2006 (Fall 2006). The third campaign reported was over 26-days during the following spring after snowmelt, initialization of soil thaw and prior to agronomic field operations, between April 12 and May 8, 2007 (Spring 2007). The two latter non-growing season campaigns (Fall 2006 and Spring 2007) were the main focus of this study. Missing TDL data occurred during periods of system maintenance, mechanical malfunction, and power

disruptions. A liquid nitrogen dewar cooled the laser and required re-filling twice per week. The data recorded during re-filling episodes and for the following two hours were discarded from further analysis due to the influence of resulting vibrations and temperature perturbations inside the enclosure on gas concentration calculations. Other less frequent examples of system maintenance introducing gaps to the trace gas concentration time series included: changing the atmospheric sample pump oil and parts; replacing the reference gas cylinder; changing sample intake heights; performing gradient and timing tests; and changing air filters. After discarding data due to system maintenance and mechanical malfunctions, average 30-minute [$^{12}CO_2$] and [$^{13}CO_2$] data coverage from the TDL was approximately 96 %, 54 %, and 74 %, for the Corn Crop 2006, Fall 2006, and Spring 2007 measurement campaigns, respectively.

3.3.4 Supporting Environmental Measurements

A weather station was located at the site near the centre of the four plots on an undisturbed, grassed area. The following is a description of the meteorological instruments used in this study. Air temperature was measured with a combined temperature and relative humidity probe (Model HMP45C, Vaisala Inc., Woburn, Massachusetts, USA) mounted within a radiation shield (Model 41003-5 10-Plate Gill Radiation Shield, R.M. Young Company, Traverse City, Michigan, USA) 2 m above the ground surface to a tripod stand (Model CM110 Tripod and Grounding Kit, Campbell Scientific Inc., Logan, Utah, USA). A cumulative precipitation gauge (Model T-200B Series Precipitation Gauge, Geonor Inc., Milford, Pennsylvania, USA) was installed approximately 3 m away from the main weather station tripod on an independent pedestal. A soil temperature profile consisting of 6 thermistors (Model 107B Soil/Water

Temperature Probe, Campbell Scientific Inc., Logan, Utah, USA) made measurements at 0.02 m, 0.05 m, 0.1 m, 0.2 m, 0.5 m and 1 m depths.

The total aboveground corn biomass produced during the growing season was calculated from hand-clipped samples taken prior to mechanical harvesting in October 2006. Samples were taken from 12 random locations in each of the tillage treatments and air-dried at 40°C. The amount of aboveground corn residue input to the cropland in each tillage treatment was taken as the difference between total aboveground biomass and the bulk grain removed (1230 kg C ha^{-1}, Chapter 2) from the system. Belowground biomass production was estimated assuming a shoot-to-root ratio of 5.6 for grain corn (Bolinder et al., 2007).

The determination of the $\delta^{13}C$ signature of indigenous SOC ($\delta^{13}C_{SOC}$) at the site and the corn CRC ($\delta^{13}C_{CRC}$) was done with IRMS by the Stable Isotope Facility (SIF) in the Department of Plant Sciences at the University of California, Davis, California, USA (SIF, 2010). Soil samples from 0 – 0.1 m, 0.1 – 0.2 m, and 0.2 – 0.4 m depths were collected from 6 random locations from each tillage treatment in November 2005 (6 months prior to planting corn) for $\delta^{13}C_{SOC}$ analysis. Soil samples were dried, finely ground with a ball mill, and packaged in metal capsules prior to shipment to the UC Davis SIF for analysis. For $\delta^{13}C_{CRC}$, separate samples of the aboveground biomass from 12 corn plants taken from the site at harvest in October 2006 were dried, homogenized, finely ground with a Wiley mill or coffee grinder, and packaged in metal capsules prior to shipment to the UC Davis SIF for analysis.

The $\delta^{13}C$ signature of soil respiration ($\delta^{13}C_{R\text{-}SOIL}$) was evaluated prior to corn planting (May 6, 2006) and following faba emergence (July 9, 2007) from measurements

of dark CO_2 fluxes made with static, two-piece (collar and lid) reflective PVC chambers (20 cm i.d. x 10 cm high). For the chamber measurement campaigns, six collars were placed on each of the four plots at the site within a 10 to 50 m radius of the micrometeorological flux tower. Collars were inserted into the soil to a depth of 3 to 4 cm to ensure a seal with the soil, approximately 5 to 7 days prior to gas sampling. Weeds and seedlings were removed from the interior and area surrounding the collars (approximately 30 cm radius) approximately 18 to 36 hours prior to sampling campaigns. During chamber CO_2 flux measurement campaigns, lids were secured to each collar and 20 mL head-space gas samples were drawn into a syringe (Becton-Dickinson, Franklin Lakes, New Jersey, USA) at regular intervals (0, 15, 30, and 45 min.) through a rubber septum. Chambers were vented to the atmosphere with a small piece of tubing to maintain pressure equilibrium between the head-space and the atmosphere. Syringe samples collected were immediately injected into 12 mL pre-evacuated and helium flushed vials (Labco Exetainer, High Wycombe, UK). To ensure integrity and quality assurance of the samples, known low and high gas standard mixtures were injected into vials, taken to the field on sampling dates, handled, and analyzed in the same manner as the field samples. Vials were kept in the dark at room temperature until shipment to the SIF at UC Davis (SIF, 2010) for analysis of total $[CO_2]$ and $\delta^{13}[CO_2]$ with IRMS. The $\delta^{13}C_{R\text{-}SOIL}$ was determined using the Keeling plot technique, taken as the y-intercept of OLS regressions between $\delta^{13}[CO_2]$ and the reciprocal of the total $[CO_2]$ over time (n = 4) for each chamber on the sampling dates. The $\delta^{13}C_{R\text{-}SOIL}$ values for the RT and IT plots were estimated as the mean y-intercept from the collars measured within each treatment that had Keeling plots with minimum r^2 values of 0.8.

3.3.5 Data Analysis

3.3.5.1 Calculation of the Stable C Isotope Signature of Ecosystem Respiration The flux ratio technique (Eq. 2; Griffis et al., 2004; Drewitt et al., 2009) was used to quantify the $\delta^{13}C$ signature of ecosystem respiration ($\delta^{13}C_R$). Similarity was assumed between the two CO_2 isotopologues, and the $\delta^{13}C_R$ relationship was simplified to the ratio of 30-minute mean vertical mixing ratio gradients, ie. $\Delta[^{13}CO_2]/\Delta[^{12}CO_2]$, eliminating errors associated with estimating *K* values. The micrometeorological measured net ecosystem CO_2 exchange (NEE) between cropland and the atmosphere is the net balance of gross primary production and respiration (R). In the absence of photosynthesis during nocturnal hours or the non-growing season, NEE = R. As the present study was concerned with examining $\delta^{13}C_R$, data analysis was limited to data recorded during nocturnal (Corn Crop 2006) or non-growing season (Fall 2006 and Spring 2007) conditions.

A signal-to-noise relationship between the magnitude of ecosystem CO_2 fluxes and discerning $\delta^{13}C_R$ values has been observed by others using the TDL and flux-ratio technique (Griffis et al., 2004, 2005; Zhang et al., 2006; Drewitt et al., 2009). From the data collected in the current study, visual assessment of the relationship between 30-minute $\delta^{13}C_R$ and $\Delta[^{12}CO_2]$ values revealed a tremendous amount of variability in $\delta^{13}C_R$ values obtained when $\Delta[^{12}CO_2]$ was less than approximately 1 μmol mol^{-1} (Δz = 0.65 m), and the noise increased exponentially as $\Delta[^{12}CO_2]$ approached zero (data not shown). The ability of the TDL to resolve vertical mixing ratio gradients of $^{12}CO_2$ and $^{13}CO_2$ was assessed by zero vertical gradient tests, the standard deviation (S.D.) of $\Delta[^{12}CO_2]$ and $\Delta[^{13}CO_2]$ when the two intakes were at the same measurement height, $\Delta z \approx 0$ m, performed with the system at the site in September 2006. The $\delta^{13}C_R$ values calculated

when the vertical mixing ratio gradient of $^{12}CO_2$ was greater than this resolution (S.D. of 30-minute [$^{12}CO_2$] zero-gradients = 0.45 μmol mol^{-1}, n = 141) were aggregated in bins (n = 10) by $\Delta[^{12}CO_2]$ (Figure 3.1). A minimum gradient threshold for reliable $\delta^{13}C_R$ data for each measurement campaign was determined from the standard error (S.E.) of the means for the bins, which generally decreased with increasing $\Delta[^{12}CO_2]$ (Figure 3.1). The cutoff was selected as the point at which S.E. of $\delta^{13}C_R$ binned by $\Delta[^{12}CO_2]$ decreased to 3 ‰ or less. This approach resulted in minimum [$^{12}CO_2$] gradient (Δz = 0.65 m) thresholds of 1 μmol mol^{-1} for the nocturnal Corn Crop 2006 and Fall 2006 periods, and 1.6 μmol mol^{-1} for the Spring 2007 measurement campaign. The use of the minimum gradient thresholds constrained the S.E. of the mean 30-minute $\delta^{13}C_R$ for each of the three measurement campaigns to less than 2 ‰.

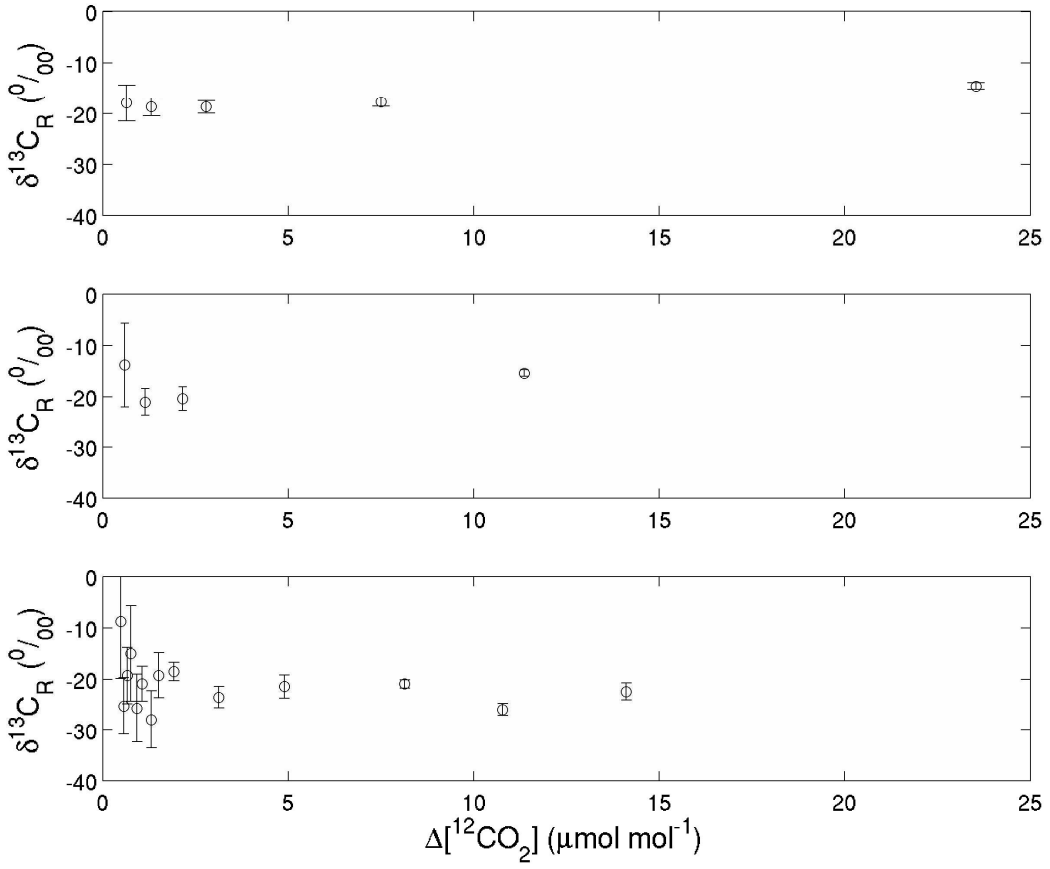

Figure 3.1 Average 30-minute stable C isotope ratio signature of ecosystem respiration ($\delta^{13}C_R$) binned by mean $\Delta^{12}[CO_2]$ (± 1 S.E.; n = 10) for three measurement campaigns (top = nocturnal Corn Crop 2006; middle = Fall 2006; bottom = Spring 2007).

3.3.5.2 Partitioning Ecosystem Respiration Budgets During the Non-growing Season

Continuous, multi-year net CO_2 flux measurements from the other TDL (parameterized for $[CO_2]$ and $[N_2O]$) at the research site were partitioned into GPP and R, and gap-filled using a modified version of the standard Fluxnet-Canada protocol (methods and data processing were described in Chapter 2). Daily averages of gap-filled R were used to partition CRC and SOC sources from the two tillage treatments during the non-growing season periods (Fall 2006 and Spring 2007) with acceptable $\delta^{13}C_R$ measurements. Daily

means of $\delta^{13}C_R$ were obtained from days with more than one 30-minute observation meeting the minimum mixing ratio gradient thresholds for both tillage treatments. An OLS regression was fit between the daily average $\delta^{13}C_R$ values and time for the Fall 2006 and Spring 2007 measurement campaigns. The fraction of daily R due to oxidation of CRC (R_{CRC}) was determined from a two-member $\delta^{13}C$ linear mixing model ($\delta^{13}C_R$ - $\delta^{13}C_{SOC}$ / $\delta^{13}C_{CRC}$ - $\delta^{13}C_{SOC}$), and that due to metabolism of SOC (R_{SOC}) as the difference between total R and R_{CRC}. The error of the total cumulative R (ΣR) was estimated from the S.E. of the mean R budgets obtained from the two individual plots of each tillage treatment. The uncertainty associated with ΣR_{CRC} and ΣR_{SOC} for each tillage treatment and period was estimated by propagating the fractional errors contributing to estimation of the budgets (S.E. of ΣR, S.E. of $\delta^{13}C_R$ for the period, and the S.E. of the slope and y-intercept from the regression between $\delta^{13}C_R$ and time).

3.3.5.3 Statistical Tests

Differences among means of initial $\delta^{13}C_{SOIL}$ values for the three sampling depths were tested within each tillage treatment using one-way analysis of variance with the *anova1* function from MATLAB® (Verson 7.6.0, Statistics Toolbox 6.2 (R2008a), The Mathworks Inc., Natick, Massachusetts, USA). Means of initial $\delta^{13}C_{SOIL}$ values for each sampling depth and total aboveground crop biomass were tested between the two tillage treatments using *ttest.* P-values less than 0.05 were considered significant for tests of $\delta^{13}C_{SOIL}$ and aboveground biomass means. Sample medians of daily R and $\delta^{13}C_R$ from the two tillage treatments were compared for the two non-growing season periods with non-parametric rank-sum tests, using the *ranksum* function. Correlation coefficients and

significance levels between daily $\delta^{13}C_R$, air and soil temperatures were calculated with *corrcoef*. P-values less than 0.1 were considered significant for tests of the micrometeorological flux (R and $\delta^{13}C_R$) medians and for correlations between $\delta^{13}C_R$ and variables.

3.4 Results

3.4.1 Environmental Conditions during the Non-growing Season Campaigns

The Fall 2006 (November 10 to December 10, 2006) and Spring 2007 (April 12 to May 8, 2007) measurement campaigns represented the transition from autumn to winter (decreasing air temperatures and freezing of subsoil), and winter to spring (increasing air temperatures and thawing of subsoil) seasons at the southern Manitoba site, respectively (Figure 3.2). The average of the 30-minute means of air temperatures measured at a height of 2 m at the site during the Fall 2006 period was -7.8°C and exhibited a range of approximately 40°C, from -27.8°C to 12.2°C. The mean air temperature during the Fall 2006 period was similar to the 30-year normal (1971 – 2000) of -5.3 ± 3.3 (S.D.)°C for the region (Winnipeg, Manitoba, Canada) in November (Environment Canada, 2010). The Spring 2007 period was warmer than the 30-year normal for April for the (4.0 ± 2.7°C), with a mean air temperature of 11.6°C, and similarly extreme as the Fall 2006 campaign, ranging 34.5°C, from -3.4°C to 31.1°C. The Fall 2006 period was relatively dry, with 6.2 mm of precipitation measured on-site, compared to the 30-year normal (1971 – 2000) of 26 mm for November (Environment Canada, 2010). However, prior to

the Fall 2006 measurement campaign, the site received 36.4 mm of precipitation during October, which is normal. Unfortunately the precipitation gauge at the site was malfunctioning during the Spring 2007 campaign. The area (Morris, Manitoba, Canada) received 27 mm of precipitation during the Spring 2007 measurement period (MAFRI, 2010), slightly less than the normal amount of 30 mm (Environment Canada, 2010).

The average CO_2 mixing ratios ($[CO_2]$) measured with the micrometeorological system (h ~ 1 m) at the site were 5 to 6 μmol mol^{-1} higher during both measurement campaigns (Table 3.1) than background levels for Alert, Canada (November 2006: $[CO_2]$ = 383.71 μmol mol^{-1} and April 2007: $[CO_2]$ = 389.63 μmol mol^{-1}; Keeling et al., 2008). The mean $[CO_2]$ measured during Spring 2007 was 6.9 μmol mol^{-1} greater than the Fall 2006 (Table 3.1), similar to northern hemisphere background trends for the period (Keeling et al., 2008). The average stable C isotope ratio of the atmospheric surface layer ($\delta^{13}[CO_2]$) at the site was more depleted in $^{13}CO_2$ during both measurement campaigns (Table 3.1) relative to the backgrounds of -8.33 ‰ and -8.67 ‰ for November 2006 and April 2007 at Alert, respectively (Keeling et al., 2010). The mean value during Spring 2007 was 0.7 ‰ lower than the Fall 2006 period at the site, in accordance with the higher overall average $[CO_2]$. Keeling plots (OLS regression between $\delta^{13}[CO_2]$ and inverse of $[CO_2]$) indicated a $\delta^{13}C$ of approximately -25 ‰ (y-intercept) for CO_2 sources at the site and surrounding vicinity ($\delta^{13}C_{KEELING}$) during the two measurement campaigns (Table 3.1).

Table 3.1 Concentrations and stable C isotope ratio characteristics of the atmospheric surface layer CO_2 monitored at the site during the two post-harvest study campaigns. Values represent the mean $[CO_2]$ (± 1 S.E.), $\delta^{13}[CO_2]$ (± 1 S.E.), and $\delta^{13}C_{KEELING}$ (± y-intercept S.E.) values combined from upper and lower intake heights at the four measurement towers.

Period	$[CO_2]$ (μmol mol^{-1})	$\delta^{13}[CO_2]$ (‰)	$\delta^{13}C_{KEELING}$ (‰)	$[CO_2]$ range (μmol mol^{-1})	n
Fall 2006	388.77 ± 0.09	-8.80 ± 0.01	-25.62 ± 0.39	53	1554
Spring 2007	395.66 ± 0.33	-8.87 ± 0.01	-25.05 ± 0.21	149	1960

The initial stable C isotope signatures of SOC ($\delta^{13}C_{SOC}$) determined from soils collected in November 2005 (Table 3.2) were statistically similar between the RT and IT plots for the 0.0 – 0.1 m (P = 0.77), 0.1 – 0.2 m (P = 0.53) and 0.2 – 0.4 m (P = 0.70) depths. As well, the $\delta^{13}C_{SOIL}$ values did not vary significantly (P > 0.05) with depth prior to the establishment of the RT (P = 0.06) and IT plots (P = 0.09) at the site.

Table 3.2 Total organic C content and stable C isotope ratio signatures of soil samples (mean $\delta^{13}C_{SOC}$ ± 1 S.E.) from the two tillage treatment plots collected in November 2005, 6 months prior to seeding of corn in spring 2006.

Date	Treatment	Soil Depth (m)	Total Organic C (%)	$\delta^{13}C_{SOIL}$ (‰)	n
November 2005	Intensive tillage	0.0 – 0.1	3.80 ± 0.28	-25.34 ± 0.16	6
		0.1 – 0.2	2.69 ± 0.37	-24.92 ± 0.21	6
		0.2 – 0.4	1.63 ± 0.22	-24.82 ± 0.11	6
	Reduced tillage	0.0 – 0.1	3.68 ± 0.28	-25.26 ± 0.15	6
		0.1 – 0.2	2.80 ± 0.26	-24.66 ± 0.21	6
		0.2 – 0.4	1.94 ± 0.20	-24.73 ± 0.17	6

The $\delta^{13}C$ signature of the soil respiration CO_2 flux in May 2006 (prior to seeding of corn) determined with chamber measurements, IRMS and Keeling plot analysis ($\delta^{13}C_{R\text{-}SOIL}$) was similar to the surface $\delta^{13}C_{SOC}$ values and did not vary with tillage treatment (Table 3.3). The conservation of $\delta^{13}C_{SOC}$ with depth and relative concurrence of initial $\delta^{13}C_{R\text{-}SOIL}$ and $\delta^{13}C_{SOC}$ ($\delta^{13}C \approx$ -25 ‰) at the site indicates that the isotopic disequilibrium between soil respiration and bulk SOM often reported for forest ecosystems (Ehleringer et al., 2000; Boström et al., 2007) was not a significant issue for this mechanically and naturally well-mixed vertisolic agricultural soil.

Table 3.3 Stable C isotope ratio signatures of the soil respiration flux (mean $\delta^{13}C_{R\text{-}SOIL}$ ± 1 S.E.) and ranges of [CO_2] measured with chambers in the two tillage treatments prior to seeding of corn in 2006 and during the summer of 2007. The $\delta^{13}C_{R\text{-}SOIL}$ values were calculated as the mean y-intercept from chambers with minimum Keeling plot r^2 values of 0.8.

Date	Treatment	$\delta^{13}C_{R\text{-}SOIL}$ (‰)	[CO_2] range (μmol mol^{-1})	n
May 6, 2006	Intensive tillage	-25.61 ± 0.21	2098	12
	Reduced tillage	-25.59 ± 0.42	1760	8
July 9, 2007	Intensive tillage	-17.34 ± 0.28	3797	12
	Reduced tillage	-16.95 ± 0.48	6074	9

The total aboveground biomass at the end of the 2006 growing season (Table 3.4) was not statistically different between the tillage treatments (P = 0.19). The stable C

isotope signature of the corn CRC ($\delta^{13}C_{CRC}$) determined from aboveground biomass collected in October 2006 from the site was -12.70 ± 0.04 ‰ (±S.E., n = 12).

Table 3.4 Components of corn crop biomass C at the site at the end of the 2006 growing season. The total aboveground corn biomass produced during the growing season was calculated from hand-clipped samples taken prior to mechanical harvesting in October 2006. The amount of aboveground corn residue input to the cropland in each tillage treatment was taken as the difference between total aboveground biomass and the bulk grain removed (1230 kg C ha^{-1}, Chapter 2) from the system. Belowground biomass production was estimated assuming a shoot-to-root ratio of 5.6 for grain corn (Bolinder et al., 2007). Total crop residue input is the sum of aboveground residue input and estimated belowground biomass production.

Treatment	Aboveground biomass (kg C ha^{-1})	Aboveground residue input (kg C ha^{-1})	Belowground biomass (kg C ha^{-1})	Total crop residue input (kg C ha^{-1})	n
Intensive tillage	2760 ± 180	1530	490	2020	12
Reduced tillage	3030 ± 160	1800	540	2340	12

3.4.2 Trends in Soil Respiration and C Isotope Fluxes

The gap-filled mean daily ecosystem respiration (R) during the Fall 2006 measurement campaign was 2.8 ± 0.3 kg C ha^{-1} day^{-1} (± 1 S.E., n = 30) and 4.3 ± 0.5 kg C ha^{-1} day^{-1} (± 1 S.E., n = 30) for the RT and IT treatments, respectively. Mean daily R was greater for both tillage treatments during Spring 2007 compared to Fall 2006, with average values of 15.2 ± 0.7 kg C ha^{-1} day^{-1} (± 1 S.E., n = 26) and 14.9 ± 0.9 kg C ha^{-1} day^{-1} (± 1 S.E., n = 26) for the RT and IT plots at the site, respectively. The average stable C isotope ratio of the R ($\delta^{13}C_R$) at the site was more enriched in $^{13}CO_2$ ($\delta^{13}C_R$ less negative) relative to the indigenous SOC (Table 3.2) during both the Fall 2006 and Spring

2007 measurement campaigns, for both tillage treatments (Table 3.5), indicating that recently fixed corn CRC ($\delta^{13}C_{CRC}$ = -12.70 ± 0.04 ‰) was being oxidized. In comparison to the $\delta^{13}C_R$ values for the post-harvest Fall 2006 and Spring 2007 measurement campaigns (Table 3.5), the nighttime respiration signature of the maturing corn canopy in September 2006 (plant and soil respiration) was more enriched (Corn Crop 2006: $\delta^{13}C_R$ = -17.02 ± 0.6 ‰ (± 1 S.E.), n = 38). The relative enrichment in $^{13}CO_2$ was similar for the R flux from the IT and RT plots during both Fall 2006 (P = 0.41) and Spring 2007 (P = 0.44) measurement campaigns (Table 3.5). The relative enrichment in $^{13}CO_2$ was greater in Fall 2006 than Spring 2007 for the IT treatment (P = 0.03), and nominally but not significantly greater (P = 0.56) for the RT plots between the respective periods (Table 3.5).

Table 3.5 Stable C isotope ratio signatures of the ecosystem respiration (mean $\delta^{13}C_R$ ± 1 S.E.) and ranges of the vertical [CO_2] gradients measured over the two tillage treatments during the two post-harvest study periods.

Period	Treatment	$\delta^{13}C_R$ (‰)	$\Delta[CO_2]$ range (μmol mol^{-1})	n
Fall 2006	Intensive tillage	-17.97 ± 1.71	16	13
	Reduced tillage	-19.82 ± 1.92	21	16
Spring 2007	Intensive tillage	-22.25 ± 1.02	21	28
	Reduced tillage	-21.02 ± 1.11	29	29

Daily average R values from both tillage treatments corresponded with mean air temperatures at the site for both field campaigns (Figure 3.2). In Fall 2006 the general

trend was increasing daily R and air temperature from November 10 to November 22, peaking at approximately 8.6 kg C ha^{-1} $day^{-1}$and 13.3 kg C ha^{-1} day^{-1} for the RT and IT plots at the site, respectively. Following the maximum values for the Fall 2006 period, mean air temperature and R declined for the remainder of the field campaign, and the subsoil began freezing progressively with depth (Figure 3.2). In Spring 2007, mean daily R oscillated with air temperatures for both tillage treatments, and gradually increased towards the end of the period with the thawing of subsoil layers (Figure 3.2). Highest R values for the RT plots were observed on April 20, 2007 at 23.1 kg C ha^{-1} day^{-1}, a day with similar fluxes from the IT plots (22.3 kg C ha^{-1} day^{-1}; Figure 3.2). Peak fluxes from the IT plots occurred on the final day of the Spring 2007 measurement campaign, May 7, the day on which the mean air temperature was also the greatest (Figure 3.2), and were 23.3 kg C ha^{-1} day^{-1}, which is higher than R fluxes estimated from the RT plots (20.5 kg C ha^{-1} day^{-1}) on that day. The results of non-parametric rank sum tests of the daily R from the treatments revealed a significant difference between the RT and IT treatment plots for Fall 2006 ($P = 0.02$), and no significant difference for the Spring 2007 period ($P = 0.87$).

Values of $\delta^{13}C_R$, calculated from days with more than one 30-minute observation with sufficient vertical [CO_2] gradients from both tillage treatments, exhibited trends of increasing depletion of $^{13}CO_2$ with $\delta^{13}C_R$ becoming more negative over the duration of both field campaigns (Figure 3.2). The relationship between $\delta^{13}C_R$ and time (day) was fit with OLS linear regression for both measurement periods. The slope ± S.E. indicated a slight difference in the relative rate of $^{13}CO_2$ depletion between the RT ($\delta^{13}C_R$ = -0.26 (± 0.07) x day - 13.40 (± 1.25) ‰, $r^2 = 0.94$) and IT ($\delta^{13}C_R$ = -0.07 (± 0.11) x day - 15.33 (± 1.98) ‰, $r^2 = 0.3$) plots over the Fall 2006 period, however only the slope from the RT

treatment linear relationship was significant (P = 0.08). During the Spring 2007 campaign, the linear regressions of the relationships between $\delta^{13}C_R$ and time for the two treatments were similar for RT ($\delta^{13}C_R$ = -0.42 (± 0.12) x day – 16.69 (± 1.84) ‰, r^2 = 0.66) and IT ($\delta^{13}C_R$ = -0.56 (± 0.13) x day – 14.05 (± 1.97) ‰, r^2 = 0.77) plots at the site (Figure 3.2), and both slopes were significant (P < 0.01 for both the RT and IT plots).

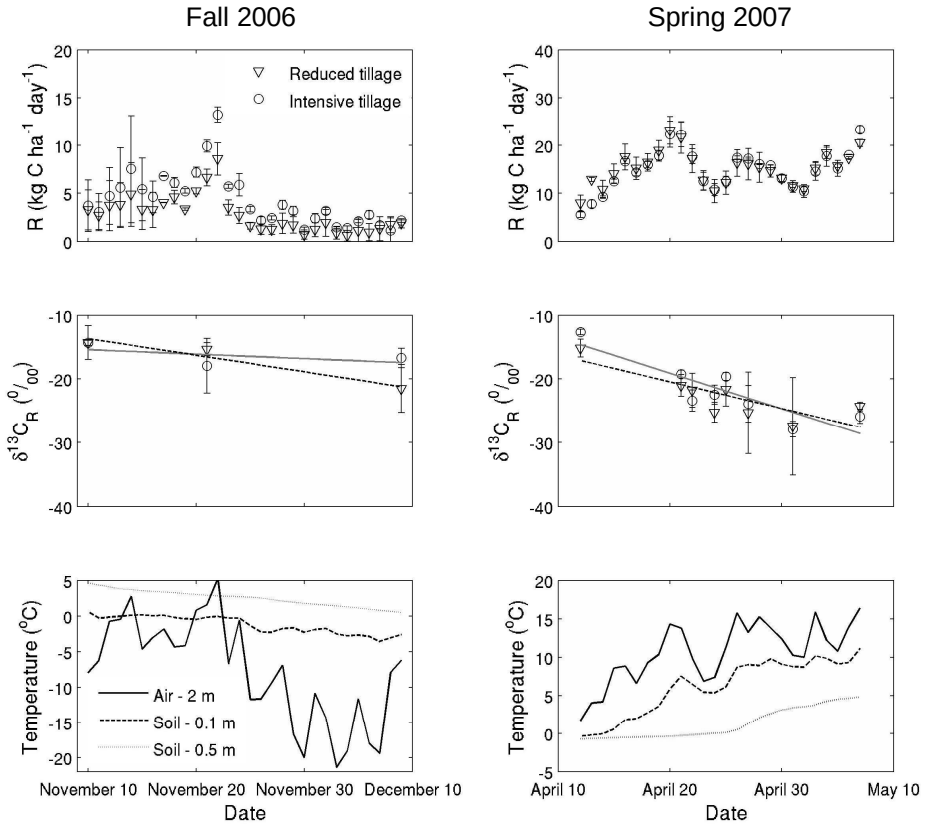

Figure 3.2 Time series of the gap-filled, average daily soil respiration (R ± 1 S.E.; top panels), the stable C isotope ratio of soil respiration ($\delta^{13}C_R$ ± 1 S.E.; middle panels), air (at 2 m height) and soil (at 0.1 m and 0.5 m depths) temperatures (bottom panels) at the site during the Fall 2006 and Spring 2007 non-growing season measurement campaigns.

The declining $\delta^{13}C_R$ values for both tillage treatments over time corresponded to decreasing air and soil temperatures during Fall 2006, and conversely, increasing air and

soil temperatures during the Spring 2007 measurement campaign (Figure 3.2). Positive correlations between daily $\delta^{13}C_R$ and mean temperatures for the RT treatment were significant ($P < 0.1$) for soil temperatures at 0.05 m ($r = 1.00$; $P = 0.04$), 0.1 m ($r = 1.00$; $P = 0.07$), and 0.2 m ($r = 1.00$; $P = 0.06$) depths during Fall 2006. Correlations between daily $\delta^{13}C_R$ and mean air and soil temperatures for the IT treatment were not significant ($P > 0.1$) during Fall 2006. Negative correlations between daily $\delta^{13}C_R$ and mean temperatures for the RT treatment were not significant ($P > 0.1$) for air temperature at 2 m height ($r = -0.56$, $P = 0.15$) or soil temperature at the 0.5 m depth ($r = -0.63$, $P = 0.1$), but were significant ($P < 0.1$) for soil temperatures at 0.05 m ($r = -0.77$; $P = 0.03$), 0.1 m ($r = -0.80$; $P = 0.02$), and 0.2 m ($r = -0.82$; $P = 0.01$) depths during Spring 2007. Negative correlations between daily $\delta^{13}C_R$ and mean temperatures for the IT treatment were significant ($P < 0.1$) for air temperature at 2 m height ($r = -0.63$; $P = 0.09$), and for soil temperatures at 0.05 m ($r = -0.84$; $P = 0.01$), 0.1 m ($r = -0.86$; $P = 0.006$), 0.2 m ($r = -0.89$; $P = 0.003$), and 0.5 m ($r = -0.75$; $P = 0.03$) depths during Spring 2007.

3.4.3 Component Soil Respiration Budgets

The cumulative total ecosystem respiration (ΣR) was three to four times higher over Spring 2007 than during the Fall 2006 measurement campaign, for both tillage treatments (Table 3.6; Figure 3.3). The ΣR was higher for the IT compared to RT plots at the site in Fall 2006, but the two treatments had a similar ΣR over Spring 2007 (Figure 3.3) or for the two periods combined (Table 3.6). The IT plots had a higher cumulative respiration derived from crop residue carbon (ΣR_{CRC}) than the RT treatment (Figure 3.3; Table 3.6), however, there was overlap between the propagated error estimates around

ΣR_{CRC} (Table 3.6). The RT plots had a lower cumulative respiration derived from native SOC (ΣR_{SOC}) compared to the IT treatment during Fall 2006, and a higher ΣR_{SOC} over Spring 2007 (Figure 3.3), however, there was overlap between the error estimates around ΣR_{SOC}, as there was for ΣR_{CRC}, indicating that an effect of tillage was not detectable (Table 3.6). Within the RT and IT treatments, ΣR_{CRC} and ΣR_{SOC} were different during each measurement campaign (according to ±1 S.E.), as were the changes in the ratios of ΣR_{CRC} : ΣR_{SOC} between the Fall 2006 and Spring 2007 periods. For the RT treatment, approximately 69 %, 24 %, and 32 % of total ΣR was derived from ΣR_{CRC} for the Fall 2006, Spring 2007, and for the two periods combined, respectively. For the IT treatment, approximately 71 %, 29 %, and 40 % of total ΣR was from ΣR_{CRC} for the Fall 2006, Spring 2007, or for the two periods combined, respectively.

Over Fall 2006, the general trends of ΣR, ΣR_{CRC}, and ΣR_{SOC} displayed by both tillage treatments was an increasing rate until November 22, followed by a decrease with the onset of colder temperatures and winter (Figure 3.3). In contrast, over Spring 2007, ΣR continued to increase with air and soil temperatures as the season progressed towards summer, however, the continued increase was driven by ΣR_{SOC}, as there was a leveling off of ΣR_{CRC} for both tillage treatments by the end of the measurement campaign (Figure 3.3). Estimates of the temporal trend of daily $\delta^{13}C_R$ over Spring 2007 (Figure 3.2) indicated no contribution of the corn CRC towards ΣR (or $\Sigma R = \Sigma R_{SOC}$) after May 2 for both the RT and IT plots (Figure 3.3).

Table 3.6 Components of the cumulative ecosystem respiration flux for the two tillage treatments at the site during the two post-harvest study periods. The cumulative ecosystem respiration (ΣR) was calculated from average daily values of R derived from partitioned and gap-filled net CO_2 flux measurements at the site (shown for stable C isotope study periods in the top panels of Figure 3.2; measurements and data analysis were described in Chapter 2). Daily values of $\delta^{13}C_R$ were estimated from OLS linear regressions between means from days with more than one 30-minute $\Delta^{13}[CO_2]$ / $\Delta^{12}[CO_2]$ observation obtained when the minimum $\Delta^{12}[CO_2]$ threshold was met for both tillage treatments and time (middle panels, Figure 3.2). The CO_2 fluxes derived from crop residue carbon (ΣR_{CRC}; middle panels) and resident soil organic carbon (ΣR_{SOC}; bottom panels) were calculated using a linear two-member mixing model and the estimated temporal trend in $\delta^{13}C_R$. Errors given are the root-sum-square error of the variables (ΣR, $\delta^{13}C_R$, and $\delta^{13}C_R$x time regressions) utilized for partitioning soil respiration (Section 3.3.5.2).

Period	Treatment	ΣR (kg C ha^{-1})	ΣR_{CRC} (kg C ha^{-1})	ΣR_{SOC} (kg C ha^{-1})
Fall 2006	Intensive tillage	129 ± 32	92 ± 29	37 ± 12
	Reduced tillage	84 ± 1	58 ± 9	26 ± 4
Spring 2007	Intensive tillage	388 ± 2	112 ± 22	276 ± 55
	Reduced tillage	396 ± 40	93 ± 19	303 ± 61
Fall & Spring	Intensive tillage	517 ± 129	204 ± 73	313 ± 113
	Reduced tillage	480 ± 48	151 ± 38	329 ± 85

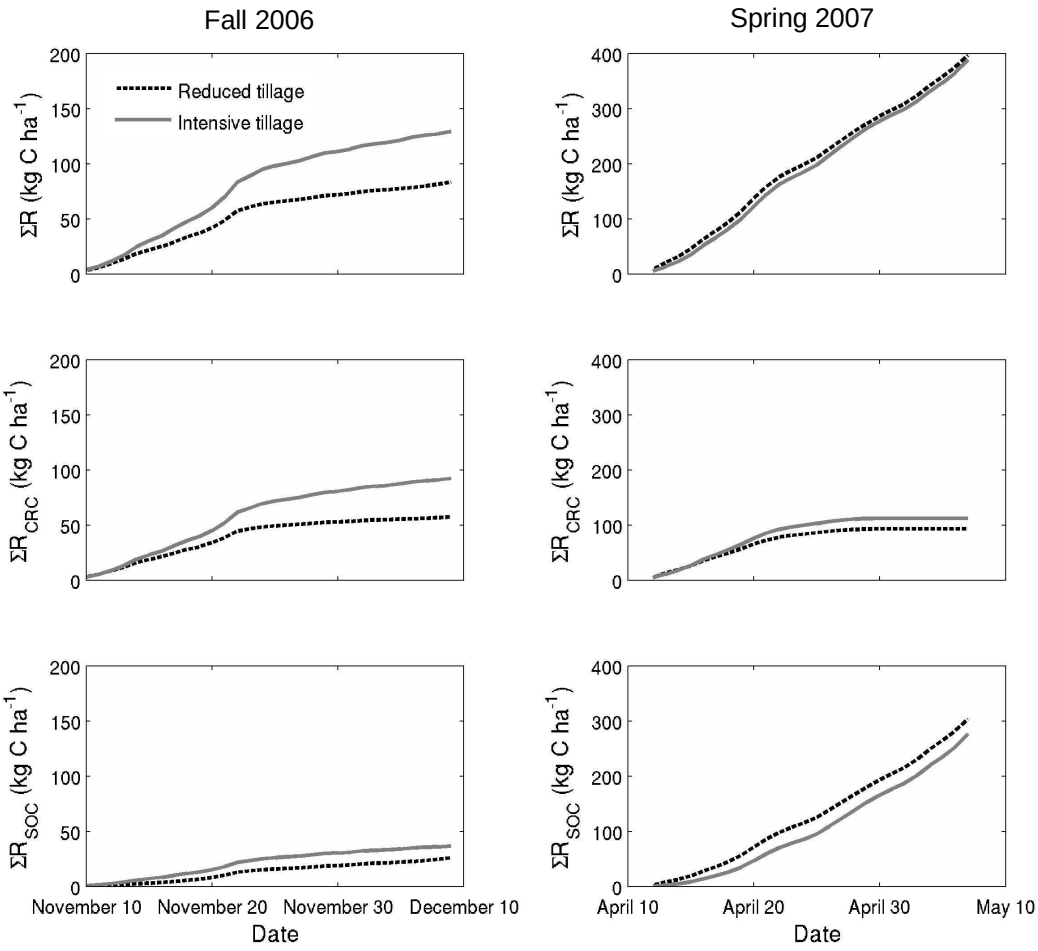

Figure 3.3 Components of the cumulative ecosystem respiration flux for the two tillage treatments at the site during the Fall 2006 and Spring 2007 study periods. Cumulative ecosystem respiration (ΣR; top panels) was calculated by summing average daily values of R derived from partitioned and gap-filled net CO_2 flux measurements at the site (measurements and data analysis were described in Chapter 2). The CO_2 fluxes derived from crop residue carbon (ΣR_{CRC}; middle panels) and resident soil organic carbon (ΣR_{SOC}; bottom panels) were derived from a temporal trend in the stable C isotope ratio of the soil respiration flux ($\delta^{13}C_R$; Figure 3.2).

3.5 Discussion

The average daily R and ΣR were higher for the intensive tillage (IT) compared to the reduced tillage (RT) treatment at the site during the Fall 2006 measurement campaign (Section 3.4.2), perhaps due to enhanced decomposition of organic matter following mechanical tillage and disking of the plots. Tillage has been shown to stimulate decomposition and decay of organic matter due to fragmentation and mixing of CRC with the top-soil (Schnürer et al., 1985; Aulahk et al., 1991; Neely et al., 1991; Beare et al., 1992; Garnier et al., 2003). However, this difference in R between tillage treatments was short-lived and relatively insignificant for the long-term C budgets at the site, as ΣR was three to four times higher over Spring 2007 than during the Fall 2006 measurement campaign, and similar in magnitude for both tillage treatments (Table 3.6; Figure 3.3).

The majority of ecosystem respiration following autumn harvest was due to the decomposition of recently fixed corn CRC (≈ 70%) compared to native SOC (≈ 30%). However, this trend did not persist into the following spring after winter, when a greater proportion of the respiration flux originated from indigenous C_3-derived SOC substrates (> 70%), with less originating from the C_4 tissue compared to the previous fall (Table 3.5; Table 3.6; Figure 3.3). From a study in southern Minnesota using similar micrometeorological methodology, the post-harvest $\delta^{13}C_R$ in the fall was dominated by a signature similar to that of the previously grown soybean (C_3) crop (Griffis et al., 2004). The following spring, the calculated $\delta^{13}C_R$ values fluctuated between a C_3 signature similar to that of the previously grown soybean crop and that of the ambient SOC (Griffis et al., 2005), which was a juxtaposition of C_3 and C_4 derived C and reflects the influence

of historic C_4 dry-land prairie and the contemporary corn-soybean rotation at the site. In a field campaign conducted with the same measurement system as the present study one year earlier in southern Ontario, 57 % and 25 % of the measured respiration flux during the post-harvest autumn originated from corn CRC for conventional and no-tillage plots, respectively (Drewitt et al., 2009). The following spring, the amount of heterotrophic respiration attributed to each substrate source for the conventional and no-tillage treatments declined to 22 % and 0 %, respectively (Drewitt et al., 2009). In the current study, there was no detectable difference between the two tillage treatments, with similar contributions of CRC to total respiration for both the Fall 2006 (71% for the IT plots and 69% for RT plots) and Spring 2007 (29% for the IT plots and 24% for RT plots) measurement campaigns. In this respect, both tillage treatments in the current study behaved in a similar fashion as the conventional tillage plots reported on by Drewitt et al. (2009). The similarity in the partitioning of heterotrophic respiration for the tillage treatments reported herein is most likely due to the early, transitional stage of the recently established RT plots in Manitoba (approximately one year old at the time of the study), which contrasts with the no-tillage plots in southern Ontario, which were over 6 years old when $\delta^{13}C_R$ measurements were made.

Measurements of daily $\delta^{13}C_R$ in both Fall 2006 and Spring 2007 indicated a decline in the contribution of the C_4 CRC to the respiration flux as the seasons progressed (Figure 3.2). In Fall 2006, this trend coincided with decreasing air temperatures and the progressive freezing of the soil horizon with depth. In contrast, during Spring 2007 the trend was correlated with increasing temperatures and the progressive thawing of the soil horizon with depth. The changing $\delta^{13}C_R$ values over both periods likely reflects

differences in the depth distribution of C_4-CRC and C_3-SOC sources contributing to total soil R at the site, with the C_4 substrates relatively concentrated near the soil surface. In Fall 2006, the top layers of soil froze first which may have caused the decrease in the contribution of corn CRC to the total R over time. In Spring 2007, the top layers of soil thawed first, while the soil was frozen at greater depths, gradually thawing as the season progressed, influencing daily $\delta^{13}C_R$ values in a similar manner as Fall 2006, even though the temporal trend in soil thermal regimes were opposite. By the end of the Spring 2007 period, prior to seedbed preparation and planting, 100 % of the respiration flux was apparently from native SOC sources, with no detectable contribution from the corn C_4-CRC (Figure 3.2; Figure 3.3), similar to spring measurements over no-tillage plots in southern Ontario (Drewitt et al., 2009). Of course, the corn residue left behind following grain harvest (Table 3.4) had not been completely decomposed by May 2007, but perhaps the most labile fraction of the above and belowground necromass had been exhausted as an energy source. Corn stover (cobs, stalks, etc.) was still present on the surface at the site for the following two growing seasons (faba in 2007 and wheat in 2008) and the C_4-C would have further contributed to total ecosystem respiration during those cropping periods. Indeed, chamber soil respiration measurements during the summer of 2007 indicated a shift in the C substrate contributing to $\delta^{13}C_R$ compared to the final period of micrometeorological measurements in early May 2007, with a C_4 influence detectable (Table 3.3).

The stable C isotope signature of atmospheric [CO_2] sources at the site and surrounding vicinity derived from the Keeling plot method did not detect a difference between the Fall 2006 and Spring 2007 periods (Table 3.1). The discrepancy between the

Keeling plot method ($\delta^{13}C_{KEELING}$, Table 3.1) and the flux-ratio ($\delta^{13}C_R$, Table 3.5) method has been noted by other researchers (Griffis et al., 2005; Zhang et al., 2006; Drewitt et al., 2009), as the former is based on concentrations which have a much larger footprint contributing to point measurements than a flux based approach (Griffis et al., 2007). In the current study, the footprint for $\delta^{13}C_{KEELING}$ would have overlapped between the tillage treatments and extended beyond the area of the experimental field. In contrast, the footprint for $\delta^{13}C_R$ was constrained to each of the four (two intensive tillage and two reduced tillage) experimental plots of interest at the site. The $\delta^{13}C_{KEELING}$ signatures (Table 3.1) did not reveal any influence of C fixed by the corn crop on the ambient [CO_2] measured at the site during Fall 2006 or Spring 2007, but were very similar to the value for the indigenous SOC (Table 3.2). This suggests that the calculated $\delta^{13}C_{KEELING}$ values were mainly the cumulative result of soil respiration from the site, neighboring C_3 croplands and nearby natural ecosystems, although anthropogenic combustion sources in the region may have also contributed to the Keeling plot signatures and their influence cannot be ruled out or distinguished.

3.6 Conclusions

Non-growing season ecosystem respiration rates were found to be higher from intensive tillage than reduced tillage plots in the fall of 2006 following corn harvest. However, during the following spring respiration fluxes were significantly higher and similar in magnitude for the two tillage treatments, resulting in equivalent cumulative

CO_2 budgets over the non-growing season periods studied. The stable C isotope signatures of ecosystem respiration from the two tillage treatments were similar in both fall 2006 and spring 2007, indicating that the relative proportion of C substrate sources (CRC vs. SOC) contributing to the total respiration flux were not significantly different. Both tillage treatments had a higher amount of C oxidized that was derived from C_4-CRC than C_3-SOC in fall 2006, whereas the stable C isotope signature of ecosystem respiration was dominated by the native SOC signal in the spring of 2007. This indicates that the most labile fraction of C_4-CRC from the previously grown crop had turned over during the six month period although corn residues remained in the system and contributed to the total respiration flux during the following summer and crop years.

3.7 Acknowledgements

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4. NITROUS OXIDE EMISSIONS FROM AN ANNUAL CROP ROTATION IN THE RED RIVER VALLEY, MANITOBA, CANADA

4.1 Abstract

Nitrous oxide (N_2O) emissions were measured using the flux-gradient micrometeorological method over three years (2006–2008) in an annual (corn – faba - spring wheat) crop rotation located within the Red River Valley, Manitoba, Canada. The N_2O vertical gradient was measured using tunable diode laser absorption spectrometry to estimate 30-min-average the net N_2O flux sequentially over each of four 4-ha plots. Measurements were used to determine reduced and intensive tillage treatment effects in 2006 and 2007 and continued for intensively tilled plots in 2008 to determine cumulative N_2O flux over the three study years. Annual gap-filled N_2O budgets were 5.5, 1.4, and 4.3 kg N ha^{-1} in the corn, faba and spring wheat crop years, respectively. Emissions from fertilizer nitrogen addition and soil thaw the following spring were responsible for the greater cumulative flux in the corn and spring wheat years. A recent conversion from intensive tillage to a reduced tillage practice showed no difference in N_2O emissions because of relatively large variability among the experimental plots. Using three approaches to approximate the background cumulative annual N_2O emissions for the site resulted in estimates of 3.5–3.8% and 1.4–1.8% of applied fertilizer N being emitted for the corn and spring-wheat crop years, respectively. The results indicate that the Red River Valley may need revised coefficients for estimating direct soil N_2O emissions from fertilizer N compared to other soils on the Prairies.

4.2 Introduction

Nitrous oxide (N_2O) is an important atmospheric pollutant that is a greenhouse gas (GHG) in the troposphere, and contributes to the destruction of ozone in the stratosphere (Forster et al., 2007). With a long residency time in the troposphere, combined with unique radiative properties of the N_2O molecule, this trace gas has a global warming potential (GWP) over 100-years that is approximately 300 times that of carbon dioxide (CO_2). The agricultural sector is estimated to be the largest anthropogenic source of N_2O to the atmosphere, the majority of which is attributed to biogeochemical transformations of nitrogen (N) added to cropland soils (Forster et al., 2007; Smith et al., 2007; Davidson, 2009). Projections of future human population dietary requirements and trends (increasing rate of meat consumption) indicate that N_2O emissions will increase as a result of greater synthetic fertilizer and manure application to soils, unless effort is exerted to reduce this source (Smith et al., 2007; Davidson, 2009).

There are two major processes that contribute to N_2O emissions from soils: nitrification and denitrification (Focht and Verstraete, 1977). Nitrification is the aerobic oxidation of ammonium (NH_4^+) to nitrite (NO_2^-) and NO_2^- to nitrate (NO_3^-). Soil nitrification is mostly carried out by chemoautotrophic bacteria, although heterotrophic nitrification is known to occur (Focht and Verstraete, 1977; Prosser, 1989; Robertson and Groffman, 2007). Nitrifying bacteria have also been shown to produce NO and N_2O, as gaseous "losses" or side products from the nitrification process (Prosser, 1989; Davidson, 1992). The major environmental factors known to influence nitrification are oxygen (O_2) availability and pH (Focht and Verstraete, 1977). Nitrification is the result of microbial aerobic respiration, therefore it only occurs under sufficiently oxic conditions. The

optimum soil pH for nitrification is between 6.6 and 8.0 (Prosser, 1989). During the growing season in agroecosystems, much of the NO_3^- produced via nitrification is taken up by the actively growing crop and microbial biomass (Focht and Verstraete, 1977). However, because NO_3^- is an anion, it is present in soil water unassociated with soil constituents, and can be readily lost out of the system through leaching and denitrification (Focht and Verstraete, 1977; Prosser, 1989; Robertson and Groffman, 2007), especially during shoulder seasons lacking crop cover, which has tremendous implications for N conservation in agricultural soils.

Denitrification is the reduction of oxidized forms of N, an integral part of the global biogeochemical N cycle as the primary mechanism that returns dinitrogen (N_2) gas to the atmosphere, and occurs via both physical-chemical and biological means. Chemodenitrification is a non-enzymatic process where NO_2^- is dismutated to nitric oxide (NO) and N_2 (Robertson and Groffman, 2007). It can occur through several abiotic chemical pathways, however, chemodenitrification is not believed to play an important role in net N_2O emissions from soils compared to biological denitrification (Beauchamp, 1997; Chapin et al., 2002; Robertson and Groffman, 2007). The majority of biological denitrification that takes place in agricultural soils is the result of facultative anaerobic microbial metabolism. This type of denitrification refers to the sequential dissimalatory respiratory reduction of oxygen containing N compounds (NO_3^-, NO_2^-, NO, N_2O) via electron transport phosphorylation when O_2 is limiting, and is carried out by many genera of bacteria (Focht and Verstraete, 1977; Zumft, 1997). Denitrification is therefore intrinsically linked to nitrification rates in soils which produces the substrate NO_3^- (Focht and Verstraete, 1977; Prosser, 1989). In anaerobic environments, denitrifiers generate energy as adenosine tri-phosphate (ATP) by transferring electrons (e^-) from an organic or

inorganic source (e^- donor) through the cytochrome system to NO_3^-, NO_2^-, or gaseous N oxides (e^- acceptor). There are four microbial enzymes utilized in the process, each a unique type of oxide reductase. The reductase enzymes act in consortium, decreasing the oxidation state of a series of nitrogen intermediates decrementally. Most denitrifying bacteria possess the ability to produce a suite of reductases and are capable of completing the entire reductive sequence, or any distinct portions of it (Zumft, 1997), depending on substrate availability and environmental conditions. As a result of this biochemical complexity, denitrification occurs to varying degrees of completion in agricultural soils, and the e^- acceptors of lower oxidation states often go unused by the microbial community and are released to the soil solution (NO_2^-) and atmosphere (NO and N_2O). Although the potential exists for three gaseous denitrification products to be released to the atmosphere, N_2O and N_2 are regarded as the most substantial species released during the process. There is considerable variation in the reported relative amounts of N_2O and N_2 emitted during biological denitrification in soils (Aulakh et al. 1992; Beauchamp, 1997), with the mole fraction of the gases varying from 0 to 1, depending on soil moisture conditions (O_2 availability). With decreasing oxidation-reduction potential, a higher proportion of soil denitrification proceeds completely through to N_2 gas. Other factors that control the relative abundance of end products from soil denitrification are the ratio of oxidant (nitrate) to reductant (organic or inorganic e^- donor), soil pH, and temperature (Chapin III et al., 2002).

For biological denitrification to occur in soils, a number of conditions must be met. As O_2 is a superior terminal e^- acceptor (yields more energy), denitrification is restricted to sufficiently anoxic sites and a N oxide must be present to act as an oxidant (Zumft, 1997). A reductant must also be present, such as an organic C source (for

organotrophs), or S, HS^-, and NH_4^+ for lithotrophic microorganisms (Richards, 1987). Most denitrification in agricultural soils is carried out by organotrophic microorganisms, so the reaction is linked to decomposition processes, and highly dependent on the quantities and quality of soil organic C pools (Aulakh et al., 1991; Beauchamp, 1997; Robertson and Groffman, 2007). Soil denitrification is mainly a function of the within-site content or status of these essential factors (anaerobiosis and the presence of appropriate e^- donors and acceptors), as affected by process-regulating abiotic and biotic controls (Beauchamp, 1997). Climate exerts a significant influence on soil denitrification; precipitation dictates soil moisture levels and O_2 availability, while temperature affects denitrification rates directly and indirectly. The direct effect of temperature on denitrification is similar as for other biochemical reactions, in that an exponential relationship of increasing reaction rates with increasing temperature is found (Focht and Verstraete, 1977). Increasing temperature also affects denitrification indirectly by decreasing the solubility of N_2O and O_2 in the soil aqueous phase (Grant and Pattey, 2003). Another effect of climate on N_2O emissions that occurs in northern temperate regions is the occurrence of substantial fluxes during spring snowmelt and soil thaw (Nyborg et al., 1997; Wagner-Riddle and Thurtell, 1998; Grant and Pattey, 1999; van Bochove et al., 2000; Pattey et al., 2007; Wagner-Riddle et al., 2007; Pattey et al., 2008), a process that is currently not well understood or modelled, but generally attributed to biological denitrification (Rover et al., 1998; Wagner-Riddle et al., 2008; Tenuta, 2010). An earlier hypothesis to explain this phenomenon partly attributed the significant observed spring thaw burst to N_2O produced and accumulated at depth over the winter being released as ice barriers in soil layers thawed (Goodroad and Keeney, 1984; Burton and Beauchamp, 1994). Recent studies have indicated that the majority of these N_2O

fluxes are more likely due to enhanced denitrification in the near surface layer of the soil during thawing periods (Furon et al., 2008; Wagner-Riddle et al., 2008; Tenuta, 2010). Mechanisms proposed to explain the phenomenon include a combination of factors that increase the denitrification product ratio of N_2O:N_2 (Tenuta, 2010), increase substrate (e^- donor and acceptor) availability (van Bochove et al., 2000; Teepe et al., 2001), and the presence of water-saturated surface soil as snow melts and frozen subsoil impedes drainage (Nyborg et al., 1997).

The Government of Canada ratified the United Nations Framework Convention on Climate Change (UNFCC) in 1992 and the Kyoto Protocol in 2002 (Environment Canada, 2008; UNFCC, 2009 and 2010). In compliance with Article 5, paragraph 1 of the Kyoto decisions (United Nations, 1998), which required Annex I Parties (developed countries) to have "a national system for the estimation of anthropogenic emissions by sources and removals by sinks of all greenhouse gases not controlled by the Montreal Protocol" in place by 2007, Canada submits an annual inventory of all anthropogenic GHG sources and sinks in the nation-state to the UNFCC secretariat (Environment Canada, 2008). Following recommendations from the Intergovernmental Panel on Climate Change (IPCC, 2006) and permission from the UNFCC, Canada estimates direct N_2O emissions from cropland soils using a Tier II (country-specific) approach instead of using the original or revised default Tier I methodology (ie. 1 – 1.25 % of applied N released as N_2O-N on an annual basis). The Tier II methodology estimates direct soil N_2O emissions at finer spatial and temporal scales than the IPCC default from baseline regional emission-factor relationships between annual cumulative N_2O flux and N application rate, modified by climatic data (ratio of precipitation to potential evapotranspiration), topographic landscape positions, soil texture and management

practices (Environment Canada, 2008; Rochette et al., 2008a). Mean direct soil N_2O emission estimates from 1990 – 2005 using the Tier II approach were found to be lower and higher than the original and revised IPPC default (Tier I) methodologies, respectively (Rochette et al., 2008b). The Tier II inventory indicates that the application of fertilizer N was the largest source of direct soil N_2O emissions in Canada over the 15-year period, and that emissions from the source have increased by over 20 % since 1990 (Environment Canada, 2008; Rochette et al., 2008b). The emission of N_2O from cropland soils accounted for approximately half of the GHG source from the 8 % contribution of the agriculture sector to the national inventory (Environment Canada, 2008).

Although the more detailed Tier II approach is a great improvement on previously used methodology for estimating the national soil N_2O emission inventory, emission-factors are derived from a limited number of experiments. This highlights the need for more reliable measurements of the net flux of N_2O from agroecosystems, to help refine and revise estimates for regional inventories, particularly for contributions related to hydrology, soil texture, climate, and management activities. For example, some agricultural soils may sequester atmospheric carbon dioxide with the implementation of conservation tillage management (West and Post, 2002), but it remains unclear how tillage practices devised to increase the C sink strength of soils may affect net N_2O fluxes. Recent studies report both increased (Six et al., 2004; Rochette, 2008; Kong et al., 2009; Tan et al., 2009) and decreased (Wagner-Riddle et al., 2007; Rochette, 2008; Ussiri et al., 2009) rates of N_2O emissions with adoption of conservation tillage practices, with various explanations provided for observations. The Canadian Tier II methodology for the estimation of direct N_2O emissions from agricultural soils uses a correction factor related to tillage practices. The tillage ratio factor results in higher and lower rates of N_2O flux

for eastern Canada (provinces of Ontario and Quebec) and the western Prairies (provinces of Alberta, Saskatchewan and Manitoba), respectively, when no-till and reduced tillage techniques are used on cropland (Environment Canada, 2008; Rochette et al., 2008a). More field studies with robust measurements could lead to a better understanding of the role of tillage intensity and other management activities on the regulating controls of N_2O fluxes and the coupling to organic C cycling in cropland soils, which is required for complete elucidation of net GHG budgets and predicting impacts of global change phenomena and land-use decisions.

The majority of direct measurements of N_2O exchange between agricultural ecosystems and the atmosphere have been conducted with soil chamber or cover (enclosure) techniques. For example, time-dependent head-space samples obtained from chambers (with a syringe) can be readily analyzed for N_2O concentrations with electron capture detector gas-chromatography (Aulakh et al., 1992). However, there is significant spatial-temporal variability in measured N_2O fluxes under field conditions (Rover et al., 1999; Pattey et al., 2007; Dunmola et al., 2010) that is difficult to capture with chambers due to limited replication. Furthermore, using chamber techniques can physically disrupt and alter the micro-climate around the experimental area and within the enclosed volume, potentially introducing biases and artifacts to studies. Chambers are challenging to deploy and sample during the winter and early spring in temperate climates, so there is limited *in situ* field measurements of spring thaw N_2O emissions. Lastly, recent studies have indicated that plants can also be a source of N_2O, either through physiological mechanisms or as the result of soil-generated N_2O released to the atmosphere via the transpiration stream (Pihlatie et al., 2005a), indicating that soil chamber measurements may underestimate true ecosystem emissions.

Tower-based micrometeorological methods provide an alternative method for obtaining the net exchange of N_2O between the surface and the atmosphere (Denmead, 2008). Micrometeorological techniques enable the continuous quantification of net cropland-atmosphere N_2O exchange, integrated over the landscape scale. Such methods can enable workers to overcome two of the greatest challenges to accurately estimating N_2O fluxes at meaningful landscape and regional scales- spatial and temporal heterogeneity. In recent decades, the net flux of N_2O between the surface and lower atmosphere has been evaluated with a variety of micrometeorological techniques (eg. flux-gradient, eddy covariance, relaxed eddy accumulation, nocturnal boundary layer methods) in agricultural (Christensen et al., 1996; Wagner-Riddle et al., 1997; Grant and Pattey, 1999; Laville et al., 1999; Kelliher et al., 2002; Grant and Pattey, 2003; Pattey et al., 2007; Phillips et al., 2007; Wagner-Riddle et al., 2007; Pattey et al., 2008; Denmead et al., 2010; Desjardins et al., 2010), natural (Pihlatie et al., 2005b), and urban (Famulari et al., 2010) environments.

The emission-factors derived for the Canadian Tier II inventory are mainly based on growing season chamber (small-enclosure) flux campaigns, but do consider data from a few continuous tower-based micrometeorological studies conducted in southern Ontario. Like most Annex I Parties, there are a limited number of continuous, field-scale N_2O flux measurements in Canada, particularly from the Prairies (agricultural regions in the provinces of Alberta, Saskatchewan, and Manitoba) where the emission-factors were developed entirely from chamber studies. There is also a geographical bias in the flux measurements used to derive the Prairie region emission-factors, because the majority of experiments used were conducted in Alberta and Saskatchewan, with limited available data from Manitoba. With a relatively small population and low industrial emissions,

Manitoba is unique in the Canadian context, in that agriculture rivals the transportation sector and is the second largest GHG source, accounting for an estimated 33.3 % of the 2007 provincial inventory, the majority of which is attributed to soil N_2O emissions (Manitoba Agriculture, Food and Rural Initiatives, 2010). Clearly more field-scale data will benefit policy-makers and GHG inventories in Manitoba and Canada.

In the present study, the net flux of N_2O between the surface and atmosphere was independently evaluated from separate micrometeorological towers in the same agricultural field, over a period of three crop seasons. The net flux of CO_2 between the surface and atmosphere for the same field and period was reported in Chapter 2. This chapter reports on findings from the first tower-based micrometeorological N_2O flux study conducted in western Canada, and the only field-scale investigation to examine freeze-thaw N_2O emissions from the vertisolic clay soil of the Red River Valley floodplain of southern Manitoba. Research queries addressed were: what effect does reduced tillage practices have on N_2O fluxes during a transition from intensive cultivation? What is the influence of crop management (species grown and production inputs used) and climate on field scale N_2O emissions during the growing season in the region? How significant are spring thaw emissions of N_2O for this soil and climatic zone and how are they modulated by substrate availability, air and soil temperature? How do annual cumulative N_2O emissions compare to estimates used for national GHG inventories? And how much do the N_2O emissions offset the net CO_2 fluxes measured at the site when expressed as global warming potential equivalents?

4.3 Materials and Methods

4.3.1 Site Description

The experimental field (49.64°N, 97.16°W; 235 m a.s.l.) where N_2O flux measurements were performed was located at the University of Manitoba Glenlea Research Station, approximately 16 km south of Winnipeg, Manitoba, Canada. The research site was situated in the Red River Valley, a near-level to very gently sloping (0 to < 2 % slope, typically < 1 m km^{-1}), glaciolacustrine clay floodplain. The soils at the site were of the Red River association, consisting of a combination of Osborne clay and Red River clay soil series depending on local drainage characteristics and the micro-relief of the landscape (Ehrlich et al., 1953; Michalyna et al., 1971). The hydrology ranges from poorly (micro-lows, Osborne clay series) to imperfectly (micro-highs, Red River clay series) drained soils. The Red River clay soil series is classified as a Gleyed Humic Vertisol (Canadian system) or a fine smectitic frigid Typic Epiaquert (USDA system), while the Osborne clay series is classified as a Gleysolic Humic Vertisol (Canadian system) or a fine smectitic frigid Typic Endoaquert (USDA system). The average bulk density and soil organic carbon content of the surface (0 – 0.2 m) layer of soil when the study was initiated were approximately 1.2 Mg m^{-3} and 3.2 %, respectively. The pH was 6.2 and there was an absence of carbonate minerals in the surface layer. The particle size distribution was 60 % clay, 35 % silt and 5 % sand.

4.3.2 Agronomic History

Details of the agronomic history and management practices at the site during the study period were given in Chapter 2, Section 2.3.2. An abbreviated version follows

herein. After a fallow year that included weed management by tillage and chemical means in 2005, different soil management treatments were initiated in the spring of 2006 with the establishment of four 200 m by 200 m (4 ha each, or 16 ha area total) experimental treatment plots inside of a larger 30 ha field. Two plots were managed as intensive tillage (IT) treatments and two plots were managed as reduced tillage (RT) treatments. The IT plots were tilled in April 2006 and all plots were sown to corn (*Zea mays* L. cv 'DKC27-12 (Roundup Ready®)', DEKALB®) on May 16. A granular fertilizer blend (32-25-10-10, N-P-K-S; Viterra Inc.) was side-banded with the seed at planting at a rate of 185 kg ha^{-1} (60 kg N ha^{-1}). Granular urea (46-0-0) was broadcast applied at 110 kg ha^{-1} (50 kg N ha^{-1}) on May 17 and lightly tine-harrowed to incorporate into the soil on all plots; herbicide was applied on June 13, 2006. Grain was harvested from all plots on October 6, and on October 25, 2006 standing aboveground corn biomass (stalks and leaves) on all plots was shredded with a flail-mower. The IT plots were double-disced on October 27 and tilled on October 28, 2006. After cultivating the IT treatment and harrowing all plots on May 9, 2007, faba (*Vicea faba minor* L. cv 'CDC Blitz', Crop Development Centre, University of Saskatchewan) was planted to all plots on May 11. A self-adhering peat-powder inoculant (Becker Underwood Canada Ltd., Saskatoon, Saskatchewan) was hand applied as the faba bean was being augered into the seeder. No fertilizer or herbicide was applied to the faba crop. The faba crop was harvested on August 27, post-harvest herbicide was applied to all plots on September 6, and the IT plots were double-disced on October 25, 2007. In spring 2008, the tillage treatment comparison was discontinued at the site. Only the two IT plots remaining in annual crop production during 2008 were considered for the purposes of this study. On May 16, 2008 the plots were cultivated and tine-harrowed. Wheat *(Triticum aestivum* L. cv '5602 RS - Hard Red Spring', Viterra (Proven® seed) Inc.) was sown to the

annual plots on May 21, and a granular fertilizer blend (60-10-0, N-P-K) was side-banded with the seed at planting at a rate of 165 kg ha^{-1} (100 kg N ha^{-1}). Herbicide was applied on June 23 and grain was harvested on September 16, 2008. Straw from the crop was subsequently baled and the plots were cultivated on November 3, 2008.

4.3.3 Nitrous Oxide Flux Measurements

Micrometeorological equipment to measure net N_2O fluxes from the four plots was deployed at the site beginning in August 2005. A tunable-diode-laser based trace gas analyzer (Model TGA100A, Campbell Scientific Inc., Logan, Utah, USA) was installed inside a grid-powered instrumentation trailer located in the centre of the four experimental plots. The air temperature inside the trailer was kept at approximately 20°C for the duration of monitoring with electric heat and air-conditioning as required. The laser and associated optical hardware and electronics for the trace gas analyzer (TGA) were further housed within an insulated, temperature-controlled enclosure. The lead-salt tunable-diode-laser of the TGA (Model IR-N2O/CO2, Laser Components GmbH., Olching, Germany) was operated at a cryo-cooled temperature of -189.15°C in a dual-ramp, jump-scanning mode (eg. Fried et al., 1993) and parameterized for the concurrent measurement of atmospheric concentrations of N_2O and CO_2 at a frequency of 10 Hz.

The flux gradient (FG) micrometeorological technique was used to determine the net exchange of N_2O between the soil-crop system and the lower atmosphere over 30-minute intervals. Using the FG method, the flux of N_2O between a crop system and the lower atmosphere (F_N) can be represented as:

$$F_N = -K \frac{\Delta[N_2O]}{\Delta z}$$

where, K is the turbulent transfer coefficient or "eddy diffusivity" for N_2O, $\Delta[N_2O]$ is the concentration gradient of N_2O in the surface layer, and Δz is the vertical distance between N_2O concentration observation heights (0.65 m).

The eddy diffusivity (K) term was estimated using a similarity theory, eddy covariance based aerodynamic method (Monteith and Unsworth, 2008). A three-dimensional sonic anemometer-thermometer (CSAT-3, Campbell Scientific Inc., Logan, Utah, USA) was mounted within the surface layer to an instrumentation tower in each tillage treatment and used to calculate the covariances required to estimate K (friction velocity (u_*) and vertical sonic temperature flux). Integrated similarity functions were applied to correct K calculations for dynamically stable and unstable atmospheric conditions based on the Obukhov length (Denmead, 2008). Linear regressions between the sonic anemometer-thermometer from each management treatment indicated no significant difference (slope = 1 ± 10 %) in 30-minute K values over the course of the study (Appendix A), so the average value was used for flux calculations. Equality in the turbulent transport of momentum, heat, and mass was assumed. Snow depth, stubble and crop height (h_c) were measured manually with a ruler or a tape twice-weekly to weekly during the course of the study. These surface parameter records were used to estimate the zero-plane displacement height (d) and calculate the effective observation heights (z - d) to be used in the evaluation of stability corrections and determination of K. For periods of snow cover, d was assumed to be equal to the depth of snow, during the rest of the year it was assumed to be $0.66h_c$ (Garratt, 1992; Denmead, 2008) and interpolated between periods when manual surface observations were made.

For the calculation of $\Delta[N_2O]$, two stainless steel gas sample intakes (12.5 mm internal diameter (i.d.)) were mounted at different heights within the atmospheric surface layer to a triangular, aluminum instrumentation tower located at the approximate centre of each experimental plot. Care was taken to ensure a balance between measuring gradients far enough above the surface to minimize roughness sub-layer effects but low enough to contain the flux footprint to each experimental plot of interest. Because of the large size of the experimental plots (4 ha) and location of the FG towers in the centre, fetch to effective observation height ratios of approximately 90:1 to 100:1 were generally maintained for all plots, in all cardinal directions during monitoring. Further details of the sampling and control system utilized, and additional theoretical considerations noted were reported in Chapter 2.

4.3.4 Supporting Environmental Measurements

A weather station was located at the site near the centre of the four plots on an undisturbed, grassed area. The following is a description of the meteorological instruments used in this study. Air temperature and relative humidity were measured with a combined probe (Model HMP45C, Vaisala Inc., Woburn, Massachusetts, USA) mounted within a radiation shield (Model 41003-5 10-Plate Gill Radiation Shield, R.M. Young Company, Traverse City, Michigan, USA) 2 m above the ground surface to a tripod stand (Model CM110 Tripod and Grounding Kit, Campbell Scientific Inc., Logan, Utah, USA). A cumulative precipitation gauge (Model T-200B Series Precipitation Gauge, Geonor Inc., Milford, Pennsylvania, USA), was installed approximately 3 m away from the main weather station tripod on an independent pedestal. A soil temperature

profile consisting of 6 thermistors (Model 107B Soil/Water Temperature Probe, Campbell Scientific Inc., Logan, Utah, USA) with measurements at 0.02 m, 0.05 m, 0.1 m, 0.2 m, 0.5 m and 1 m depths was placed into the solum. Station pressure was measured with a barometric pressure sensor (Model 61205, R.M. Young Company, Traverse City, Michigan, USA) that was mounted within a fibreglass enclosure housing a datalogger, with the pressure port vented to the outside environment with a piece of PVC tubing. Weather station data were recorded by a programmed datalogger (Model CR1000, Campbell Scientific Inc., Logan, Utah, USA) at a frequency of 0.1 Hz.

Six soil samples from the 0 to 0.3 m depth were taken from each of the four plots at bi-weekly to monthly intervals between April and November of each study year. The six benchmark sample locations were randomly selected within the flux footprint of each plot, and repeatedly sampled for the duration of the study. Samples were kept on ice in an insulated chest while in the field and during transport prior to the laboratory. The samples were dried at 40^{o}C for 48 to 72 hours in a drying room before being ground and passed through a 2 mm mesh screen. The air-dried and screened soil samples were extracted with a 2 M KCl solution at a 5:1 extractant to soil ratio. Concentrations of NH_4^+-N and NO_3^--N in the extract were determined by the automated phenate and copperized cadmium reduction to nitrite methods, respectively, with a Technicon^{TM} Autoanalyzer II (Pulse Instrumentation Ltd., Saskatoon, SK, Canada). The concentrations of mineral N were expressed as mg kg^{-1} dry soil after correcting the air-dried moisture content based on oven-dried sub-samples.

4.3.5 Data Analysis

4.3.5.1 Data Filtering and Processing Missing TGA and sonic data occurred during periods of field operations (tillage, seeding, and harvest), system maintenance, mechanical malfunction and power disruptions. Significant ongoing systematic gaps that caused data removal were system maintenance and a turbulence threshold based on u_*. A liquid nitrogen dewar cooled the laser and required re-filling twice per week. The data recorded during re-filling episodes and for the following hour were discarded from further analysis due to the influence of resulting vibrations and temperature perturbations inside the enclosure on gas concentration determinations. Other less frequent examples of system maintenance introducing gaps to the flux time series included: changing the atmospheric sample pump oil and parts, replacing the TGA reference gas cylinder; raising sample intakes; performing gradient and timing tests; and changing air filters. After discarding data due to system maintenance and mechanical malfunctions, average 30-minute [N_2O] data coverage from the TGA was approximately 75 % for the duration of the three-year study. When including quality turbulence data from the sonic anemometer-thermometers (complete high-frequency half-hour time-series, no diagnostic warnings), data available for the calculation of net N_2O fluxes was approximately 66 % of possible half-hours.

Filters were applied to the half-hourly time series to assure the N_2O flux data was of high quality. Trace gas concentration data ([N_2O]) were rejected when the TGA operating temperature and pressure were outside of acceptable ranges (±0.5°C and ±2 kPa, respectively). The concentration gradient ($\Delta[N_2O]$) data were rejected if the difference in the internal operating system pressure when switching between upper and

lower intakes was greater than 5 Pa. Aerodynamic fluxes were rejected if the standard deviation of the 30-minute mean upper or lower intake [N_2O] was greater than 20 ppb, and when the mean u_* was less than thresholds previously determined acceptable for CO_2 fluxes at the site (Chapter 2). It was not possible to independently determine u_* thresholds for F_N due to the episodic and short-lived nature of events, and the log-normal distribution of fluxes during the years where the site received synthetic fertilizer (2006 and 2008), although visual inspection of the faba year (2007) data indicated a u_* threshold close to 0.1 m s^{-1} (data not shown) was appropriate. Similarity was assumed for the surface-layer behavior of CO_2 and N_2O, therefore the u_* threshold filters determined for the former were deemed adequate and applied to the latter. This approach resulted in u_* thresholds of: 0.15 m s^{-1} and 0.12 m s^{-1} for the corn growing season and non-growing season respectively; 0.18 and 0.12 m s^{-1} for the faba growing and non-growing seasons respectively; and 0.15 and 0.12 m s^{-1} for the spring wheat growing and non-growing seasons respectively. After application of the u_* filters, the total data coverage of acceptable measured F_N utilized in this study was approximately 50 % of possible 30-minute periods. The acceptable measured F_N data coverage for the individual experimental plots monitored was approximately 12.5 % of possible 30-minutes periods.

In contrast to the growing body of work on gap-filling micrometeorological net ecosystem CO_2 exchange (NEE) data, no procedures have been developed or standardized for 30-minute N_2O fluxes. This is likely due to the high spatial-temporal variability of N_2O fluxes, the relatively few number of continuous micrometeorological studies monitoring this trace gas, and a lack of known ecosystem-scale relationships with commonly measured meteorological variables that could be used to model and fill the time-series. Therefore, presented are the 30-minute fluxes from each of the individual

four plots at the site averaged separately for each day of the study when available. Daily fluxes were then estimated for the site as the mean and standard error of the average values obtained for the individual plots. For comparison of tillage treatments over the first two years of the study (corn and faba), the means and standard error of the average daily 30-minute fluxes from the intensive-tillage and reduced-tillage plots were calculated. Using this approach, data coverage of daily F_N means for the entire site or the two tillage treatments was approximately 70 % of possible days during the study.

Seasonal and annual micrometeorological N_2O-N flux budgets for the site and tillage treatments were estimated by summing the daily means with both no interpolation of missing data, and with gap-filling the daily time-series by linear interpolation of missing periods. The uncertainty of the N_2O-N flux budgets were estimated as the standard error of budgets obtained from the integration of daily mean flux values from the individual plots measured. Crop years were defined as the period from May 1 of the year the crop was planted to April 30 the following calendar year: the corn year was May 1, 2006 to April 30, 2007, the faba year was May 1, 2007 to April 30, 2008, and the spring wheat year considered for annual N_2O-N budgets was May 1, 2008 to April 30, 2009. Crops were seeded and fertilizer was applied within the first three weeks of the start of the study year (the specific dates are noted in Section 4.3.2).

4.3.5.2 Relationships between Nitrous Oxide Flux and Temperature Non-linear regressions for F_N-temperature response relationships were performed with the *nlinfit* function from MATLAB® (Verson 7.6.0, Statistics Toolbox 6.2 (R2008a), The Mathworks Inc., Natick, Massachusetts, USA) with no bounds placed on the ordinary least-squares (Gauss-Newton with the Levenberg-Marquardt modification) parameter

estimates. The 95 % confidence intervals for parameter estimates were calculated from the residuals and estimated coefficient covariance matrix using the *nlparci* function. Correlation coefficients and significance levels between F_N, air and soil temperatures were calculated with *corrcoef*.

4.4 Results

4.4.1 Weather and Environmental Conditions

The average daily air temperature at the site was 3.3, 2.4 and 1.5^{o}C for the crop years 2006, 2007 and 2008, respectively. During 2006, air temperature was higher than the 30-year normal (average being 2.6^{o}C) for the area (Environment Canada, 2010), while the air temperature in 2007 was lower and closer to normal and 2008 was a cooler year than the long term average. Total precipitation at the site was 306, 669, and 740 mm for the 2006, 2007, and 2008 crop years, respectively. Total precipitation was only 60 % of the normal annual (average of 514 mm) amount (Environment Canada, 2010) over the 2006 crop year, and above average during the 2007 and 2008 crop years. During the 2006 corn growing season (seeding to harvest), the site only received 150 mm of precipitation. The precipitation in the corn growing season was less than half as much as either the 2007 faba or 2008 spring wheat crops, which received 390 mm and 365 mm over growing season periods that were approximately 8 and 6 weeks shorter in duration, respectively.

Soil extractable mineral N (ammonium and nitrite plus nitrate) was highest following fertilizer application for the corn crop in spring 2006 (Figure 4.1). Extractable ammonium declined with crop growth and remained less that 20 mg N kg^{-1} dry soil for

the remainder of the crop year. In contrast, the NO_3^- concentration initially decreased rapidly but increased later in the growing season, followed by a decline of approximately 20 mg N kg^{-1} (≈70 kg N ha^{-1} to 0.3 m depth) between October 1, 2006 and April 18, 2007 (Figure 4.1). For the remainder of the study, the concentration of both extractable forms of mineral N were approximately 20 mg kg^{-1} or less, with slight increases of 15 mg kg^{-1} (≈60 kg N ha^{-1}) and 6 mg kg^{-1} (≈20 kg N ha^{-1}) following faba harvest in August 2007 and fertilizer application to the spring wheat crop in May 2008, respectively.

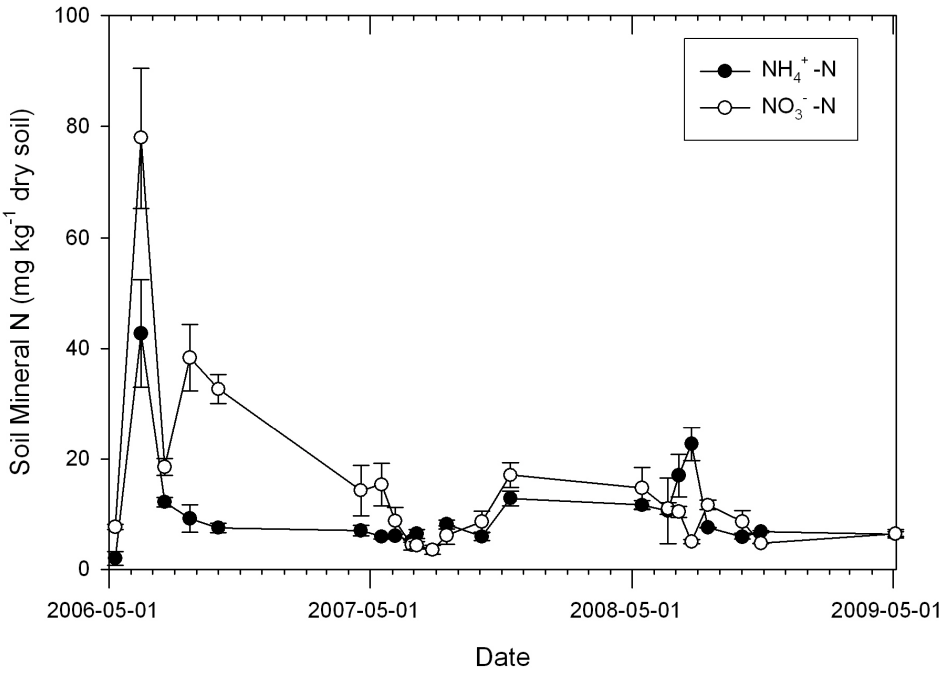

Figure 4.1 Time series of the mineral nitrogen (N) content of the 0 to 0.3 m soil depth over the course of the experiment. Open circles represent NH_4^+-N concentrations; closed circles correspond to NO_3^--N concentrations. Values represent the mean and error bars are the standard deviation (n = 24 in 2006 and 2007; n = 12 for 2008 and 2009).

4.4.2 Nitrous Oxide Emission Episodes

The N_2O flux (F_N) measured at the site over the three crop years was episodic in nature and predominately a net source from the crop system into the atmosphere. The

average F_N was essentially neutral (0 ± 10 g N ha^{-1}) for approximately 90 % of days measured during the triennium, with emissions greater than 50 g N ha^{-1} occurring on only 5 % of the days having observations (Figure 4.2). The standard error of F_N scaled with the magnitude of the average daily values, with higher spatial (between plots) and temporal variability observed during periods with high emissions. The periods with the most significant N_2O emissions followed N fertilizer application in late May and early June 2006 (peaking at 740 ± 170 g N ha^{-1} on June 6, 2006), the subsequent spring thaw in April 2007 (peaking at 230 ± 50 g N ha^{-1} on April 18, 2007), and in mid-June 2008 following fertilizer application (peaking at 440 ± 180 g N ha^{-1} on June 10, 2008; Figure 4.2).

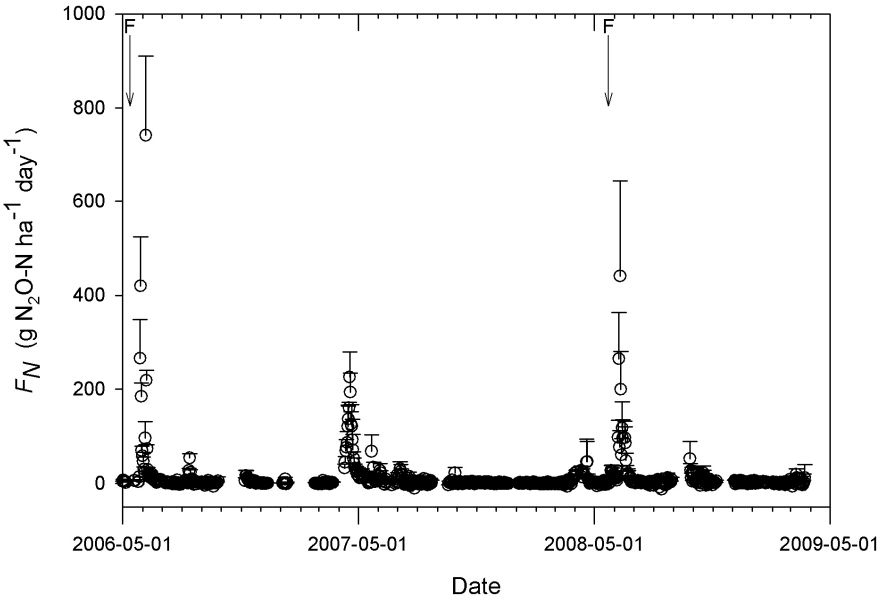

Figure 4.2 Time series of the average daily N_2O flux (F_N) at the site. Error bars are shown in the positive direction only, and correspond to one standard error of the daily mean values from the four plots in 2006-2007 and the two plots in annual production in 2008-2009. Fertilizer applications (F) are denoted with downward arrows.

The post-fertilizer N_2O emissions in the late spring of 2006 and 2008 occurred within two to three weeks after application, following significant rain events. In 2006, there were two emission peaks; one in late May and one in early June (Figure 4.2; Figure 4.3). The first episode began the afternoon of May 28, approximately 12 days after fertilizer N application, and lasted through to June 1 (Figure 4.3). The site had received 18 mm of rain in a one hour period on the morning of May 28. The second N_2O peak in 2006 began on June 5 following an additional 16 mm of rain and the emission period lasted until June 8. In 2008, the post-fertilizer emission fluxes began 16 days following application, starting June 7 and lasting until June 14 (Figure 4.3). The 2008 event began after 42 mm of rain on June 6, continuing with an additional 34 mm of rain on June 9 and 16 mm on June 11. The F_N events in 2006 and 2008 both showed positive correlations with air temperature, with exponential relationships providing the best regression fits (Figure 4.4).

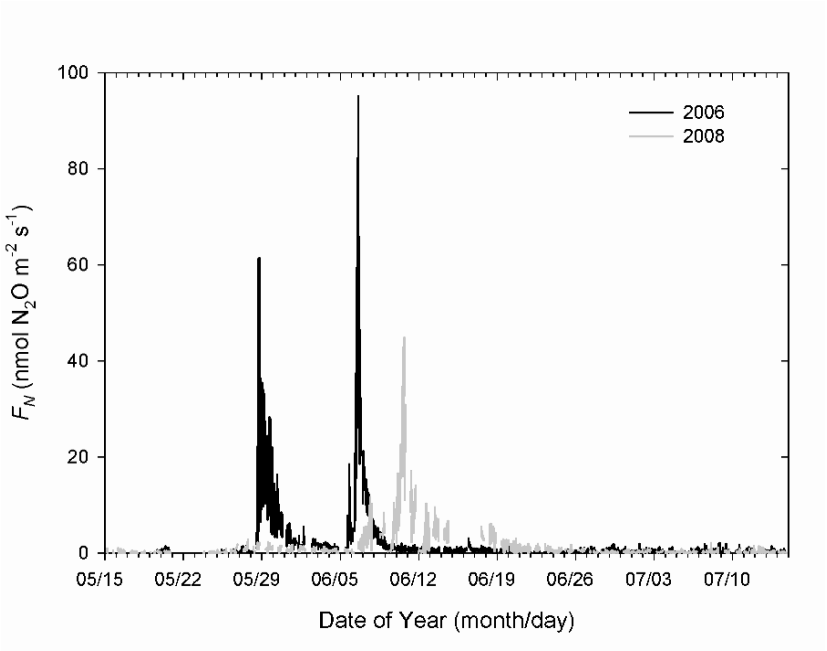

Figure 4.3 Time series of the filtered 30-min. N_2O flux (F_N) calculated at the site showing periods of nitrogen fertilizer induced emission episodes during the early growing seasons of 2006 and 2008.

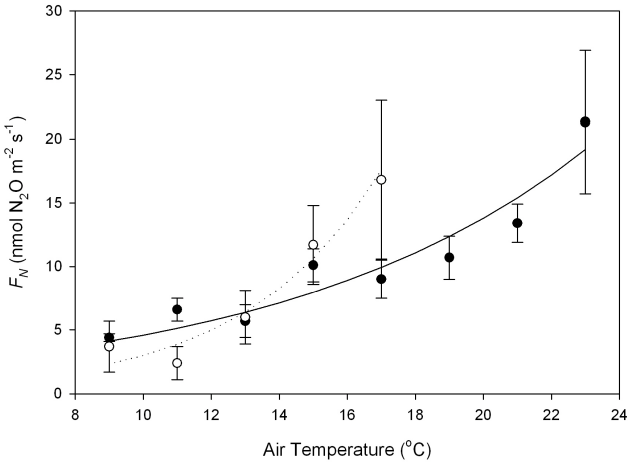

Figure 4.4 Bin-averaged (2°C bins) temperature-response curves of post-fertilization N_2O fluxes in 2006 (closed circles) and 2008 (open circles). The 2006 data corresponds to an emission event from 12:00 pm on May 28 through 12:00 pm on June 1 aggregated with a second event June 6 through June 9 (Figure 4). The 2008 data corresponds to the N_2O flux from 12:00 pm on June 10 to 12:00 pm on June 13 (Figure 4). Error bars represent the standard error for each binned average (n = 7 – 71 for 2006; n = 7 – 15 for 2008). Lines are fitted non-linear regression curves (r^2 = 0.89 for 2006; r^2 = 0.94 for 2008).

Mean daily N_2O emissions were lower during the faba crop year (May 2007 to May 2008) at the site (Figure 4.2). Peak daily emissions during the faba crop year (70 ± 40 g N ha^{-1} on May 22, 2007) occurred approximately two weeks after seeding. The site received 20 mm of rain between May 10 and May 20 and more than 50 mm on May 21 into May 22, prior to this N_2O efflux event. There were only six days with mean N_2O fluxes greater than 20 g N ha^{-1} considering the entire 2007 growing season, while there was a consecutive week of average daily emissions greater than 20 g N ha^{-1} during April 2008, during the spring thaw period following the faba crop.

4.4.3 Cumulative Nitrous Oxide Flux and Greenhouse Gas Budgets

Over the three crop years studied, the annual plots at the site were a cumulative source of 8.8 kg N_2O-N ha^{-1} to the atmosphere (Table 4.1), when only considering days

with accepted measurements from all plots (Figure 4.2), and no interpolation of the time-series. Approximately 57% of the N_2O was released during the corn crop year (5.0 kg N_2O-N ha^{-1}), 14% during the faba crop year (1.2 kg N_2O-N ha^{-1}) and 30% during the spring wheat crop year (2.6 kg N_2O-N ha^{-1}, Table 4.1). Nearly half of the cumulative N_2O emissions during the 2006 and 2008 crop years occurred during the brief emission episodes following N fertilizer application and significant precipitation events (Figure 4.2; Figure 4.3). Over the three crop years, the N_2O emissions within two to three weeks of N fertilizer applications in 2006 and 2008 accounted for more than 40% of the total cumulative flux. The spring thaw flux at the end of the corn crop year (Figure 4.2; Figure 4.5) comprised approximately 35% and 20% of the cumulative annual and triennial N_2O emissions at the site, respectively. This contrasted to the spring thaw flux following the faba crop year, which accounted for approximately 12% and 2% of the cumulative annual and three-year N_2O flux, respecitively.

Table 4.1 Measured ecosystem nitrogen and carbon flux components: N fertilizer applied ($F_{N\text{-}FERTILIZER}$), cumulative net N_2O flux (ΣF_N), gap-filled cumulative net N_2O flux (ΣF_N-GF), gap-filled cumulative net CO_2 ecosystem exchange ($\Sigma F_{C\text{-}NEE}$), and C removed by harvest ($F_{C\text{-}HARVEST}$) for each of the three crop years (May 1 to April 30). Negative fluxes represent ecosystem N and C gain, positive fluxes are loss. Error values given are ± 1 S.E.

	2006	2007	2008	Net Study Period
$F_{N\text{-}FERTILIZER}$, kg N ha^{-1}	-110	n/a	-100	-210
ΣF_N, kg N ha^{-1}	5.0 ± 0.6	1.2 ± 0.2	2.6 ± 0.5	8.8 ± 0.1
ΣF_N-GF, kg N ha^{-1}	5.5 ± 0.7	1.4 ± 0.4	4.3 ± 0.8	11.2 ± 1.3
$\Sigma F_{C\text{-}NEE}$, kg C ha^{-1}	-720 ± 170	70 ± 30	-2400 ± 430	-3050 ± 1400
$F_{C\text{-}HARVEST}$, kg C ha^{-1}	1230 ± 90	3070 ± 90	1920 ± 250	6220 ± 930
$F_{C\text{-}ECOSYSTEM}$, kg C ha^{-1}	510 ± 130	3140 ± 1100	-480 ± 110	3170 ± 1520

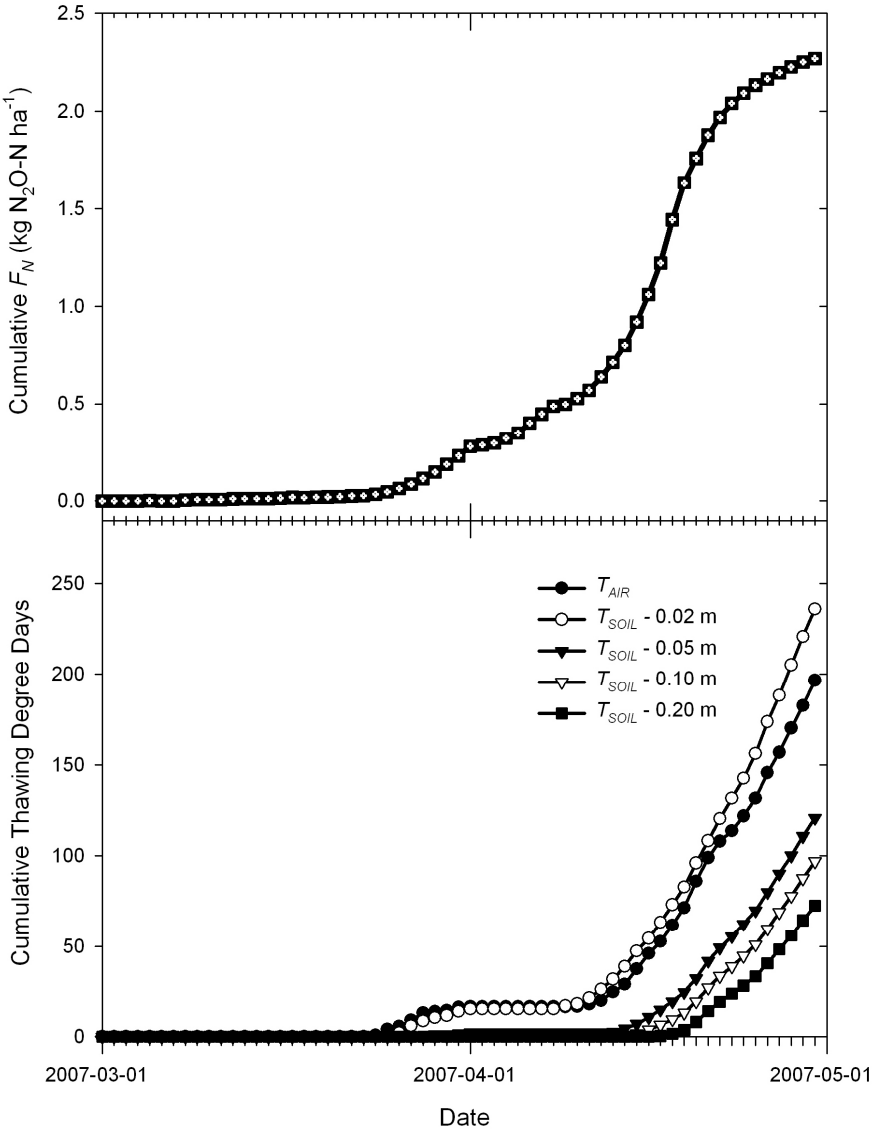

Figure 4.5 Cumulative N_2O flux (top panel) and thawing degree days (growing degree days > 0°C) for air and soil temperatures (bottom panel) during spring thaw in 2007.

With interpolation of the average daily fluxes and conversion to CO_2-equivalents based on the commonly used IPCC Second Assessment Report 100-year GWP of 310, the N_2O emissions at the site significantly offset the net CO_2 uptake (negative NEE) by the

crop canopy during the corn (2006) and spring wheat (2008) crop years (Figure 4.6). Based on the interpolated flux, the site was estimated to be a N_2O source of 2.7 and 2 t CO_2-eq. ha^{-1} for the corn and spring wheat crop years, respectively. The cumulative NEE for the corn and spring wheat crop years was -2.6 and -8.8 t CO_2 ha^{-1}, respectively. Therefore, the percentage net GHG offset due to N_2O emissions was approximately 110 % in 2006 and 23 % in 2008; or around 40 % of the total NEE of the annual crops over the three years studied (Figure 4.6). The cumulative N_2O emissions during the faba year (≈ 0.7 t CO_2-eq. ha^{-1}), when NEE was essentially CO_2 neutral (Chapter 2), contributed to the site being a net GHG source during the field production period of the crop's life cycle in 2007.

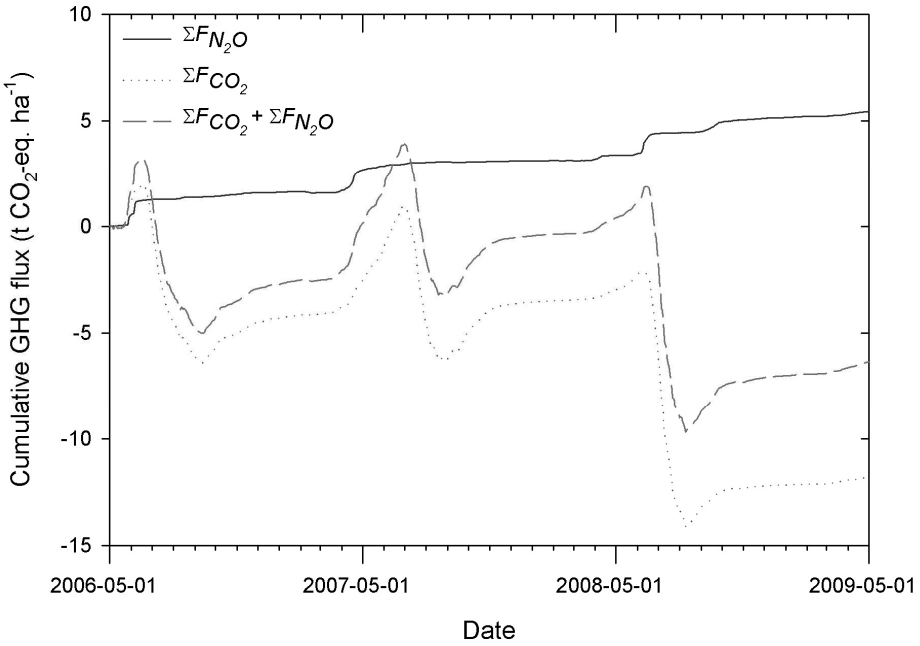

Figure 4.6 Cumulative N_2O, CO_2 and net GHG (CO_2 + N_2O) exchange between the site and the atmosphere for the three-years of annual crop production studied. The net CO_2 balance represents cumulative daily sums of gap-filled half-hourly fluxes (gap-filling procedure described in Chapter 2). The N_2O budget was constructed by summing interpolated daily average values and was converted to CO_2-equivalents assuming the IPCC Second Assessment Report GWP of 310X.

4.4.4 Influence of Tillage Regime on Nitrous Oxide Emissions

There was no detectable difference in episodic or cumulative F_N between the two tillage treatments over the first two years of the study. Landscape-scale spatial variability between plots for the two treatments was greater than differences between treatments, similar to findings for net CO_2 flux measurements at the site (Chapter 2). Peak flux episodes and cumulative totals showed greater variability for the reduced tillage (RT) treatment than for the intensively tilled (IT) plots. Highest daily mean F_N occurred during the corn crop year on June 6, 2006, approximately a fortnight post-fertilization for both the RT and IT treatments, and were 840 ± 360 g N ha^{-1} d^{-1} and 650 ± 140 g N ha^{-1} d^{-1}, respectively. During the following spring thaw, N_2O emissions peaked for the IT plots on April 18, 2007 at 230 ± 100 g N ha^{-1} d^{-1} and for the RT plots the following day (April 19) at 220 ± 30 g N ha^{-1} d^{-1}.The cumulative N_2O flux over the two-year study of the reduced tillage transition at the site was 6.3 ± 1.7 kg N ha^{-1} and 6.2 ± 0.4 kg N ha^{-1}, for the RT and IT treatments. This two-year N_2O flux was comprised of 5.0 ± 1.2 kg N ha^{-1} and 5.0 ± 0.1 kg N ha^{-1} during the corn crop-year, and 1.4 ± 0.5 kg N ha^{-1} and 1.2 ± 0.3 kg N ha^{-1} for the faba year, from the RT and IT plots, respectively.

4.5 Discussion

4.5.1 Agronomic and Environmental Controls of N_2O Emissions

The largest N_2O fluxes during monitoring occurred shortly after synthetic N fertilizer application in 2006 and 2008 (Figure 4.2; Figure 4.3), and following significant precipitation events. The timing of the fertilizer-driven emission episodes, allowing for

differences in the timing and amount of precipitation events and the transformation of different forms of synthetic N (entirely ammoniacal-based versus NO_3^--containing product), was similar to other agricultural field studies conducted with soil chambers (MacKenzie et al., 1997; Smith et al., 1998; Tan et al., 2009; Kong et al., 2009; Ussiri et al., 2009) and micrometeorological techniques (Laville et al., 1999; Grant and Pattey, 2003; Wagner-Riddle et al., 2007; Denmead et al., 2010). However, the magnitudes of the peak fluxes observed in the present study (740 ± 170 g N ha^{-1} d^{-1} in 2006 and 440 ± 200 g N ha^{-1} d^{-1} in 2008) were generally greater than previous reported values from Canada based on similar instrumentation and methodology. For example, peak daily N_2O fluxes from a clay-loam near Ottawa, Ontario, Canada following fertilizer application (155 kg N ha^{-1} urea) for a corn crop were between 200 and 500 g N ha^{-1} d^{-1} (Grant and Pattey, 2003). On a silt-loam near Guelph in southwestern Ontario, Wagner-Riddle and co-workers (2007) reported peak daily average N_2O fluxes between 100 and 150 g N ha^{-1} d^{-1} following fertilizer application to corn crops and similar amounts of precipitation as reported herein. A greater amount of fertilizer N was applied to their conventional corn plots (150 kg N ha^{-1} as broadcast granular urea), than to the corn (110 kg N ha^{-1} total, with 60 kg N ha^{-1} banded with the seed and 50 kg N ha^{-1} broadcast applied) and spring wheat crops (100 kg N ha^{-1} banded with the seed) studied herein. The difference in peak N_2O fluxes between the two sites was most likely related to differences in soil properties, with the fine-textured soil of the Red River Valley, Manitoba (60 % clay compared to 19 % clay for the Guelph silt-loam) having a greater organic C content and poorer drainage, which may have contributed to the higher daily average emissions observed in 2006 and 2008.

A strong positive relationship between N_2O fluxes and air temperature was observed during the fertilizer driven events in 2006 and 2008 when aggregated into 2°C bins (Figure 4.4). This suggests that substrates (N and C) and moisture were not limiting, and temperature was the primary environmental control on field-scale emissions during these periods. Both nitrification and denitrification have been shown to be dependent on temperature when substrates are not limiting (Focht and Verstraete, 1977). However, the temperature fits are confounded by diurnal trends (that also include solar radiation, photosynthesis, plant water uptake and transpiration) and may also be the result of degassing of N_2O from the soil matrix with declining gaseous solubility (Grant and Pattey, 2003) and decreasing water-filled pore-space during the daytime hours (Denmead et al., 2010). The N_2O fluxes observed following fertilizer application were likely the result of both nitrification and denitrification, with the coupling of the latter to the former. In 2006, both extractable NH_4^+-N and NO_3^--N in the top 0.3 m of the soil increased between May 10 and June 15 during the period of peak flux (May 28 to June 9; Figure 4.2 and Figure 4.3) to levels that were much greater than the amount of fertilizer applied (Figure 4.1). This indicates that the net mineralization of soil organic N and a considerable amount of nitrification took place over this period, despite the actively growing crop sink for available N. The enhanced decomposition and mineralization of soil organic matter following fertilizer application was likely a result of the prior fallow year (2005) and absence of crop residue inputs to the soil. The additional available soil mineral N (e^- acceptor) and available organic C (e^- donor) due the relatively high organic content of the soil at the site would have contributed to the intensity of N_2O emissions due to denitrification in 2006. In 2008, extractable soil NH_4^+-N and NO_3^--N decreased between May 15 and June 20 during the period of peak flux in 2008 (June 10 to June 13;

Figure 4.2 and Figure 4.3) following fertilizer application. This was likely due to a mixture of plant and microbial uptake of available N, as well as, nitrification and denitrification. A much greater amount of precipitation was received at the site subsequent to N fertilization in 2008 (92 mm compared to 34 mm in 2006), available soil NO_3^--N decreased more than NH_4^+-N, and the emission episode was sustained over a longer temporal period than the two peaks in 2006. For these reasons, perhaps a larger proportion of the post-fertilizer flux was due to denitrification than nitrification in 2008 than in 2006.

The second most important temporal period of N_2O emissions occurred during spring-thaw at the end of the corn crop year, in April 2007 (Figure 4.2; Figure 4.5). The spring-thaw emissions in 2006 (after the 2005 summer-fallow year; data not shown) and 2008 (following the legume faba crop; Figure 2) were detectable, but minor in comparison. The timing, duration and intensity of the emission episodes during the 2007 spring-thaw were similar to significant N_2O flux events observed at other northern temperate agricultural sites (Nyborg et al., 1997; Wagner-Riddle and Thurtell, 1998; Grant and Pattey, 1999; Pattey et al., 2007; Wagner-Riddle et al., 2007).

The spring-thaw N_2O flux in the present study following the 2006 corn crop lasted approximately two weeks (Figure 4.5), peaking at 230 ± 50 g N ha^{-1} d^{-1} on April 18, 2007 (Figure 4.2). In comparison, the peak flux reported from five spring periods monitored using the flux-gradient technique in southern Ontario, Canada (43.7°N latitude) occurred on a conventional-tilled plot following a winter-wheat crop and was approximately 320 g N ha^{-1} d^{-1} (Wagner-Riddle et al., 2007). The duration and magnitude of emissions during that particular thaw flux period were significantly higher than any other reported by Wagner-Riddle et al. (2007) for their corn-soybean-wheat rotation, and were attributed to

the relatively high intensity of soil freezing on the conventionally-tilled plots the previous winter. For a field slightly further north in Ontario (45.3°N latitude), located near Ottawa, Grant and Pattey (1999) measured peak spring-thaw emissions near 170 g N ha^{-1} d^{-1}, following a barley crop (70 kg N ha^{-1} applied) using the flux-gradient method. At the same site the next year following a corn crop (138 kg N ha^{-1} applied), peak N_2O emissions were approximately 110 g N ha^{-1} d^{-1} and occurred slightly later in the spring (Pattey et al., 2007).

The degree of over-winter cropland soil freezing has been shown to influence the intensity and amount of spring-thaw N_2O emissions in southern Ontario, especially when residual autumn soil NO_3^--N concentrations are less than 10 mg N kg^{-1} (Wagner-Riddle et al., 2007). During the experiment reported here, the cumulative freezing degree-days < 0°C (FDD) at the 0.05 m soil depth were nearly thrice as high over the post-corn winter (2006/2007; FDD ≈ 520) than over the winter following the faba crop (2007/2008; FDD ≈ 180). Although the accumulated FDD may have contributed to the intensity and amount of N_2O emissions in April 2007 (Figure 4.2; Figure 4.5), it was not likely a limiting factor or responsible for the differences observed between years. There was approximately twice as much NO_3^--N (oxidant) present in the soil in fall 2006 (33 mg N kg^{-1}), than in fall 2007 (17 mg N kg^{-1}; Figure 4.1), which was likely the most significant contributor to differences in observed emissions during the two spring thaws, as has been found in other studies examining freeze-thaw N_2O flux events (Wagner-Riddle and Thurtell, 1998; Tenuta, 2010). As well, a much greater amount of crop residue C (reductant) was present following the corn crop, which was harvested for grain, than after the faba crop grown in 2007, which was harvested for animal feed silage (virtually all aboveground biomass removed from the system). This difference in available substrates (e^- donors and e^-

acceptors) is the most likely explanation for the contrasting intensity and duration of N_2O emissions between years monitored in this study.

The 2007 spring thaw N_2O emission event (Figure 4.2) was closely linked to air and shallow soil temperature, with fluxes declining while deeper soil layers (from 0.05 m to 0.2 m) thawed (Figure 4.5). The N_2O flux during the period of emissions 50 g N ha^{-1} d^{-1} or greater (April 12 to 24, 2007) exhibited significant positive correlations with air ($r = 0.83$, $p = 0.002$) and 0.02 m soil temperature ($r = 0.72$, $p = 0.02$) when aggregated into 2°C bins. The correlation between F_N and 0.05 m soil temperature was positive but not significant ($r = 0.77$, $p = 0.2$), while relationships with lower soil depth temperatures were negative and insignificant. As there was no burst or additional intensity of emissions observed following thawing of the lower soil layers, it does not appear that the thaw flux event in the present study was the result of N_2O produced at depth over the winter being trapped by frozen soil and then suddenly released with thawing. It also does not support the hypothesis of substantial production of N_2O during thawing of soil at deeper layers being emitted at the soil surface. Perhaps the N_2O produced in deeper soil layers was completely reduced to N_2 before being released to the atmosphere (Wagner-Riddle et al., 2008). As well, the deeper soil layers at the site likely have a lower denitrification intensity and potential for producing N_2O due to less conducive physical (eg. higher bulk density) and biochemical (eg. lower organic C content) characteristics than the near surface horizon (Cho et al., 1979; Tenuta, 2010).

The data suggests that the 2007 spring thaw N_2O burst was a near-surface denitrification phenomenon of biological origin. The top-soil was saturated following snow-melt, there was measured nocturnal warming of the atmosphere by the surface (positive sensible heat flux), and standing water observed over portions of the field

because of drainage impeded by the frozen sub-soil, that would have induced denitrification. Residual soil NO_3^--N was high the previous fall, and the freezing and thawing cycle could have further enhanced denitrification during the period by lyzing bacterial cells, disrupting soil aggregates and fragmenting crop residues, as has been noted by other investigators (van Bochove et al., 2000; Teepe et al., 2001). The rapid decomposition and mineralization of labile organic pools results in the production of CO_2 and a reduction in O_2 levels due to accelerated aerobic respiration, further increasing the demand for NO_3^- as an alternate electron acceptor. Relatively high CO_2 fluxes (compared to the other two years with spring thaw measurements and considering soil profile temperatures during the period) were observed in the present study concurrently with the 2007 spring thaw N_2O flux event (data not shown), which is indicative of high rates of microbial activity in the form of both aerobic (with associated O_2 consumption) and anaerobic (denitrification) respiration. Simultaneous N_2O (from reduction) and supporting CO_2 (oxidation of C) fluxes have been noted in other studies examining the freeze-thaw emission episodes (Grant and Pattey, 1999; van Bochove et al., 2000; Teepe et al., 2001; Furon et al., 2008). Furthermore, low temperatures have been shown to increase the denitrification product ratio of N_2O:N_2, by inhibiting the reduction of the former to the latter (Tenuta, 2010), which may have also contributed to the relatively large N_2O emissions observed during the thaw period in April 2007 of the present experiment.

4.5.2 Relevance of Cumulative N_2O Flux to N Management and GHG Budgets

During the 2006 corn crop year (May 1, 2006 to April 30, 2007) the cumulative N_2O-N emissions (ΣF_N) represent approximately 4.5 % of applied fertilizer N (Table 4.1).

To put this in perspective for the cropping system N budget, using a crude protein estimate of 10 % for corn grain the N (assuming 160 g N kg protein) removed at harvest in fall 2006 (≈ 44 kg N ha^{-1}) was approximately 40 % of the N fertilizer applied the previous June (110 kg N ha^{-1}). Therefore, the accumulated N emissions released to the atmosphere as N_2O over the year from the crop system correspond to the equivalent of 10 % of the fertilizer N applied that was not harvested as grain. The remaining input N unaccounted for by grain harvest and F_N, was left in the ecosystem as plant litter, potentially immobilized by clay particles, organic matter, and microbes, and lost from the system in run-off water and to the atmosphere as NH_3 (volatilization), NO (nitrification and denitrification), and N_2 (denitrification). The equivalent of 2.6 % of applied fertilizer N was accounted for by cumulative F_N during the spring wheat crop year (May 1, 2008 to April 30, 2009). In contrast to the corn year where a substantial amount of applied N was left unaccounted for by F_N and grain harvest, the estimated crude protein N in aboveground biomass removed from the spring wheat crop as grain (71 kg N ha^{-1}) and straw bales (11 kg N ha^{-1}) in September 2008 was approximately 80 % of the amount of synthetic N applied the previous June (100 kg N ha^{-1}). The cropland supported a significant cumulative F_N in the early stages of crop growth that was most likely from fertilizer N, and additional mechanisms of retention and loss from the system discussed previously in relation to the corn year, would have occurred to varying degrees in 2008, as well. The spring wheat crop would have incorporated additional N from the soil system, provided by the mineralization of faba residue from the previous year and soil organic matter. Of course real-world N dynamics are complex, and even though it is important to compare cumulative F_N and harvested biomass protein to amounts of applied synthetic fertilizer for estimations of agroeconomic efficiency and potential impacts of

excessive N in the environment, the ratios reported herein do not necessarily imply substrate origins.

Although the amounts of measured N_2O-N lost from the annual agroecosystem during production of the corn and spring wheat crops are insignificant from an agroeconomic perspective, commonly assuming fertilizer N use-efficiency to be ≈ 50 %, they are significant for GHG accounting purposes. The net N_2O emissions over the course of the three-year study offset nearly half of the net CO_2 uptake by the annual crops grown at the site (Figure 4.6). With accounting for C removed from the agroecosystem during harvest episodes (Table 4.1), the cumulative N_2O emissions exacerbate the net global warming potential of the annual cropping system.

As the measurements of F_N in the present study represent the total N_2O flux, which could originate from fertilizer N or soil organic matter, an estimated "background" flux must be subtracted from the annual cumulative totals before comparing to Tier I or Tier II emission-factors. As there were no control plots (no N fertilizer application) during the corn and spring wheat crop years in the present study, three possible background levels were used, to estimate a range relating the amount of N fertilizer applied directly to N_2O emissions. The three estimates of the percentage of N fertilizer applied being released as N_2O were derived by: applying the global background flux level for soils originally proposed by Bouwman (1996) and used for IPCC Tier I methods of 1 kg N_2O-N ha^{-1} yr^{-1}, using the cumulative flux during the faba crop year (1.2 kg N_2O-N ha^{-1} yr^{-1}; Table 4.1), and the emissions at 0 kg applied N derived by Rochette et al. (2008a) for Quebec-Ontario (y-intercept of their Figure 1 or 0.8 kg N_2O-N ha^{-1} yr^{-1}). The emission-factor for Quebec-Ontario was used in this case, as the regression between N fertilizer rate and cumulative N_2O emissions was only significant for that region, and was

not for the Prairie soil zones (Figure 1 from Rochette et al., 2008a). Using these three approaches for approximating the background (soil organic matter derived) ΣF_N for the site results in estimates of 3.5 – 3.8 % and 1.4 – 1.8 % of applied fertilizer N being emitted as N_2O for the corn and spring wheat crop years, respectively.

The ΣF_N for the 2006 corn year (Table 4.1) was approximately two to three times greater than what would be predicted by the original (1.25 % of applied fertilizer N emitted as N_2O-N) and revised (1 % of applied fertilizer N emitted as N_2O-N) default IPCC Tier I emission-factors, respectively. During the 2008 spring wheat crop year, ΣF_N, was also greater than the Tier I default factors, but only the emission-factor estimate using the lowest background flux level (from Rochette et al. 2008a) was greater than one standard error (Table 4.1) . Using the Tier II (regional-scale) approach, Rochette et al. (2008b) estimated mean annual total N_2O emissions between 1.5 and 2 kg N ha^{-1} for the Red River Valley of southern Manitoba from 1990 – 2005. These estimates are less than half of the ΣF_N measured during the corn crop year, and slightly less than the total flux observed during the spring wheat year in the present study. The estimated amounts of synthetic N applied emitted as N_2O during both the corn (3.5 – 3.8 %) and spring wheat (1.4 – 1.8 %) crop years are higher than the effective emission-factors estimated for Manitoba for the years 1990 through 2005 (mean: 1 %, minimum: 0.6 %, maximum: 1.3 %) using the Canadian Tier II approach (Rochette et al., 2008b). The fertilizer derived N_2O flux during the corn and spring wheat crop years are twice as high and similar, respectively, than would be predicted with Ontario-Quebec emission-factors (Environment Canada, 2008; Rochette et al., 2008a) assuming a precipitation (P) to potential evapotranspiration (PET) ratio of 1 (1.7 % of applied fertilizer N released as

N_2O-N). It should be noted that the annual N_2O emissions reported here did not necessarily increase as a function of P:PET. With a mean annual PET in the Winnipeg area of approximately 550 mm (Natural Resources Canada, 1974), the ratio of P:PET was about 0.6 during the corn crop year, and greater than 1 during the faba (1.2) and spring wheat (1.4) years. Although the corn crop year had the highest ΣF_N (Table 1), it had a P:PET ratio that was half or less than the other two crop years.

The higher ΣF_N during the corn year compared to the faba year was due to fertilizer N application and the greater availability of NH_4^+ and NO_3^- in the soil (Figure 4.1). Higher ΣF_N during corn vs. spring wheat crop production in this study may have been partially due to a greater amount of fertilizer being applied (10 kg N ha^{-1} more), and the relative performance of the two crops under the climate regimes of the growing seasons. The spring wheat crop had a cumulative NEE that was approximately three times greater than the corn (Table 4.1), a higher photosynthetic capacity (Chapter 2), and similar grain mass harvest (Chapter 2). Perhaps counter-intuitively, low precipitation during the corn growing season may have caused higher annual N_2O emissions by enhancing the subsequent spring thaw flux because of poor crop performance and associated limited uptake of available N leaving a large residual soil NO_3^- pool in the fall of 2006.

Mean daily N_2O emissions were significantly lower during the faba crop year (May 2007 to May 2008) than the prior and subsequent annual crop years at the site (Table 4.1; Figure 4.2) which received fertilizer N. Peak daily emissions during the faba crop year occurred approximately two weeks after seeding and were therefore most likely sourced from residual N in the soil, not biological N_2 fixation. Between planting of the

faba crop and the N_2O emission episode (less than two weeks) the site received more than 70 mm of rain. These environmental conditions would have inhibited seedling emergence, plant growth and symbiotic N fixation, but would have promoted nitrification and denitrification. The cumulative N_2O flux during the faba crop year in this study was similar to previously reported values for annual legumes of approximately 1 kg N_2O-N ha^{-1} yr^{-1}, and supports the proposal of Rochette and Janzen (2005) to remove the biological N fixation process from the default IPCC Tier I methodology and country-specific GHG inventories (Environment Canada, 2008; Rochette et al., 2008a). The total annual N_2O emission during the faba crop year (1.2 kg N_2O-N ha^{-1}) was similar in magnitude to the error estimate (± 0.9 kg N_2O-N ha^{-1}) for the three-year budget at the site (Table 4.1), and to the estimated global background flux levels for agricultural soils of 1 kg N_2O-N ha^{-1} yr^{-1} (Bouwman, 1996) used in IPCC Tier I estimates.

4.5.3 Underestimation of Nitrous Oxide Fluxes

Although the mean daily N_2O fluxes measured in the current study were higher than many previously reported values, and cumulative annual emissions were significantly greater than IPCC Tier I and Canadian Tier II emission-factors, the net N_2O flux between the crop system and atmosphere was likely underestimated due to missing data and potential methodological shortcomings. The system was not operational during April 2009 due to emergency flood preparations in the Red River Valley, and the spring thaw flux following the spring wheat crop is missing from the cumulative budget. Although residual soil NO_3^- levels were much lower in the autumn of 2008 following the spring wheat than in fall 2006 after the corn crop (Figure 4.1), the accumulated freezing degree-days at 0.05 m soil depth over the winter of 2008-2009 was substantially higher

(FDD ≈ 850) than the previous two years (2006/2007 FDD ≈ 520 and 2007/2008 FDD ≈ 180) which suggests a significant spring-thaw N_2O emission episode is missing from the cumulative annual and triennial flux budgets reported herein, although the magnitude is a mystery. Another contributing factor to likely underestimation of ΣF_N budgets is the treatment and consideration of days with missing data (30% of possible days over the three-years). Although, with the unknown exception of April 2009, the periods with the most significant emission episodes (post-fertilizer in 2006 and 2008, and spring thaw 2007) were adequately captured, a linearly interpolated (daily means) budget results in a ΣF_N higher (about 20 % higher for the three-year budget) than that used to estimate fertilizer emission-factors (Table 4.1). Lastly, the N_2O fluxes reported from this study may have been underestimated due to theoretical uncertainties inherent to the flux-gradient micrometeorological technique. Two factors that may have caused an underestimation of the net N_2O flux were possible roughness sublayer effects when the corn canopy was at peak height, and the assumption of similarity in K values for momentum, energy and mass (Denmead, 2008). Theoretical, worst-case "correction" factors were applied to the N_2O flux time-series in a manner similar to those used to estimate uncertainty due to potential underestimation of CO_2 fluxes at the site (Chapter 2). An enhancement factor of 2X was applied to F_N for the period during the corn crop in 2006 when the lower [CO_2] intake was mounted at $1.2h_c$, and all eddy diffusivity (K) values for the three crop years were increased by a factor of 1.4X to account for the possible difference between the turbulent transfer of momentum and mass. Possible roughness sublayer effects during peak corn crop height (late July to harvest) were found to be insignificant (solely applying an enhancement factor of 2X during that period

increased the non-gap-filled cumulative annual and triennial N_2O estimates by 4 % and 2 %, respectively), as noteworthy N_2O flux episodes during the study occurred during non-cropping (spring-thaw) or low crop height periods (post-N-fertilization). However, potential violation of the similarity assumption between momentum and mass was important as N_2O fluxes from the present study were generally unidirectional, unlike the bidirectional nature of CO_2 fluxes reported in Chapter 2. Applying both factors (2X enhancement to compensate for roughness sublayer effects during the corn crop year, and 1.4X to account for the potential difference between the turbulent transfer of momentum and mass) to the flux time series increased ΣF_N for the corn, faba, spring wheat crop years by 2.3 kg N_2O-N ha^{-1}, 0.5 kg N_2O-N ha^{-1}, and 1.1 kg N_2O-N ha^{-1}, respectively. Therefore, assuming equivalent K coefficients for momentum and mass may have resulted in the underestimation of cumulative annual and triennial N_2O emissions from the cropping system to the atmosphere (Table 1) by more than 40 %.

4.6 Conclusions

The results from this study indicate that the Red River Valley shared by Canada and the United States may need revised coefficients for estimating soil N_2O emissions from applied fertilizer N in keeping with the unique topography of the landscape and fine-textured vertisolic soils compared to other soils in the Prairies and Northern Great Plains. The spring thaw N_2O flux following the corn crop in spring 2007 highlights the need to have continuous whole-year measurements when estimating cumulative annual emissions

in the Red River Valley, and likely for all of western Canada, which is currently neglected in the Canadian Tier II methodology (spring thaw flux is included for Eastern Canada). This requires additional consideration for N_2O inventories for the Red River Valley region, in light of the propensity for overland flooding and poor field drainage, prior and during spring soil thaw periods. Furthermore, additional micrometeorological measurements of F_N at different fields and soil zones in Canada (and agricultural regions elsewhere) will aid in improving and revising emission-factors derived primarily from chamber studies.

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5. SYNTHESIS

5.1 Important Findings and Implications

This dissertation reported and analyzed the findings from three years of continuous measurements of biogenic CO_2 and N_2O fluxes from a northern prairie cropping system in the Red River Valley of southern Manitoba, Canada. As the first multi-year micrometeorological assessment of net CO_2 and N_2O exchange for the Canadian Prairies, it is a valuable contribution to the currently limited but expanding international literature on seasonal and annual dynamics of trace gas fluxes between agroecosystems and the atmosphere. These intensive flux campaigns complement long-term soil C and N inventory research by filling the temporal frequency gap and capturing the short-term influence of agronomic management decisions and inter-annual variability in crop performance against the backdrop of global change forcing.

The net C balance (NEE + harvested C) at the site (Chapter 2) exhibited large inter-annual variability that was mainly dependent on crop species and growing season environmental conditions. The site was, on average, an annual source of CO_2 ($\approx$ 1000 kg C ha^{-1} yr^{-1}) which differs from the commonly assumed C equilibrium of mature croplands. This research highlights the importance of directly measuring or doing an adequate job modelling ecosystem respiration when estimating net C budgets of crop production. Plant and soil respiration are inevitable C costs required to produce and maintain crop tissues to maturity and have been neglected or poorly represented by the majority of agricultural GHG inventories. As well, crop rotations and the amount of above-ground biomass harvested have a large impact and legacy on the multi-year ecosystem C balance. For example, in 2007 when this agroecosystem was the largest C source (> 3000 kg C ha^{-1}),

virtually all of the aboveground faba biomass was harvested for animal feed silage. The NEE of the faba year was essentially C neutral, indicating that that there was a balance between photosynthesis and respiration in this crop year before accounting for harvest biomass removal. Larger rates of respiration may have been a combination of the legacy of plant litter from the previously grown corn crop in 2006, which was harvested for grain only, and a potentially higher rate of plant and microbial respiration associated with legume production. In contrast, the following crop year (2008) was the only year out of the three in which the annual cropping system was a small C sink after accounting for harvest, and may be attributable to a combination of better overall crop performance (higher rates of photosynthesis), and lower rates of respiration because of cooler air and soil temperatures and a relatively small amount of plant residue substrate left in the system following faba harvest.

An influence on total rates of soil respiration between conservation tillage and intensive tillage practices employed at the site was detected in the autumn of 2006 following corn harvest (Chapter 3). Although total soil respiration rates were different in fall 2006, the relative proportion of different C sources being metabolized (CRC vs. SOC) was similar between the treatments indicating that although reduced tillage had slowed down overall cycling, it was not compartment specific. This difference in total soil respiration rates between treatments did not persist into the following spring of 2007. As soil respiration rates were much higher during the spring measurement campaign, this negated any reduction in the non-growing season CO_2 emissions observed the previous fall due to the conservation tillage practices at the site. A much higher proportion of total respiration originated from corn residues in the fall of 2006 ($\approx$ 70 %) than the following spring ($<$ 30 %) for both tillage treatments, indicating a fairly fast (months to $<$ 1 year)

rate of turnover for the most labile fractions of the above and below-ground biomass. Although the most easily decomposable C from the corn crop oxidized over the period of stable C isotope measurements, it represents a small portion of the necromass left in the system and the more recalcitrant tissues will continue to decay over time. Interestingly, the sources of C contributing to the respiration signal changed over time from being CRC to SOC dominated during both the fall 2006 and spring 2007 intensive stable C isotope measurement campaigns. This finding coincided with transitional seasonal thermal regimes in the soil profile (freeze-up in the fall, thaw in the spring), and conceptual sources of C that would be contributing to the respiratory CO_2 signal at different depths.

In addition to the continuous monitoring of net CO_2 fluxes at the Red River Valley site, N_2O emissions were simultaneously measured using equivalent micrometeorological techniques and annual budgets were constructed for the three crop years comprising the field data obtained in this thesis study (Chapter 4). Significant N_2O emissions measured at the site were episodic in nature, occurring after N fertilizer application and during spring-thaw periods, similar to results obtained from other studies conducted in northern temperate agricultural regions (Wagner-Riddle et al., 1997; Grant and Pattey, 1999; Grant and Pattey, 2003; Wagner-Riddle et al., 2007). The cumulative N_2O budgets estimated for the corn and spring wheat crop years, in which N fertilizer was applied, were substantially greater than would be predicted using default Tier I IPCC or region specific Tier II Environment Canada emission factors. The post-N-fertilizer events in the spring and early summer exhibited diurnal trends and were correlated with air temperature, illustrating the importance and relevance of the continuous N_2O flux measurements obtained during emission episodes in the present study compared to estimations based on intermittent measurements. Such diurnal trends highlight the uncertainty in the majority of

agricultural soil N_2O budgets reported thus far, which are most commonly constructed from the linear interpolation of snapshot (usually weekly to bi-weekly, sometimes twice-weekly or daily) chamber measurement campaigns. Spring-thaw emissions measured in April 2007 following a corn crop the previous year were substantial, and closely related to air and surface soil temperatures, but not deeper soil layer temperatures. This data set therefore supports the hypothesis that freeze-thaw N_2O emission episodes are a near surface biological process, not due to the physical release of gas trapped by ice. Perhaps spring-thaw N_2O emissions are the product of facultative denitrifier populations that comprise an energetic ecological niche in agricultural soils during these seemingly inhospitable periods. Relatively large CO_2 fluxes were concurrently measured with the spring-thaw N_2O emission event in April 2006, compared to other years of monitoring at the site (Chapter 2) suggesting that both aerobic and anaerobic (denitrification) respiration may have contributed to the net flux. The stable C isotope signature of the ecosystem respiration flux (Chapter 3) during the period coinciding with the large spring-thaw N_2O flux episode was approximately -20 ‰, indicating that a mixture of recently fixed corn CRC (40 %) and SOC (60 %) were substrates for the aerobic and anaerobic respiration processes. However, it is not possible to distinguish between the CO_2 produced by aerobic respiration and that originating from denitrification during the spring-thaw period in April 2007, nor whether C substrates utilized by the two biochemical pathways differed.

On an annual basis, the years where N fertilizer was applied (2006 for corn and 2008 for spring wheat) had cumulative N_2O emissions three to four times higher than the year in which a legume (faba in 2007) was grown and no fertilizer was applied. Assessing the global warming potential (GWP) of this agroecosystem based on N_2O emissions alone

would lead to the conclusion that annual legume crops may be a significant mitigation option or beneficial management practice (BMP) for the area. However, with consideration of the concurrent NEE of CO_2 and accounting for harvested C in biomass removed from the agroecosystem, the faba year actually had the highest GWP. The NEE during the faba year was essentially C neutral, however the majority of aboveground biomass was harvested for animal feed silage. This single harvest episode in 2007 removed a CO_2-C amount from the ecosystem that is twice the equivalent in cumulative N_2O emissions for the corn and spring wheat years combined, and represents 66 % of the three-year GWP (net CO_2 and N_2O) of the site. For the corn crop year in 2006, the cumulative N_2O emissions completely offset the NEE of CO_2, and harvested C contributed to the site being a significant GHG source. In 2008, the cumulative N_2O flux during spring wheat production only offset the NEE by approximately 24 %; however, a substantial grain and straw harvest contributed to an annual GHG budget that was essentially GWP neutral. It is notable that the products harvested from this site have a significantly higher GWP than that reported for the cropland processes reported in this dissertation. A full life cycle analysis would include both upstream (e.g. manufacture and transport of fertilizers, pesticides, peat powder inoculant, etc.) and the downstream usage of the harvested biomass. For example, a significant proportion of the harvested crops in the present study were processed through an additional trophic level that would have produced significant amounts of CO_2, CH_4 and N_2O, before eventually being consumed by the human population.

Anthropogenic production, harvest, and consumption of agricultural products exert a dominating influence on the net GWP of established croplands such as the site studied. The net C and N budgets resulting from such land-use decisions are therefore

significantly different from those encountered in unmanaged, natural ecosystems. These findings demonstrate the value of having accurate assessments of the net balance between photosynthesis and respiration during the growing season, robust measurements of soil respiration during the non-growing season, and accounting of biomass harvest in order to recommend GHG emission reduction and mitigation strategies that are holistically effective. It was not possible to distinguish net GHG fluxes between the conservation tillage treatment recently implemented at this site from a more intensive tillage practice ("management-as-usual" for the Red River Valley) during this study. Despite numerous advantages of the high-frequency micrometeorological flux budgets obtained from this study, it is not without practical experimental limitations compared to long-term soil inventory or intermittent chamber studies for investigating the influence of reduced or no-tillage on ecosystem C and N budgets. In an ideal world, the micrometeorological campaign and reduced tillage treatment at the site would have continued for a decade at least, and perhaps over time a difference in the net CO_2 and N_2O fluxes between the treatments would manifest. However, this is an unrealistic scenario given the costs associated and level of expertise required to operate such infrastructure, changing research funding priorities, and the need to immediately reduce GHG emissions. In order to offset the GWP of this Red River Valley cropland site, any tillage treatment implemented would need to consistently (temporally and spatially) sequester and stabilize organic C at a rate twice that of the most optimistic reported in the often-cited West and Post (2002) study. Clearly such rates are unachievable for the site in the present study given the short length of the growing season in southern Manitoba, even with a possible climate change induced extension, biomass harvest requirements, and variability in crop physiology and environmental conditions. Although the reduced tillage treatment was

admittedly dissimilar from a more mature conservation tillage cropland, the inability to detect a difference over the two-years of that phase of the study was apparently due to landscape-scale heterogeneity in net CO_2 and N_2O fluxes, likely because of variability in topography and hydrology (drainage). Only recently have micrometeorological theory and methods been developed to address such landscape variability within natural ecosystems (Hollinger and Richardson, 2005) and between experimental plots or treatments in agricultural settings (Davis et al., 2010; Glenn et al., 2010), even though the importance is intuitive and evident.

It is anticipated that the data obtained during the course of this thesis will be valuable to the scientific community to calibrate and validate remote-sensing products and computational models. Such models of cropland GHG exchange may be coupled to general circulation models at time steps of decades to centuries and used to identify practices and climatic conditions that are conducive to lower or higher GHG emissions in the long-term, as well as, to predict the effects of global change on cropland C and N cycling. In particular, the *in situ* measurements of net CO_2 flux from this study will help fill the void in available data on crop photosynthesis, plant and soil respiration under the field conditions encountered on the Canadian Prairies. The data obtained from the micrometeorological stable C isotope campaigns may be valuable for modelling and testing hypotheses on the rates of turnover for different organic matter fractions in the soil. The N_2O flux data-set is a valuable contribution to the climate change research community as there is a lack of such continuous monitoring campaigns, and this data gives a more complete accounting of the emission episodes in the field than common static chamber-based approaches, particularly for fluxes during spring-thaw periods in temperate regions. In a broader sense, this work as a whole represents a move towards

understanding the integration of multi-elemental cycling and energy flows within ecosystems (Allen and Gillooly, 2009), with the need for simultaneous study of C and N cycling interactions being identified as a top research priority (Gärdenäs et al., 2010).

5.2 Ongoing and Future Research

Ongoing and future research at the Red River Valley site used in this study will address such issues as the net methane (CH_4) flux of the soil, the influence on the net GHG balance of including perennial legume-based forage stands in crop rotation compared to continuous annual species, the influence of fall vs. spring application of N fertilizer on net N_2O emissions, and life-cycle assessments. While it is commonly assumed that agricultural soils represent a small CH_4 sink, little is known about the magnitude of fluxes, and in the case of the Red River Valley, where soils are often saturated and subjected to overland flooding, it may be hypothesized that the system is a source of CH_4. Inclusion of CH_4 flux studies at the site is required to better estimate the true net GHG budget and C balance of the ecosystem. The use of perennial legumes in the cropping rotation is anticipated to provide a significant reduction and possible mitigation of GHG emissions compared to continuous production of annual species by: providing a longer season of net CO_2 uptake, greater belowground biomass production, and a reduction in N_2O emissions in the absence of N fertilization. However, it is unknown whether or not such benefits will be sustained after the system is ploughed under and the cropping system re-planted to annual species. Understanding the influence of the timing of N fertilizer application on N_2O emissions will be a very important and practical research question to address with the site infrastructure. In the current study, N fertilizer was applied in the spring at the time of planting of corn and spring wheat crops, which

may be considered a BMP on the Prairies. However, the reality in Manitoba is that most farmers apply N fertilizer the previous fall prior to spring planting for economic (fertilizer is cheaper in the fall compared to the spring) and seasonal division of labour (less field work to do and more time to do it) reasons, and is potentially subject to greater loss through leaching and denitrification. A comparison between fall and spring application of fertilizer N would be useful for testing such hypotheses, developing N_2O emission reduction strategies and incentives, and for modifying emission-factors if necessary. Lastly, the crops produced at the site during and subsequent to this study require varying amounts of inputs, non-renewable energy-use, and have different fates post-harvest (human food, animal feed, and biofuel) that could be accounted for in full GHG life-cycle assessment (LCA) of the agroecosystem. The net biogenic CO_2 and N_2O fluxes during the field production of the crops are one of the most challenging portions of a LCA to reliably estimate, and this study and subsequent data from the site fills that knowledge gap. Furthermore, much of the harvested biomass is cycled locally at the experimental farm through livestock, and the manure is applied to the soil on the research station land. Other research teams at the station study the diets and GHG emissions from livestock and excreta, so there is capacity for a broader multidisciplinary, collaborative synthesis of data at the site.

Of course, ongoing and future research campaigns, and the modelling efforts based on the data obtained from this study will take place during an era on the Earth undergoing unprecedented change, with agricultural production on croplands facing numerous challenges and unknowns such as climate warming, elevated CO_2 concentrations, and increasing rates of N deposition. Recent findings on the potential influence of asymmetric diurnal warming (nocturnal temperatures are increasing at a

greater rate than daytime temperatures in the Northern Hemisphere) on photosynthesis and respiration (Wan et al., 2009; Xia et al., 2009), and the effect of elevated [CO_2] on crop N uptake (Bloom et al., 2010) illustrate some uncertainties associated with conducting scientific research in a changing world and model assumptions. However, it is often said that modelling efforts will only be as good as the data they are based on, and this highlights the importance of robust micrometeorological studies under contemporary and increasing forcing to better elucidate underlying mechanisms and patterns associated with biogeochemical trace gas fluxes and coupling with the climate system.

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APPENDIX A

Table A.1 Geometric mean (model II) regressions between the eddy diffusivities (m s^{-1}) calculated from sonic anemometers located on separate plots (IT and RT) at the site for each calendar year of the study.

Year	slope ± S.E.	y-intercept ± S.E.	r^2	n
2006	0.9967 ± 0.0014	0.0004 ± 0.0002	0.9789	10,839
2007	1.0581 ± 0.0020	-0.0035 ± 0.0003	0.9585	11,109
2008	1.0190 ± 0.0026	-0.0014 ± 0.0003	0.9263	11,519