SPATIAL AND TEMPORAL VARIATION IN GREENHOUSE GAS EMISSIONS FROM TWO OPEN WATER PRAIRIE WETLANDS

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ABSTRACT

Prairie wetlands provide valuable habitat for waterfowl and wildlife and buffer the impacts of upland land uses. However, their contribution to Canada's greenhouse gas inventory is poorly understood. The purpose of this study was to compare the spatial and temporal variation in nitrous oxide (N_2O), carbon dioxide (CO_2), and methane (CH_4) emissions from Pond 1 at the St. Denis Wildlife Management Area, Saskatchewan and the Deep Crop Wetland (DCW) at the Manitoba Zero Tillage Research Association farm, Manitoba. Nitrous oxide flux was low on all measurements days: at Pond 1 flux ranged from -1.47 to 6.01 ng N_2O-N m^{-2} s^{-1} in 2004 and -6.98 to 5.74 ng N_2O-N m^{-2} s^{-1} in 2005 and flux from the DCW never exceeded 2.50 ng N_2O-N m^{-2} s^{-1} in 2005. Methane flux from Pond 1 was substantially higher in 2005 (-469.10 to 3776.08 μmol CH_4 m^{-2} d^{-1}) than in 2004 (-251.55 to 191.55 μmol CH_4 m^{-2} d^{-1}). This increase in methane from Pond 1 followed a major increase in water volume in 2005 after snowmelt. Methane flux in 2005 from the open water and riparian sampling points at the DCW ranged from -13.64 to 110.47 μmol CH_4 m^{-2} d^{-1} and -4.51 to 40.23 μmol CH_4 m^{-2} d^{-1}, respectively. Carbon dioxide flux from Pond 1 and the DCW in 2005 were very similar: open water flux ranged from
-96.42 to 95.42 mmol CO_2 m^{-2} d^{-1} at Pond 1 and 3.21 to 38.94 mmol CO_2 m^{-2} d^{-1} at the DCW. Despite the similarity in CO_2 flux, the DCW had 10- to 15-fold higher levels of macrophytes, phytoplankton and metaphyton biomass and similar levels of periphyton to Pond 1 in 2005. These biomass differences were not, however, reflected in the CO_2 or CH_4 flux. Pond 1 and the DCW were net sources for greenhouse gases but contributed less greenhouse gas than reports from other aquatic systems.

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1.0 INTRODUCTION

The prairie pothole region (PPR) of North America encompasses approximately 780 000 km^2 (Mitsch and Gosselink, 1993). Wetlands in the PPR are often located within agricultural fields and are at risk of eutrophication from external nutrient sources (Environment Canada, 2001), drainage, and tillage of what is often marginal farm land (Environment Canada, 1986). The PPR is known as the "duck factory" of North America, providing 10% of waterfowl nesting habitat and producing 50-80% of the North American waterfowl population (Smith et al., 1964; LaBaugh et al., 1996).

Along with providing valuable habitat for wildlife, wetlands are important in filtering water, buffering the impacts of upland land uses, removing and storing greenhouse gases from the atmosphere, and reducing soil erosion (Ducks Unlimited Canada, 2006). Costanza et al. (1997) attempted to put an economic value on ecosystem services which provide direct or indirect benefits to humans through ecosystem functions (i.e., the process itself). Wetlands were valued at almost US$15 000 ha^{-1} yr^{-1}, nearly twice the value of lakes. The three main ecosystem services provided by wetlands were identified as disturbance regulation (~US$4 500 ha^{-1} yr^{-1}), waste treatment (~US$4 200 ha^{-1} yr^{-1}), and water supply (~US$3 800 ha^{-1} yr^{-1}). Culture (aesthetics, scientific value etc.), habitat, food production (subsistence farming or fishing), and gas regulation (regulation of atmospheric gases) were also considered ecosystem services provided by wetlands.

Although the value and importance of wetlands is beginning to be understood they are still under-studied and the role they play as greenhouse gas sinks or sources is only poorly understood.

The purpose of this study was to compare the spatial and temporal variation in carbon dioxide (CO_2), methane (CH_4), and nitrous oxide (N_2O) emissions from two prairie wetlands.

The primary objectives of this study were:

1) To determine the ice-free seasonal greenhouse gas flux from the two wetlands,
2) To determine the algal and macrophyte biomass in the two wetlands and
3) To measure select biological parameters and environmental variables, and to determine which, if any, correlate to the greenhouse gas flux.

The secondary objectives of this study were:

4) To measure diurnal variability in greenhouse gas flux from the open water and
5) To compare greenhouse gas flux from the riparian area with stacking and small chambers.

To fulfill objective 1, routine gas sampling was undertaken to inventory greenhouse gas emissions from two wetlands. A general literature review is provided in Chapter 2 to introduce relevant topics to the reader. Nitrous oxide flux and cumulative emissions will be discussed in Chapter 3. Gaseous carbon losses (CO_2, CH_4) and the relationship between algal dynamics (objective 2) and water chemistry (objective 3) will be explored in Chapter 4. Chapters 3 and 4 have been written as stand alone research papers and include their own literature review to provide context and to assist in interpretation of results. Materials and methods sections also appear in both Chapters. As a result, some information will be repeated and this has been avoided when possible

by including a synthesis of results in Chapter 5 and placing the references at the end of the thesis.

2.0 LITERATURE REVIEW

2.1 Overview

Wetlands are an important facet of the global greenhouse gas budget and may act as sinks and/or sources for CO_2, CH_4, and N_2O (Bartlett and Harris, 1993; Freeman et al., 1993; Sinks Table, 1999). Emission of CH_4 and N_2O are of particular concern as their global warming potentials are 23 and 296 times higher than CO_2, respectively (IPCC, 2001). The majority of past research has focused on greenhouse gas emissions from rice paddies and peatlands, both of which are high emitters of CH_4. The large amount of organic matter and often water-saturated conditions provide the potential for anaerobic decomposition and the production of CH_4 (Aselmann and Crutzen., 1989; Christensen et al., 2003). Past studies of N_2O emissions from wetlands are generally focused on constructed wetlands (Stadmark and Leonardson, 2005) or agricultural wetlands that receive large inputs of nutrients from fertilizers (Hefting et al., 2003; Rutherford and Nguyen, 2004).

The Canadian System of Wetland Classification defines five classes of wetlands: bog, fen, swamp, marsh, and shallow water (National Wetlands Working Group, 1997). Bogs and fens are both peatlands differing mostly in their source of water input. Ombrotrophic bogs rely on inputs from precipitation while minerotrophic fens are a result of ground water interactions. Swamps are forested wetlands and peatlands, while marsh wetlands are typically eutrophic mineral wetlands which exhibit fluctuating water

regimes. This results in high amounts of dissolved salts and neutral to high alkalinity. Shallow water wetlands usually have a well developed profundal zone (deep water zone) and are transitional between permanent deep water bodies and those wetlands that are seasonally wet (National Wetlands Working Group, 1997).

Few studies have quantified the greenhouse gas emissions from marsh wetlands in the North American prairies. These mineral soil wetlands are dominated by soils of the Gleysolic Soil Order. Reducing conditions, caused by periodic or constant water saturation, are present during soil genesis, and these soils are defined by their colour and mottling (Soil Classification Working Group, 1997). Although gleysolic soils can exhibit a peaty phase which contains an organic surface layer, they do not meet the minimum criteria established for classification in the Organic Soil Order, which includes peat, bog and fen soils. The Organic Soil Order requires that the soil contain more than 17% organic carbon (30% organic matter) and the organic material must reach a depth of at least 40 to 60 cm dependent on the composition of the surface layer (Soil Classification Working Group, 1998).

2.2 Conversion of Wetlands to Agricultural Land

The original wetland area in the PPR covers approximately 80 000 km^2; more than half of this original wetland area has been drained for agriculture (Leitch, 1989). The Institute for Wetland and Waterfowl Research (IWWR) of Ducks Unlimited Canada has undertaken a large study of spatial and temporal variation in nest success of prairie ducks (SpATS) in the PPR. A subset of the SpATS wetland survey data for Saskatchewan was used to determine the number and area of wetlands and the extent of cultivation in the study sites (Phipps et al., 2005 unpublished data). Wetland survey data

was linked to soil attributes using soil survey maps of Saskatchewan. This was done to determine if an association could then be made between the distribution of wetlands and land surface attributes in order to extrapolate these results beyond specific study sites. Wetland survey data from 137 quarter-sections studied was compiled and included 2733 wetlands, 1035 of which had been tilled. This represented 38% of the wetlands at these study sites.

The number of wetlands and extent of cultivation was variable depending on region and landscape. The percentage of wetlands cultivated per study site ranged from 1% to 80%. When quarter-sections were described by soil attributes, slope class 3 (2 to 5% slope) had the highest number of tilled wetlands per quarter-section and slope class 2 (0.5 to 2% slope) had the largest mean area of tilled wetlands (~ 3000 m^2 tilled wetland area per quarter-section). There were no quarter-sections located in slope class 1 and the SpATS study did not select any study sites in areas of low duck density (< 20 pairs mi^{-2}). It is expected that agricultural land located in slope class 1 is intensively managed resulting in a high percentage of wetland cultivation and a low duck population. Including these areas would increase the estimate of percentage of wetland loss due to cultivation.

2.3 Wetland Biology

Bogs, fens and marsh wetlands differ markedly, not only in composition of developed peat or mineral soil layers but also in hydrology, pH, and nutrient status, as well as the type of plant and algal community (National Wetlands Working Group, 1997; Goldsborough and Robinson, 1996). While bogs are typically acidic and nutrient poor with the water table at or below the peat surface, fens range from poor to rich in

dissolved minerals and undergo water level fluctuations of centimeters above or below the peat surface (National Wetlands Working Group, 1997). Bogs and fens (hereafter referred to collectively as peatlands) typically support low algal diversity and are dominated by single-celled green algae (Goldsborough and Robinson, 1996). Marsh and shallow water wetlands (hereafter referred to as wetlands) can reach eutrophic states and are capable of supporting high productivity (National Wetlands Working Group, 1997). Wetlands are usually shallow, well mixed water-bodies with a large littoral relative to pelagic zone (perimeter:surface area) (Fairchild et al., 2005). The light environment is variable and may change seasonally through shading by macrophytes (Brix, 1994) and metaphyton cover (Robinson et al., 1997a) as well as attenuation of light by algae (Mazumder et al., 1990) and dissolved organic carbon (DOC) (Arts et al., 2000). Wetland biomass is dynamic and changes seasonally. Intense competition for nutrients in the water column may exist between algae and macrophytes (Robinson et al., 1997a), and zooplankton may exert strong grazing pressure on algae (Lampert et al., 1986).

The contribution of algae to total primary production in freshwater wetlands can be significant (Robinson et al., 1997b). Most algae in smaller freshwater wetlands occur in association with submersed substrates and are together referred to as periphyton (Robinson et al., 2000). Shallow wetlands with profuse littoral vegetation provide potential substrates for algal colonization, which may significantly increase wetland productivity (Sand-Jensen and Borum, 1991). Although most studies on aquatic algae focus on the free-living or pelagic phytoplankton, these algae may only contribute a minor percentage of total algal biomass. Benthic and periphytic algae often make up a large proportion of algal biomass and contribute greatly to wetland primary production (Robinson et al., 1997a). For example, Robinson et al. (1997a) found that 98% of total

algal biomass in Delta Marsh, Manitoba was comprised of benthic algae (including metaphyton and periphyton).

2.4 Biological Effects on pH and the Carbonate Equilibrium

The carbonate equilibrium (the sum of dissolved inorganic carbon) is pH dependent and largely influenced by photosynthesis and respiration within productive wetland systems (Wetzel, 1983). Algal photosynthesis assimilates CO_2, consumes H^+, and shifts the bicarbonate equilibrium to the left, resulting in an increase in pH in the water column (Figure 2.1). Respiration shifts the reaction to the right, resulting in a decrease in pH (Kalff, 2002). Bicarbonate (HCO_3^-), some of which originates from rock weathering, plays an important role in buffering aquatic systems from rapid changes in pH (Kalff, 2002). Bicarbonate can be further disassociated to yield carbonate (CO_3^{2-}). In low pH aquatic systems the dominant form of dissolved inorganic carbon (DIC) is free CO_2, whereas in high pH waters the dominant form is CO_3^{2-} (Kalff, 2002). Atmospheric CO_2 flux across the air-water boundary can be enhanced by photosynthetic consumption of CO_2 in productive waters (Wetzel, 1983).

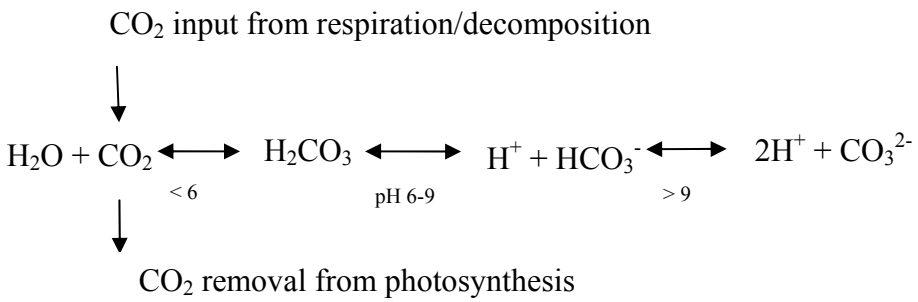

Figure 2.1 The bicarbonate equilibrium (modified from Kalff, 2002)

2.5 Biological Effects on the Redox Sequence and Gaseous Release of CO_2, CH_4, and N_2O

The redox potential of the sediments and overlying water column is governed by the presence or absence of dissolved oxygen (Kalff, 2002). Oxygen diffuses 10^4 times slower in water than air (Schlesinger, 1997). The solubility of oxygen is inversely proportional to temperature and salinity, and is affected by pressure and elevation (Kalff, 2002). As oxygen is consumed in sediments and the water column through heterotrophic respiration, a sequence of reactions takes place as lower redox potentials are achieved. Anaerobic metabolism is less efficient than aerobic respiration and free energy yielded from the reduction of inorganic substances decreases at lower redox potentials (i.e., more energy is produced from denitrification than methanogenesis) (Schlesinger, 1997). After oxygen is depleted nitrate is used as an alternative electron acceptor during the oxidation of organic matter (denitrification) (Equation 2.1); the reduction of manganese and iron follow (Schlesinger, 1997).

$$NO_3^- \rightarrow NO_2^- \rightarrow NO \rightarrow N_2O \rightarrow N_2 \qquad \text{(Eq. 2.1)}$$

When redox potentials < -220 mV are reached, sulfate then acts as an alternative electron acceptor in organic matter oxidation (sulfate reduction) (Schlesinger, 1997). Below sulfate reduction in the sediments methanogenesis occurs. Two main pathways exist for the production of CH_4: 1) acetate splitting (Equation 2.2), and 2) CO_2 reduction (Equation 2.3) (Cicerone and Oremland, 1988; Schlesinger, 1997).

$$CH_3COOH \rightarrow CO_2 + CH_4 \qquad \text{(Eq. 2.2)}$$

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \qquad \text{(Eq. 2.3)}$$

Sulfate-reducing and methanogenic bacteria are competitors for the same organic substrates and sulfate-reducing bacteria are more efficient in the uptake of H_2, resulting

in little overlap between the zones of sulfate reduction and methanogenesis (Holmer and Storkholm, 2001). Availability of labile organic carbon may also limit methanogenesis (Cicerone et al., 1992). This results in lower amounts of CH_4 production in aquatic systems with high concentrations of sulfate.

Oxygen may not always be entirely depleted from wetland sediments. A productive zone of benthic algae is often present in shallow wetlands and through photosynthesis produces an oxidized micro-zone at the sediment-water interface (Mitsch and Gosselink, 1993; Goldsborough and Robinson, 1996; Wetzel, 1996). This zone may be extremely important in chemical transformations within the sediment, and influence nutrient availability in the water column (Mitsch and Gosselink, 1993). Oxidized forms of elements are less mobile than reduced forms and often precipitate out of the water column into sediments, whereby they are reduced and become mobile again (Kalff, 2002). Presence of the oxidized micro-zone prevents their release back into the water column and their re-oxidation and immobilization (Goldsborough and Robinson, 1996).

2.6 Carbon Dioxide Emissions from Wetlands

Carbon dioxide emissions from wetlands include CO_2 from autotrophic and heterotrophic respiration as well as that produced through decomposition (Blais et al., 2005). Temperature, water table height, and quality and availability of organic substrates have been shown to be controlling factors of CO_2 emissions from peatlands (Bridgham et al., 1995; Chimner and Cooper, 2003). The effect of water table height on CO_2 has been shown in a number of peatland studies. Freeman et al. (1993) found that CO_2 emissions increased during a simulated drought. Funk et al. (1994) also found that CO_2 emissions tripled when the water table was lowered below the peat surface in

microcosm cores. Chimner and Cooper (2003) observed that CO_2 fluxes were highest when temperature was high and also when the water table was lowered to the peat surface. They attributed this to increases in mineralization of plant material in the aerobic environment. Xing et al. (2005) found a negative correlation between CO_2 fluxes and net primary production (NPP) and Chlorophyll-*a* (Chl-*a*). No high correlations were found between CO_2 fluxes and any variable measured (depth, age, pH, water temperature, wind speed, transparency, etc.) in a number of lakes, rivers, and reservoirs across Canada (Tremblay et al., 2005). pH and water temperature were significantly related to CO_2 fluxes but only explained a small proportion of the variance (Tremblay et al., 2005). When mean gross flux was analyzed, however, CO_2 flux was statistically different and higher when $pH < 7.9$. Additionally, Matthews et al. (2003) found a strong correlation between CO_2 flux and wind speed in an experimental reservoir in Ontario.

Unfortunately there is little research on CO_2 emissions from mineral wetlands. Relationships found in previous research on CO_2 emissions from peatlands, however, could provide a set of parameters to consider for possible relationships with CO_2 emissions from mineral wetlands. The physiological differences between peatlands and mineral wetlands must be considered. For example, relationships between water table height in peatlands and CO_2 emissions may not be as evident in prairie wetlands. Water table height in peatlands generally refers to water level fluctuation above or below the peat surface. In prairie wetlands water level generally refers to standing water above the soil surface.

2.7 Methane Emissions from Wetlands

Natural wetlands contribute approximately 115 Tg CH_4 to the atmosphere annually (Bartlett and Harris, 1993). The majority of these emissions are from tropical wetlands and peatlands (Bartlett and Harris, 1993). Anaerobic conditions of peatlands as well as accumulation of large amounts of organic matter provide a favorable environment for CH_4 production (Christensen et al., 2003). Wetlands often have productive zones of benthic algae inhabiting surficial sediments producing an oxygenated micro-zone (Goldsborough and Robinson, 1996; King, 1990). Atmospheric CH_4 emissions are therefore a result of CH_4 production in the anoxic sediments minus CH_4 oxidation occurring at the sediment-water interface (Bussmann, 2005) and throughout the water column. Methane oxidation that occurs at the sediment-water interface can be attributed to methanotrophic bacteria which inhabit the aerobic zone at the periphery of the anaerobic zone (Schlesinger, 1997). Methanotrophs have a high affinity for inorganic nitrogen (N) and can reduce nitrification and denitrification rates in environments where significant oxidation of CH_4 occurs (Topp and Hanson, 1991). Methane production is inhibited by sulfate as sulfate-reducing bacteria out-compete methanogenic bacteria for organic substrates (Schönheit et al., 1982).

Dominant determinants of CH_4 emissions from peatlands are water table position, soil temperature, quality and availability of substrate, and mode of gas transport to the atmosphere (Walter and Heimann, 2000). These factors are not independent of each other but rather may exert stronger control at different times of the year and at different sites depending on the condition of the wetland at the time of sampling (Walter and Heimann, 2000). Freeman et al. (1993) observed decreased CH_4 flux in peat microcosms during a simulated drought but poor correlations were found

between CH_4 flux and water table height. Similarly, Funk et al. (1994) found that peat cores with a high water table had high CH_4 fluxes. Matthews et al. (2003) found no significant relationship between CH_4 flux and water depth in an Ontario reservoir, but did find that the reservoir was acting as a sink for CH_4 while at the same time emitting CO_2. Strong correlations were not found between any of the variables measured (depth, age, pH, water temperature, wind speed, transparency, etc.) and CH_4 flux in lakes, rivers, and reservoirs across Canada (Tremblay et al., 2005). However, when the mean gross flux from the entire study was analyzed CH_4, flux was statistically different and higher when the pH < 7.9.

Researchers have found positive correlations between CH_4 flux and net ecosystem production (Whiting and Chanton, 1993), net primary production (Aselmann and Crutzen, 1989; Xing et al., 2005), and algal Chl-*a* (Xing et al., 2005). Primary production may stimulate methanogenesis by increasing available organic substrates and through the production of autochthonous organic matter (Whiting and Chanton, 1993; Xing et al., 2005).

2.8 The Role of Aquatic Macrophytes in Greenhouse Gas Emissions

Aquatic macrophytes play an important role in the production of greenhouse gases and their transport to the atmosphere (Chanton et al., 1992; Sebacher et al., 1985). These macrophytes provide organic substrates through fine roots and litter, act as a conduit for gas transport to the atmosphere (Chanton et al., 1992), and produce an oxygenated zone around the roots (Ding et al., 2005). As CH_4 travels through the shoot it bypasses the sediment-water interface, which is often a zone of CH_4 oxidation (King, 1990; Ding et al., 2005). Methane emissions from aquatic macrophytes are also

dependent on plant type and density (Grosse et al., 1991; Chanton et al., 1993; Thomas et al., 1996; Christensen et al., 2003). Relationships have been found between CH_4 emissions and net primary production (Aselmann and Crutzen, 1989), and net ecosystem production (Whiting and Chanton, 1993). Singh et al. (2000), for example, found that CH_4 emissions from the vegetated surfaces of a water body were 17 to 24 times higher than from unvegetated surfaces. Higher gas emission rates have been shown in monocotyledonous plants as compared to dicotyledonous plants (Grosse et al., 1991; Thomas et al., 1996), and in plants with active gas transport mechanisms (Sebacher et al., 1985; Brix et al., 1992). Chanton et al. (1993) reported mean CH_4 emissions of 8909 μmol CH_4 m^{-2} d^{-1} from *Typha domingensis* Pers. and 2804 μmol CH_4 m^{-2} d^{-1} from *Cladium jamaicense* Crantz in a Florida peat soil, and explained the variation in CH_4 emissions by differences in above-ground biomass and productivity. Methane emissions measured from the open water between plants in their study were 6% of the total emissions measured from *Typha domingensis*. A comparison of CH_4 emissions from the air-water interface and from *Typha latifolia* L. indicated that more than 50% of the CH_4 emissions from the littoral zone of the wetland were from the plants (Sebacher et al., 1985).

2.9 Gaseous Loss of Nitrogen from Wetlands

Denitrification has been identified as the most important process in removal of N from wetlands and riparian areas (Rutherford and Nguyen, 2004). This process produces gaseous forms of N (N_2O, N_2) which in turn are emitted to the atmosphere (Bowden, 1987). The role of N removal by wetlands and riparian areas has most often been studied in wetlands constructed for nutrient retention (Stadmark and Leonardson,

2005), and those located in agricultural fields which receive high loads of nitrate from surface and groundwater flow (Hefting et al., 2003; Rutherford and Nguyen, 2004).

High denitrification rates have been reported for organic soil swamp and mineral soil stream riparian sites (Watts and Seitzinger, 2000). Concern has arisen that high rates of denitrification could result in correspondingly high rates of N_2O emissions (Freeman et al., 1997). Groffman et al. (1998) recognized the inadequacy in the number of studies relating high denitrification rates and N_2O emissions in riparian areas and further suggests that N_2O emissions may be low due to the highly anaerobic conditions found in many riparian zone soils.

Less attention has been given to N_2O emissions from the open-water zone of wetlands. Benthic and periphytic algae play an important role in wetland N cycling (An and Joye, 2001). Studies have found high potential and actual denitrification rates in benthic and periphytic algal matrices, as they may provide important attachment sites and carbon sources for denitrifying bacteria (Toet et al., 2003; Sirivedhin and Gray, 2006). In a review by Saunders and Kalff (2001) denitrification accounted for 63% of total N removal in lakes. Combined studies of denitrification and N_2O emissions are lacking and the contribution of N_2O emissions from prairie wetlands is not well defined but is expected to be low as the water-saturated environment would promote the formation of N_2 rather than N_2O as N_2 is the dominant gas produced when the water-filled pore space exceeds 80% (Veldkamp et al., 1998). The few existing N_2O estimates from water bodies come from an extensive study by Tremblay et al. (2005) in which 125 water bodies were sampled for greenhouse gases. Their study found N_2O emissions ranging from -10 to 23 ng N_2O-N m^{-2} s^{-1} in lakes, rivers, and reservoirs across Canada.

3.0 NITROUS OXIDE FLUX FROM TWO OPEN WATER PRAIRIE WETLANDS

3.1 Introduction

Concern has arisen over the increasing concentration of atmospheric nitrous oxide (N_2O) (IPCC, 2001). Nitrous oxide is a potent greenhouse gas with a global warming potential 296 times that of carbon dioxide (CO_2) (IPCC, 2001). Wetlands have received considerable attention in their ability to remove nitrogen (N) from ground water and to improve water quality (Verhoeven et al., 2006; Freeman et al., 1997). Riparian areas surrounding wetlands and streams are generally thought to buffer water bodies from excess nutrients through immobilization of N by microbes, and plant uptake and removal of N through denitrification (Groffman et al., 1998). Denitrification, the most important process in removal of N from wetlands and riparian areas (Rutherford and Nguyen, 2004), results in production of gaseous forms of N (N_2O, N_2) which are then emitted to the atmosphere (Bowden, 1987).

Research focusing on wetland ability to remove N is most often in relation to wetlands which, due to their location in agricultural fields, are chronically loaded with nitrate from surface and groundwater flow (Hefting et al., 2003; Rutherford and Nguyen, 2004), and wetlands constructed for nutrient retention (Stadmark and Leonardson, 2005). Concern has arisen that high denitrification rates could result in correspondingly high rates of N_2O emissions (Freeman et al., 1997). Inadequacy in the number of studies

relating high denitrification rates and N_2O emissions in riparian areas has been recognized (Groffman et al., 1998). Nitrous oxide emissions may be low due to the highly anaerobic conditions found in many riparian zone soils (Groffman et al., 1998). Research on N_2O emissions from soils has shown that the production of N_2O declines beyond a water-filled pore space of 80% (proxy for O_2) and dinitrogen (N_2) is the dominant gas produced (Veldkamp et al., 1998).

Studies focusing on N_2O emissions from the open-water zone of wetlands are scarce. Benthic and periphytic algae provide important attachment sites and carbon sources for denitrifiying bacteria (Toet et al., 2003; Sirivedhin and Gray, 2006), and play an important role in wetland N cycling (An and Joye, 2001). In a review by Saunders and Kalff (2001) denitrification accounted for 63% of total N removal in lakes. Studies combining the rates of N_2O production and denitrification are lacking and prairie wetland contribution to N_2O emissions has not been established. Tremblay et al. (2005) provides the only extensive estimates of N_2O emissions for water bodies. Their study included estimates from 125 water bodies and reported N_2O emissions ranging from -10 to 23 ng N_2O-N m^{-2} s^{-1} in lakes, rivers, and reservoirs across Canada.

The purpose of this study was to assess the spatial and temporal variation of N_2O emissions in two prairie wetlands. The primary objectives were 1) to determine the ice-free seasonal N_2O flux from the two wetlands, 2) to measure select biological parameters and environmental variables and 3) to determine which of these, if any, correlated to N_2O flux. The secondary objective was to determine if there was a diurnal variation in the N_2O flux.

3.2 Materials and Methods

Greenhouse gas sampling was conducted at two research sites to inventory emissions of N_2O from the open water and associated riparian area. These inventory estimates were then used to calculate cumulative gas emissions at each site. Gas sampling over a 24-hour period was undertaken to determine if there was a diurnal emission pattern and to correct cumulative estimates for this difference.

3.2.1 Field Site

Research was conducted at two wetlands. Pond 1 is located in the St. Denis National Wildlife Area, 40 km east of Saskatoon, Saskatchewan, Canada (52º 12'N latitude, 106º 5'W longitude). Pond 1 is the largest pond at the St. Denis National Wildlife Area (Figure 3.1). Pond 1 is a semi-permanent wetland (Class IV), dominated by an open-water phase devoid of emergent vegetation (Cover Type 4), and is distinguished from a permanent wetland (Class V) by the submerged vegetation present (*Ceratophyllum* spp.) (Stewart and Kantrud, 1971). The site is characterized by a hummocky till terrain with an unsorted calcareous till and glacio-lacustrine sediment parent material (Yates et al., 2006). Slopes are strongly to moderately rolling (10 to 15%). Dominant soils are Orthic Dark Brown Chernozems on the mid and lower slopes and Calcareous Dark Brown Chernozems and Orthic Regosols on the knolls (van der Kamp et al., 2003). Mean annual precipitation in Saskatoon between 1971 and 2001 was 350 mm, of which 97 cm fell as snow (Environment Canada, 2004). Snowmelt

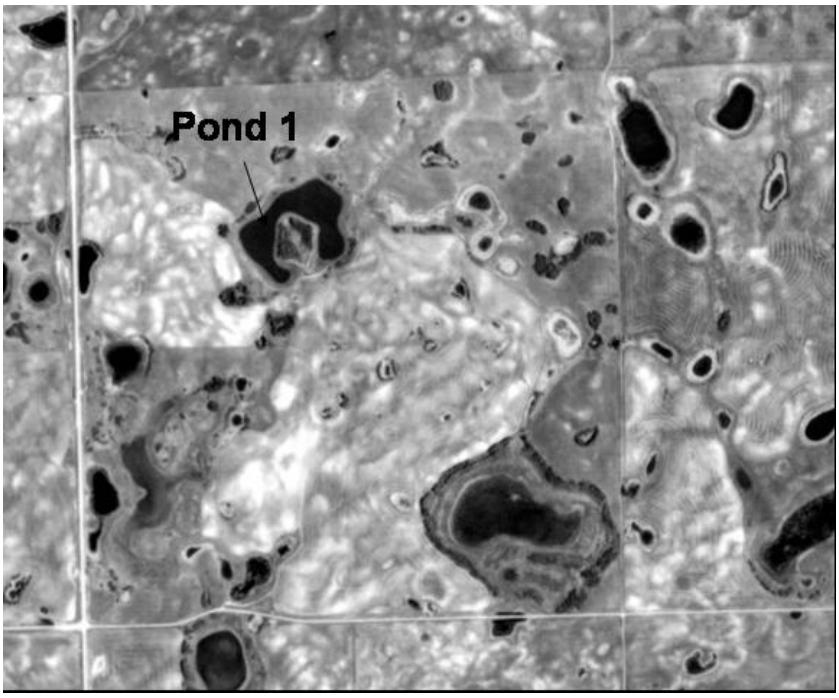

Figure 3.1 Aerial photograph of the research site at the St. Denis National Wildlife Area.

runoff is critical to recharge water levels of prairie wetlands in the spring (LaBaugh et al., 1998) as evaporative loss can be 600-1000 mm, which generally exceeds precipitation (van der Kamp et al., 2003). Mean annual temperature between 1971 and 2001 was 2.2 ºC (Environment Canada, 2004).

The second wetland was the Deep Crop Wetland (DCW), located at the Manitoba Zero Till Research Association farm (MZTRA) (Figure 3.2). The study site is located approximately 20 km north of Brandon, Manitoba, Canada. The DCW is dominated by an open-water phase at the central and deepest portion of the wetland surrounded by a deep-marsh zone composed of cattail (*Typha* spp.) and is classified as a semi-permanent (Class IV) wetland (Stewart and Kantrud, 1971). The site is characterized by a gently sloping (slope class 3: 2 to 5%), hummocky terrain formed over calcareous glacial till. Soils are typically of the Newdale Association and are dominated by Orthic Black Chernozems in mid to upper slope positions with Rego and Calcareous Black Chernozems on the knolls (Podolsky and Schindler, 1994). Mean annual precipitation in Brandon between 1971 and 2001 was 472 mm, of which 112 cm fell as snow. Mean annual temperature was 1.9 ºC over that same time period (Environment Canada, 2004).

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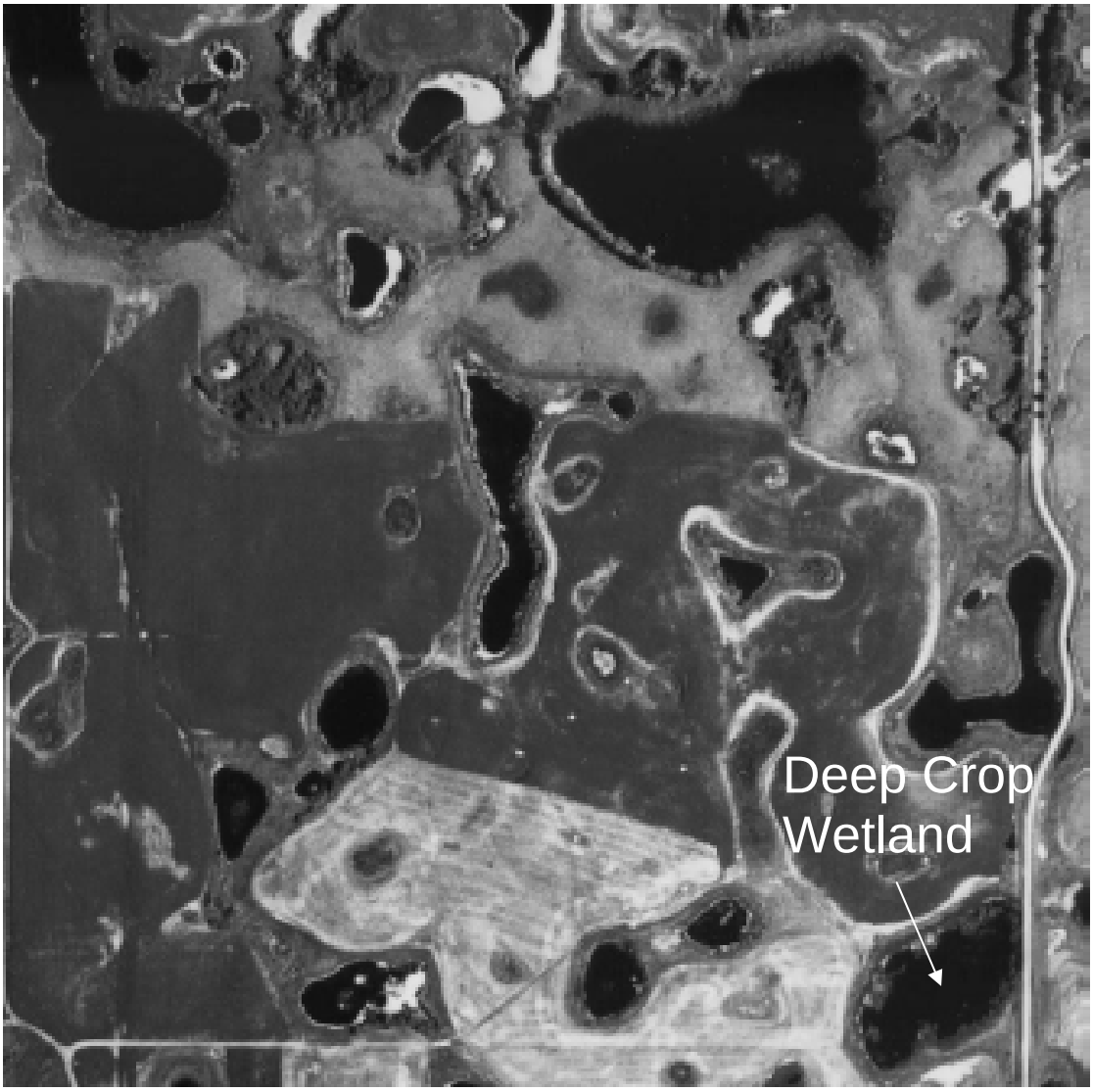

Figure 3.2 Aerial photograph of the research site at the Manitoba Zero Till Research Association farm.

3.2.2 Water Temperature, Water Depth, and Climate Data

In 2004 and 2005 water depth, ambient air temperature, and water temperature at 5-cm below the surface at Pond 1 were measured at the time of gas sampling at each pair of chamber locations along the dock using a Barnant DuaLogR™ (Barnant Company, Barrington, IL). On July 22, 2005 a HOBO® Weather Station (Onset Computer Corporation, Pocasset, MA) was set up to record hourly averages of precipitation, air temperature, relative humidity, dew point, wind speed, photosynthetically available radiation (PAR), and barometric pressure.

Water depth was measured on each sampling date at each pair of chambers at the DCW in 2005. Air temperature at the surface and 5 cm above the surface was measured at each pair of chambers along the transect.

3.2.3 Water Quality and Chemistry

Water samples were collected weekly from the open water at Pond 1 in 2004 and transported back to the laboratory on ice where they were refrigerated at 4 ºC until analysis. Samples were removed from the refrigerator prior to analysis and warmed to room temperature. pH was measured using a pH meter (pHI™, Beckman) and electrical conductivity using a conductivity meter (Radiometer, Copenhagen). Water samples for nutrient analysis were collected at least three times throughout the ice-free season at both Pond 1 and the DCW. Samples were analyzed by Enviro-Test Laboratories (Saskatoon, SK; Brandon, MB) for total nitrogen (TN), ortho-phosphorous (OP), and total phosphorous (TP), bicarbonate (HCO_3), sulfate (SO_4), chloride (Cl), sodium (Na), magnesium (Mg), potassium (K), calcium (Ca), total dissolved solids (TDS), and

electrical conductivity (EC) (APHA, 1998). Water samples were collected for analysis of dissolved organic carbon (DOC) three times throughout the ice-free season.

In 2005, dissolved oxygen, turbidity, pH, temperature, redox, and electrical conductivity were logged hourly with a Hydrolab® DS 5X (HACH Environmental, Colorado). The Hydrolab was deployed in Pond 1 from June 23 to October 11, 2005 and from July 14 to Sept 13, 2005 in the DCW.

3.2.4 Pond Sampling

Gas sampling at Pond 1 was carried out in 2004 and 2005. Sampling was conducted weekly from April 7, 2004 until October 12, 2004 at Pond 1 between 1000 and 1400 hours. A transect of 12 chambers was located along a dock that started at the water's edge. Six acrylic, non-vented chambers with a headspace volume of 10.76 L covering a surface area of 0.06 m^2 were located on each side of the dock. Maximum water depth beneath the chambers was 105 cm. Samples of headspace gas were taken with a 20-mL syringe and injected into a 12-mL evacuated tube. Twenty-milliliters of air were removed two times at each time step via syringe to clear the tygon tube prior to sampling the headspace gas. Samples of headspace gas were collected at intervals of 0, 20, 40, and 60 minutes. Two riparian area transects of 12 chambers each were also installed. Riparian area chambers were two-piece, closed, vented chambers (International Atomic Energy Agency, 1992) and were constructed from a polyvinyl chloride (PVC) ring base and vented cap similar to Hutchinson and Mosier (1981). Riparian chambers had a head space of 2.25 L covering a surface area of 0.02 m^2. At the time of the initial gas sample (t_0) the chamber was placed on the base and sealed with a

rubber ring within the cap. Samples of headspace gas were collected at time intervals of 0, 8, 16, and 24 minutes.

A rapid rise in water level in 2005 after snowmelt destroyed the dock used in 2004, thus necessitating the development of a different sampling design. The riparian area was underwater in this year and no riparian sampling was completed. Six sampling stations were accessed from a wooden dock that started at the water's edge; ten additional chambers were accessed from two floating platforms located in the open water (five chambers each). Research was conducted bi-weekly at Pond 1 from April 28 until October 11 between the hours of 1000 and 1400 hours. Acrylic, non-vented chambers with a headspace volume of 10.76 L covering a surface area of 0.06 m^2 were used to take greenhouse gas measurements. The maximum water depth beneath the chambers was 309 cm. Platform chambers were attached with a long arm and four 500-mL plastic bottles were bolted to the outside of the chamber for flotation. Samples of the headspace gas were collected at intervals of 0, 8, 16, and 24 minutes. Ambient air samples were taken at each time step.

At the DCW greenhouse gas sampling was conducted on nine sampling dates between April 15, 2005 and October 2, 2005 by University of Manitoba staff. Six soil chambers were located in the riparian area and six chambers were located over the open water. Soil chambers were two-piece, closed, vented chambers constructed from PVC. Collars were 10 cm in height of which 5 cm was inserted into the ground. The vent tube was 7.5 cm in length with a diameter of 0.4 cm. Chamber lids were flat covers fitted with a rubber band around the edge, which was in contact with a rubber ring on the topside of the collar to prevent leaking. Elastic bands were used to secure the lid to the

collar and were fastened to hooks on the outside of the chamber. Chambers had a headspace volume of 1.62 L covering a surface area of 0.03 m^2.

Open water chambers were constructed from a similar design as the soil chambers and also included PVC piping which was secured around the chamber collar to allow the chamber to float. Gas samples from the riparian and open-water chambers were collected from the headspace through a 0.13-m rubber septum using a 20-mL syringe at 30 and 60 minutes after chamber deployment. Ambient air samples were taken and those concentrations were averaged and used as the t_0 concentration for the day. Sampling was conducted between 0900 and 1400 hours. The maximum water depth beneath the chambers was 74 cm.

3.2.5 Diurnal Variation in Greenhouse Gas Emissions

Sampling was conducted over a 24-hour period on three dates during the ice-free season at Pond 1 in 2005 and one day (August 12, 2005) at the DCW. Sampling took place every two hours between 1000 and 0800 the following day. Samples were taken at intervals of 0, 8, 16, and 24 minutes with a 20-mL syringe. Collection and analysis were as described above. Mean emissions were calculated for each gas for each sampling time.

3.2.6 Gas Analysis

For samples from Pond 1, N_2O concentration was determined using a Varian CP 3800 gas chromatograph (GC) equipped with a ^{63}Ni electron capture detector (ECD) (Varian Canada Inc. Mississauga, ON). Electron capture detector temperature was 380 ºC, injector temperature was 70 ºC, and the column temperature was 290 ºC. The

analytical column was a 1.83-m x 3.18-mm i.d., 80/100 mesh Hayesep D. The carrier gas was Ar:CH_4 in a 90:10 ratio, with a flow rate of 30 mL min^{-1}. Samples (2.5 mL) were drawn using a CombiPAL^{TM} autosampler (CTC Analytics AG, Switzerland) from a 12-mL Exetainer^{TM} into a Hamilton gastight syringe and injected into a 10-port sampling valve which was then transferred to two 0.5-mL sample loops. The sample was then automatically injected onto the column via a 6-port sampling valve. System calibration was obtained using standard gases (Praxair Gases, Edmonton, AB) composed of 1.11 μL L^{-1} N_2O. Processing of data was completed using Varian Star^{TM} Chromatography Workstation (ver. 6.2) software.

Minimum detectable concentration difference (MDCD) was calculated using the standard deviation (σ) of reference gas samples in each analytical run using equation 3.1.

$$MDCD = 2\sigma \quad (3.1)$$

When calculating gas flux, the MDCD was used to filter the raw data following a standard systematic procedure developed in our laboratory to identify and correct rogue points (similar to Yates et al., 2006). The absolute concentration difference between time steps that were < MDCD were considered not significantly different from zero and a flux of zero was recorded.

Collection of gas samples at four-time intervals for each gas allowed the use of a polynomial relationship to describe the concentration vs. time curve. Generally, the 2nd order polynomial equation was a better fit. Gas flux at the water-atmosphere interface was then calculated as the slope of the line tangent to the concentration vs. time curve at time zero (t_0). Calculated flux (μL L^{-1} min^{-1}) was then multiplied by the chamber volume divided by the surface area, resulting in a flux of μL m^{-2} min^{-1}. When only three points were available for flux calculation (because of 'rogue' data points) flux was

calculated using the linear model that described the concentration vs. time relationship corrected for chamber volume and area (Hutchinson and Mosier, 1981) (equation 3.2).

$$F = (V/A)m \quad (3.2)$$

Where F is flux at t_0, V = chamber volume (L), A = cross sectional area of water covered by the chamber (m^2), m = slope of the linear regression equation ($\mu L\ L^{-1}\ min^{-1}$).

Nitrous oxide in samples from the Deep Crop Wetland was determined using a Varian CP 3800 gas chromatograph (GC) (Varian Canada Inc. Mississauga, ON). Concentration of N_2O was determined with an ECD (Varian Canada Inc. Mississauga, ON). Electron capture detector temperature was 300 ºC and column temperature was 70 ºC. The analytical column was 200-cm x 0.3175-cm, 80/100 mesh Hayesep D, and 50-cm x 0.3175-cm, 80/100 mesh Hayesep N and the carrier gas was Ar:CH_4 in a 90:10 ratio.

Minimum detectable concentration difference was calculated as described above (equation 3.1) and flux calculated using the linear model following Hutchinson and Mosier (1981) using equation 3.2. With collection of only three data points it was not possible to identify or correct rogue data points.

3.2.7 Cumulative Emissions

Daily fluxes were interpolated between sampling dates to determine cumulative emissions for the sampling period. Interpolation between sampling dates followed Yates (2006), where the mean flux for a gas on a particular sampling date was multiplied by the time interval (days) between sampling dates. To determine the cumulative estimate, results were summed over the sample collection period.

Carbon dioxide equivalents were calculated by multiplying N_2O values by 296 for a 100 year time horizon (IPCC, 2001).

3.2.8 Statistical Analysis

Statistical analysis was completed using SPSS (ver. 14.0). Nitrous oxide flux was not normally distributed, flux data was log transformed but a normal distribution was not achieved, therefore non-parametric statistics were used. To determine if there were diurnal variations in emission patterns a Mann-Whitney U test was used to test for significant differences between daytime and nighttime N_2O flux ($p=0.05$). Spearman rank correlation analysis was used to determine if relationships exist between N_2O flux and select environmental parameters (windspeed, air temperature, water temperature, pH, conductivity, turbidity, % oxygen saturation).

3.3 Results

3.3.1 Environmental Variables

Cumulative precipitation at Pond 1 for both the 2004 season (485 mm) and 2005 season (450 mm) was higher than the 30-year normal. Long-term average cumulative precipitation from April to October is 281 mm (including snowfall). June was especially wet in both years: 165 and 216 mm in 2004 and 2005, respectively. The ice-free season at St. Denis in 2004 was cooler than the 30-year average climate normal for Saskatoon (Environment Canada, 2004). In 2005, seasonal temperature was slightly below average, as was the wind speed (< 4.5 m s^{-1}). Average temperature from April to October was 9.9 ºC in 2004 and 11.2 ºC in 2005.

Cumulative precipitation from April to October as measured at the Brandon Airport was 463 mm, 80 mm greater than the average. The average temperature of the 2005 ice-free season at Brandon was 12.2 ºC, which was slightly warmer than the 30-year climate normal (Environment Canada, 2004).

3.3.2 Nutrients

Mean total nitrogen (TN) and total phosphorous (TP) concentrations were 4.39 mg L^{-1} (±1.69; n=5) and 0.60 mg L^{-1} (±0.83 STD; n=6), respectively in Pond 1 in 2004. Mean nutrient concentrations in Pond 1 in 2005 were lower than in 2004 (1.63 mg L^{-1} TN ±0.32 STD and 0.30 mg L^{-1} TP ±0.17 STD; n=3). Total phosphorous concentrations in April and June of 2005 were below the minimum detection limit of the lab (0.20 mg L^{-1}). The Redfield ratio describes marine phytoplankton requiring macro-nutrients in a molar ratio of 106C:16N:1P (Redfield et al., 1963). If the molar ration of TN:TP is > 16:1 (7.2:1 by mass) then algal growth may be P-limited, conversely, if the molar ratio is < 16:1 (7.2:1 by mass) then a N-limitation may exist. Depending on the actual concentration, Pond 1 may have been P-limited (TN:TP ratio >7.2:1 by mass) in the spring and N-limited (<7.2:1 by mass) in mid summer.

Total nitrogen and TP concentrations in the DCW increased through the season in 2005 and averaged 2.20 (±0.62 STD; n=3) and 0.28 mg L^{-1} (±0.19 STD; n=3), respectively. The TN:TP ratio in May was 21:1 by mass indicating that the DCW was P-limited. By August the wetland had switched to a slight N-limitation with a TN:TP ratio of 6:1 by mass.

3.3.3 Electrical Conductivity, Major Ions, and pH

Pond 1 water levels in 2004 were low and declined to the point where the wetland was separated into three separate water bodies. Mean EC of Pond 1 in 2004 was 4526.67 µS cm^{-1} (±847.62 STD; n=6) or moderately brackish (2,000-5,000 µS cm^{-1}) (Stewart and Kantrud, 1972). Due to high water levels in 2005, conductivity decreased to 830.00 µS cm^{-1} (± 205.18 STD; n=3), but the wetland was still slightly brackish (500-2,000 µS cm^{-1}) (Stewart and Kantrud, 1972).

Concentration of all major ions decreased from 2004 to 2005 in Pond 1, with the exception of HCO_3^- which increased slightly from 175.67 (±547.62 STD; n=6) to 194.00 mg L^{-1} (±67.02 STD; n=3). In 2004 Pond 1 was dominated by magnesium (522.50 mg L^{-1} ±147.85 STD; n=6) and sulfate (3136.67 mg L^{-1} ±942.71 STD; n=6). The rapid rise in water level in spring 2005 caused a considerable dilution effect in this year. Water chemistry was dominated by calcium (72.33 mg L^{-1} ±19.86 STD; n=3) and sulfate (267.00 mg L^{-1} ±58.85 STD). Mean DOC concentration in 2005 was 3.94 mg C L^{-1} (±1.35 STD; n=2).

At Pond 1 the seasonal mean pH in 2004 was 8.3 (±0.9 STD; n=21). The pH in Pond 1 was highest in July and August (> 9.0 in both months). In 2005 the pH was lower and the seasonal mean pH was 8.0 (±0.6 STD, n=97). It increased seasonally from 7.2 (±0.2 STD; n=26) in July to 8.6 (±0.0 STD; n=11) in October.

The percentage oxygen (O_2) saturation in Pond 1 in 2005 changed throughout the summer. Monthly mean percent O_2 saturation in the water column was 50 (± 8 STD; n=6) in July and increased to almost 95% oxygen saturation in September (± 6 STD; n=24) and October (± 7 STD; n=11). The water column was often super-saturated during the day with O_2 saturation > 100%. The high percent saturation is also reflected

in high redox potential of Pond 1, which was > 500 mV except for July. Daily mean turbidity ranged between 5 and 10 national turbidity units (NTU) with the exception of October which was very turbid, monthly mean > 95 NTU.

The EC of the DCW in 2005 was 1910.00 µS cm^{-1} (± 546.17 STD; n=3) and therefore slightly brackish (Stewart and Kantrud, 1972). The DCW was a magnesium-sulfate dominated wetland. Sulfate concentration was 892.67 mg L^{-1} (± 315.85 STD; n=3), three times the concentration at Pond 1 in 2005. Mean DOC concentration in the DCW was 2.38 mg C L^{-1} (±0.37 STD; n=3). The water column in the DCW had very low percent oxygen saturation with monthly mean percent O_2 saturation below 5.5 from July to September on dates sampled. This is also reflected in the very low redox potential. The monthly mean redox potential in July was 96 mV (±174; n=18) and decreased to -49 mV (±130; n=13) in September. Of the months when turbidity was measured, July had the highest mean turbidity (28 NTU ±7 STD; n=18) and it decreased throughout the remainder of the season.

3.3.4 Seasonal Patterns of Nitrous Oxide Emissions

Nitrous oxide flux from the open water of Pond 1 in 2004 ranged from -1.47 to 6.01 ng N_2O-N m^{-2} s^{-1} and no seasonal pattern was evident (Figure 3.3a). Nitrous oxide flux from the riparian area ranged from -0.51 to 8.11 ng N_2O-N m^{-2} s^{-1} (Figure 3.3b). Fluxes were generally higher earlier in the season. Nitrous oxide emissions from the open water of Pond 1 were low in 2005, ranging from -6.98 to 5.74 ng N_2O-N m^{-2} s^{-1} (Figure 3.3c). No seasonal pattern was evident and Pond 1 appeared to act as a sink for N_2O on most sampling days (i.e., negative flux values were observed).

Mean daily emissions from the open water at the DCW were negligible and never exceeded 1.00 ng N_2O-N m^{-2} s^{-1} (Figure 3.3d). No seasonal pattern was evident for N_2O flux. Nitrous oxide flux from the riparian area did not exhibit a seasonal pattern either and measured fluxes were never greater than 2.50 ng N_2O-N m^{-2} s^{-1} (Figure 3.3e).

3.3.5 Diurnal Emissions

Diurnal emission patterns were measured on three days at Pond 1 in 2005. The main intent was to determine if a diurnal correction should be applied to the mid-day gas measurements taken on all other sampling days.

No consistent significant differences were found between daytime and nighttime emissions for N_2O flux based on a Mann-Whitney U test at the 0.05 significance level (Table 3.1). Therefore, no correction factor was applied to the cumulative emissions.

Table 3.1 Mean daytime (0600h to 1800h) and nighttime (1800h to 0600h) nitrous oxide emissions from Pond 1 and the Deep Crop Wetland. Standard deviations are in brackets (n=6).

Date	0600 to 1800	1800 to 0600
	ng N_2O-N m^{-2} s^{-1}	
	Pond 1	
May 31	-1.20 (14.89)	-6.16 (29.09)
July 5	1.90 (58.35)	2.98 (35.34)
Aug 11	0.97 (27.17)	4.95 (25.24)
	Deep Crop Wetland	
Aug 12		
open water	-0.11 (1.62)	0.14 (1.90)
riparian area	-0.53 (1.91)	0.39 (0.85)

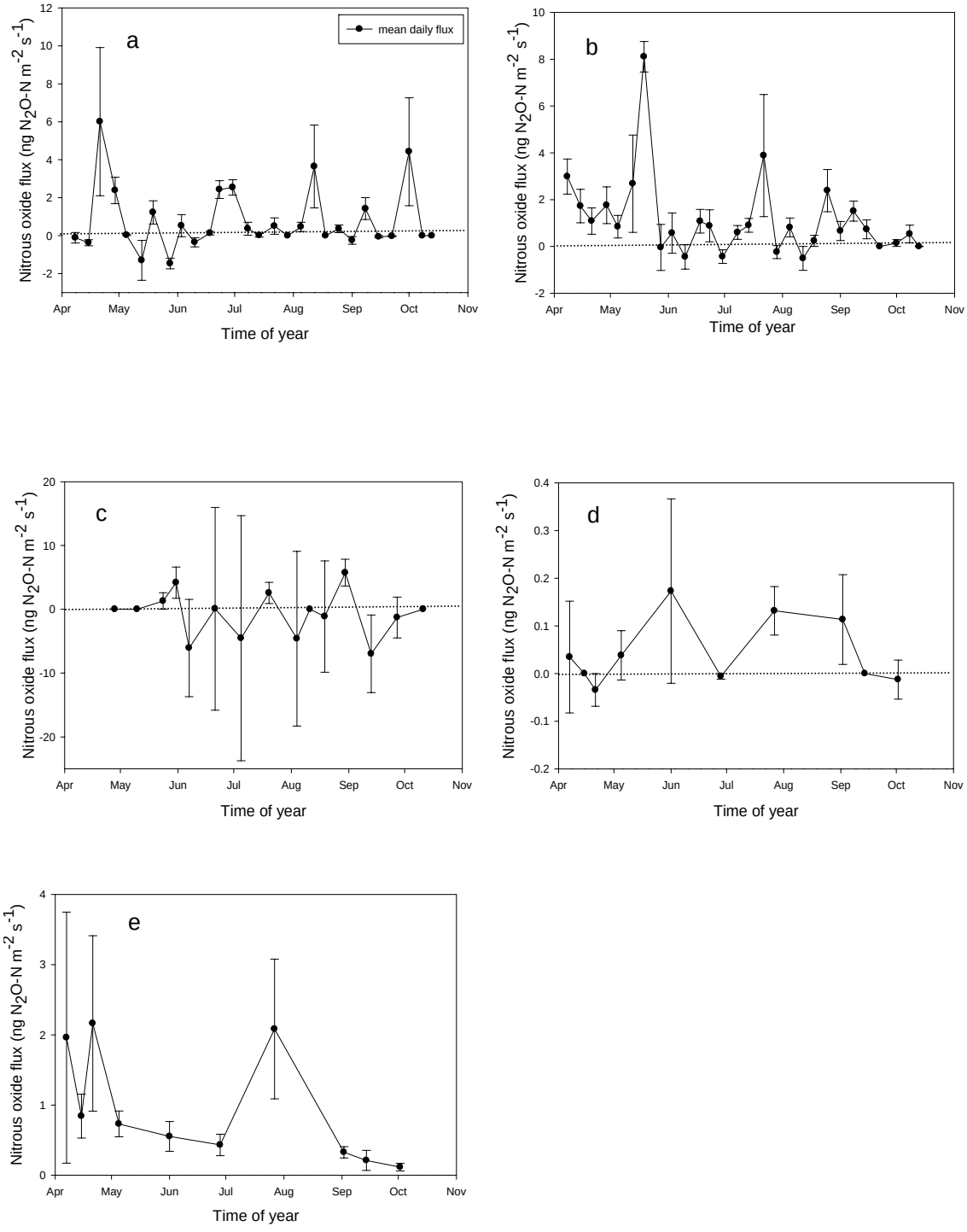

Figure 3.3 Seasonal variation in nitrous oxide flux from a) the open water of Pond 1 in 2004, b) the riparian area of Pond 1 in 2004, c) the open water of Pond 1 in 2005, d) the open water of the Deep Crop Wetland in 2005 and e) the riparian area of the Deep Crop Wetland in 2005. Error bars represent the standard error of the mean. (Note change in scale of y axis.)

3.3.6 Cumulative Emissions

Cumulative N_2O emissions were 147.49 g N_2O-N ha^{-1} 194 d^{-1} (6.86 g $CO_{2\ eq}$ m^{-2} 194 d^{-1}) from the open water of Pond 1 in 2004. Cumulative emissions from the riparian area were 203.57 g N_2O-N ha^{-1} 194 d^{-1} (9.47 g $CO_{2\ eq}$ m^{-2} 194 d^{-1}). In 2005 Pond 1 appeared to be acting as a sink for N_2O with cumulative emissions of -131.92 g N_2O-N ha^{-1} 179 d^{-1} (-6.14 g $CO_{2\ eq}$ m^{-2} 179 d^{-1}).

Cumulative emissions from the open water of the DCW in 2005 were 10.46 g N_2O-N ha^{-1} 191 d^{-1} (0.48 g $CO_{2\ eq}$ m^{-2} 191 d^{-1}) while those from the riparian area were an order of magnitude greater (144.43 g N_2O-N ha^{-1} 191 d^{-1} ; 6.72 g $CO_{2\ eq}$ m^{-2} 191 d^{-1}) and were similar to cumulative N_2O emissions from the riparian area of Pond 1 in 2004.

3.3.7 Correlation Analysis

Spearman rank correlations were used to determine if there were correlations between any of the environmental variables measured (i.e., windspeed, air temperature, water temperature, pH, conductivity, turbidity, % oxygen saturation) and daily N_2O flux from the open water of Pond 1 in 2004 and 2005. Environmental variables were measured from July 14 to September 13 at the DCW in 2005 and the majority of gas sampling dates occurred prior to this, therefore correlation analysis was not undertaken for that data set.

No significant correlations were found between N_2O flux and any of the environmental variables measured at Pond 1 in 2004 and 2005.

3.4 Discussion and Conclusions

Wetlands that hold permanent water, such as Pond 1 and the DCW are not likely significant sources of N_2O emissions. Nitrous oxide fluxes from the two study wetlands

showed no consistent diurnal or seasonal patterns. Nitrous oxide is produced when conditions are sub-optimal for denitrification, which is the dominant N_2O producing process when water-filled pore space in soils is greater than 60% (van Cleemput, 1998). When the water-filled pore space exceeds 80% in soils N_2 is the dominant gas produced (Veldkamp et al., 1998). Wetlands holding permanent water would most likely facilitate the completion of the reaction and the formation of N_2. Nitrous oxide fluxes from Pond 1 and the DCW were on the low side of the range of N_2O fluxes (-10 to 23 ng N_2O-N m^{-2} s^{-1}) observed by Tremblay et al. (2005) for 125 water bodies sampled across Canada. Tremblay et al. (2005) also found no significant relationships between N_2O fluxes and the variables measured (i.e., water and air temperature, water colour and transparency, depth, pH, alkalinity, wind velocity).

Highest mean daily N_2O flux from the open water wetlands in this study are also lower than those reported from the surrounding uplands at St. Denis and other agricultural regions. Highest mean daily N_2O flux measured in a previously cultivated landscape seeded to grass at the St. Denis site was 25.3 ng N_2O-N m^{-2} s^{-1} (Yates et al., 2006). In an agricultural region of the Alberta parkland, the highest mean flux reported was 97.2 ng N_2O-N m^{-2} s^{-1} (Lemke et al., 1998). Highest mean fluxes found in this study were 6.01 ng N_2O-N m^{-2} s^{-1} from the open water and 8.11 ng N_2O-N m^{-2} s^{-1} from the riparian area, both occurring at Pond 1 in 2004. Cumulative N_2O emissions from cultivated convex (i.e., hilltop) landscape units at St. Denis were 758.3 g N_2O-N ha^{-1} 108.5 d^{-1} in 2003, -20.2 g N_2O-N ha^{-1} 232.5 d^{-1} in 2004, and 228.4 g N_2O-N ha^{-1} 231.5 d^{-1} in 2005 (Yates, 2006), exceeding cumulative emissions from Pond 1 and the DCW in two of the three years.

Temporary or more ephemeral wetlands that are prone to drying seasonally may provide more favorable conditions for N_2O emissions. Ephemeral wetlands at St. Denis showed high N_2O flux events during the 2005 dry-down period, but this was not evident at all wetlands studied (Yates, 2006). Yates (2006) reported cumulative N_2O emissions from cultivated depressions at the St. Denis site at 1616.7 g N_2O-N ha^{-1} 231.5 d^{-1} and 2098.7 g N_2O-N ha^{-1} 231.5 d^{-1} from the basin center of uncultivated wetlands in 2005.

Pond 1 and the DCW were negligible sources of N_2O. The presence of permanent water most likely produced conditions that allowed denitrification to proceed to completion forming N_2 rather than N_2O. Climate may be an important variable regulating N_2O flux from wetlands as periods of water level dry-down have shown to promote N_2O flux events at certain times (Yates, 2006). Although it is unlikely that Pond 1 or the DCW would dry-down completely it is possible that a zone or margin around the periphery of the wetland could dry-down seasonally dependent on the environmental conditions in a given year and these areas could be sources of N_2O. This emphasizes the importance of climate as a variable when considering greenhouse gas emissions and the importance of inventorying emissions from wetlands of different permanence classes over a number of years as there could be within and between season variations in environmental conditions that may affect N_2O flux.

4.0 GASEOUS CARBON LOSSES AND RELATIONSHIP TO ALGAL DYNAMICS, WATER CHEMISTRY, AND ENVIRONMENTAL VARIABLES IN TWO PRAIRIE WETLANDS

4.1 Introduction

The prairie pothole region (PPR) of North America encompasses approximately 780 000 km^2 (Mitsch and Gosselink, 1993). This region contains a high density of wetlands and is deemed one of the world's most important wetland areas (Mitsch and Gosselink, 1993). Although the value and importance of prairie wetlands is beginning to be recognized, they are still under-studied and the role they play as greenhouse gas sinks or sources is only poorly understood.

Wetlands store carbon in living and dead organic matter and accrete organic carbon through primary production (autochthonous) and terrestrial inputs (allochthonous) (Kalff, 2002). Carbon dioxide (CO_2) emissions from wetlands arise from autotrophic and heterotrophic respiration as well as CO_2 produced through decomposition (Blais et al., 2005). Carbon transformation processes also contribute methane (CH_4) from wetlands to the atmosphere. Natural wetlands, mostly peatlands and tropical wetlands, contribute roughly 115 Tg CH_4 to the atmosphere annually (Bartlett and Harris, 1993). Methane is the end product in the anaerobic decomposition of organic matter. Accumulation of large amounts of organic matter and anaerobic conditions provide a favorable environment for CH_4 production (Christensen et al.,

2003). Wetlands often have productive zones of benthic algae inhabiting surficial sediments, producing an oxygenated micro-zone (King, 1990). Methanotrophic bacteria inhabiting this zone are active in the consumption of CH_4 and its oxidation to CO_2 (Schlesinger, 1997). Methane emissions to the atmosphere are therefore a result of CH_4 production in the anoxic sediments minus CH_4 oxidation that occurs at both the sediment-water interface and throughout the water column (Bussmann, 2005; Schlesinger, 1997).

Researchers have found positive correlations between net ecosystem production (Whiting and Chanton, 1993), net primary production (Aselmann and Crutzen, 1989; Xing et al., 2005), algal Chlorophyll – *a* (Chl – *a*) (Xing et al., 2005) and CH_4 and CO_2 fluxes. Primary production may stimulate methanogenesis through increasing organic substrates and through the production of autochthonous organic matter (Whiting and Chanton, 1993; Xing et al., 2005). This suggests that more productive wetlands may have higher CH_4 emissions due to the higher algal and macrophyte biomass and that less productive wetlands may have lower CH_4 emissions. These relationships may not hold true for the eutrophic wetlands found on the prairies; high productivity during the day can result in diurnal changes in oxygen saturation of the water column (Kalff, 2002) and may result in CH_4 oxidation (Schlesinger, 1997).

The purpose of this study was to assess spatial and temporal variation in CO_2 and CH_4 emissions from two prairie wetlands and co-variation between emissions and algal dynamics at the two sites. The two sites have strongly contrasting water chemistry and biological attributes. The specific objectives of this study were 1) to determine the ice-free seasonal greenhouse gas flux from the two wetlands, 2) to determine the algal and macrophyte biomass in the two wetlands, and 3) to measure select biological parameters

and environmental variables, and to determine which, if any, correlate to the greenhouse gas flux.

4.2 Materials and Methods

4.2.1 Field Site and Sampling Design

Research was conducted at two study sites: one in Saskatchewan and one in Manitoba. Pond 1 is located in the St. Denis National Wildlife Area, 40 km east of Saskatoon, Saskatchewan, Canada (52º 12'N latitude, 106º 5'W longitude). Pond 1 is dominated by an open-water phase and is classified as a semi-permanent wetland (Class IV), with greater than 95% open water (Cover type 4). It is distinguished from a permanent wetland (Class V) by the submerged vegetation present, which was dominated by *Ceratophyllum* spp. in 2005 (Steward and Kantrud, 1971). The surrounding landscape is hummocky till terrain with unsorted calcareous till and glacio-lacustrine parent material and is dominated by Dark Brown Chernozemic soils (Yates et al., 2006). Mean annual precipitation in Saskatoon between 1971 and 2001 was 350 mm, of which 97 cm fell as snow (Environment Canada, 2004). Snowmelt runoff is critical to recharge water levels of prairie wetlands in the spring (LaBaugh et al., 1998) as evaporative loss can be 600-1000 mm, which generally exceeds precipitation (van der Kamp et al., 2003). Mean annual temperature between 1971 and 2001 was 2.2 ºC (Environment Canada, 2004).

The second study site was the Deep Crop Wetland (DCW), located at the Manitoba Zero Till Research Association farm (MZTRA). The study site is approximately 20 km north of Brandon, Manitoba, Canada in the PPR. The DCW is a semi-permanent (Class IV) wetland dominated by an open-water zone occupying the

central and deepest part of the wetland and is surrounded by a zone of deep-marsh vegetation composed of a dense cattail (*Typha*) ring in the littoral zone (Stewart and Kantrud, 1971). The site is gently sloping (2 to 5%) hummocky terrain formed over calcareous glacial till and Orthic Black Chernozems are dominant (Podolsky and Schindler, 1994). Mean annual precipitation in Brandon between 1971 and 2001 was 472 mm, of which 112 cm fell as snow. Mean annual temperature was 1.9 ºC over that same time period (Environment Canada, 2004).

4.2.2 Water Temperature, Water Depth, and Climate Data

Water depth, ambient air temperature, and water temperature at 5-cm below the surface were measured at Pond 1 at the time of gas sampling at each pair of chamber locations along the dock using a Barnant DuaLogR™ (Barnant Company, Barrington, IL).

At the DCW in 2005 water depth was measured on each sampling date at each pair of chambers. Surface temperature and temperature at 5-cm above the surface was measured at each pair of chambers along the transect. Air temperature and soil temperature were measured at each stacking and small chamber on each sampling date using a Checktemp™ 1 Pocket Thermometer (Hanna Instruments, Mauritius).

4.2.3 Water Quality and Chemistry

Water samples were collected for nutrient analysis a minimum of three times throughout the ice-free season in 2004 and 2005 at Pond 1 and in 2005 at the DCW. Samples were analyzed by Enviro-test labs (Saskatoon, SK; Brandon, MB) for total nitrogen (TN), ortho-phosphorous (OP), and total phosphorous (TP), bicarbonate

(HCO_3), sulfate (SO_4), chloride (Cl), sodium (Na), magnesium (Mg), potassium (K), calcium (Ca), total dissolved solids (TDS), and electrical conductivity (EC) (APHA, 1998). In 2004, pH was measured using a pH meter (pHI™, Beckman) and electrical conductivity using a conductivity meter (Radiometer, Copenhagen). A Hydrolab® DS 5X (HACH Environmental, Colorado) logged dissolved oxygen, turbidity, pH, temperature, redox, and electrical conductivity on an hourly basis in both wetlands in 2005. The Hydrolab® was deployed in Pond 1 from June 23 to October 11, 2005 and in the DCW from July 14 to Sept 13, 2005.

4.2.4 Macrophyte Biomass

To assess areal macrophyte biomass (g m^{-2}), entire above-sediment portions of submersed macrophytes were collected from a known surface area from each wetland in June, July, and August of 2005. An open-ended plastic cylinder was used to delineate a known bottom area (0.23 m^2) and long-handled shears were used to cut enclosed macrophytes at the sediment surface (McDougal, 2002). For emergent macrophytes, the entire above-ground portion of the plants was harvested from a known surface area at their growth peak. All macrophyte samples were dried to a constant weight at 104 °C for determination of dry-weight biomass per unit area.

4.2.5 Algal Biomass

Chlorophyll-*a* was measured weekly during the growing season in 2005 as a determination of algal biomass. Algal assemblages measured were phytoplankton (i.e., free floating in the water column), periphyton (i.e., attached to surfaces), and metaphyton (i.e., forming filamentous mats). Phytoplankton was collected from May 12

to October 11, 2005 at Pond 1 and June 6 to October 11, 2005 at the DCW. Depth-integrated water column samples were collected with a stoppered acrylic tube (60-cm length, 7-cm inner diameter), and filtered in the dark onto 47-mm diameter 1.2-µm pore size glass microfibre filters (grade GF/C, Whatman International Ltd., England) to isolate the pelagic phytoplankton. Samples were subsequently frozen to promote cell lysis. Thawed filters were placed in 10 mL of 90% ethanol in a hot-water bath (80 ºC) and were allowed to boil for five minutes to extract the Chl-*a*. Filters were discarded and the extract volume was measured and then transferred to a borosilicate cuvette. Chlorophyll-*a* was then determined using a Turner Designs Model 10-AU fluorometer (Turner Designs Inc.) (Nusch, 1980). Chlorophyll-*a* was calculated as µg L^{-1} for phytoplankton.

Periphyton was collected by inserting pre-scored acrylic rods into the sediment thereby providing an artificial stratum for algae to colonize (Goldsborough et al., 1986). Sixty-six acrylic rods (0.64-cm diameter) were installed on May 12, 2005 at Pond 1 and on June 9, 2005 at the DCW. After colonization for one week, samples were collected weekly until October 4, 2005 at Pond 1 and October 11, 2005 at the DCW. Acrylic rods were 90 cm in length; 30 cm were inserted vertically into the sediment (50-cm apart) and the 30-cm sampling zone was pre-scored at 2.5-cm increments. Rods were installed with 10 cm to 30 cm of water above the tip of the rod. Triplicate acrylic rods were sampled each week. Three sub-samples were collected from each rod at upper, mid, and lower positions. Rod sections were placed in labeled vials and transported back to the laboratory where they were frozen until analysis. Acrylic rod sections did not withstand the boiling ethanol treatment. Consequently, Chl-*a* was extracted by placing rod sections in 10 mL of 90% ethanol for 24-hours and then sonicating for 3 to 4 minutes to

detach algae. Chlorophyll-*a* was then determined as for phytoplankton and is presented as μg cm^{-2}.

Metaphyton was collected when present. A styrofoam block (530 cm^2) was lowered into the water and was gently raised to bring metaphyton to the surface (Gurney and Robinson, 1988; Robinson et al., 1997a). Triplicate metaphyton samples were removed with a 1.27-cm-diameter copper corer from high, medium, and low mat densities. Samples were then placed in labeled vials and transported back to the lab where they were frozen until analysis. Chlorophyll-*a* was determined using the same method as for phytoplankton, except that the entire core was placed in ethanol and biomass was calculated as μg cm^{-2}.

4.2.6 Greenhouse Gas Flux

Detailed information on sampling design for gas analysis and the analytical protocols for gas chromatography is provided in Phipps (2006) (Chapter 3).

4.2.7 Pond Sampling

Greenhouse gas emissions at Pond 1 were sampled in 2004 and 2005. Sampling took place on a weekly basis from April 7, 2004 until October 12, 2004 at Pond 1 between 1000 and 1400 hours. An open water transect of 12 chambers was located along a dock that started at the water's edge. Two riparian area transects of 12 chambers each were also installed. Samples of headspace gas were collected at intervals of 0, 20, 40, and 60 minutes for open water chambers and intervals of 0, 8, 16, and 24 minutes for riparian chambers.

Snowmelt runoff caused a rapid rise in water level in 2005 and destroyed the dock used in 2004, necessitating a change in sampling design. A wooden dock was used to access six sampling stations that started at the water's edge and two floating platforms located in the open water of the pond housed five chambers each. Sampling was conducted on a bi-weekly basis from April 28 until October 11. Samples of headspace gas were taken as in 2004, except they were collected at intervals of 0, 8, 16, 24, 40, and 60 minutes.

Gas sampling was conducted on nine sampling dates at the DCW between April 15, 2005 and October 2, 2005 by University of Manitoba staff. Twelve chambers were used; six soil chambers were located in the riparian area and six chambers were located over the open water. Gas samples were collected from the headspace at 30 and 60 minutes after chamber deployment. Ambient air samples were taken and those concentrations were averaged and used as the t_0 concentration for the day. Sampling was conducted between 0900 and 1400 hours.

4.2.8 Diurnal Variation in Greenhouse Gas Emissions

Routine sampling of greenhouse gases occurred from 0900 to 1400 hours. If, however, a distinct diurnal pattern in emissions occurs then the mid-day measurements may need to be corrected to reflect true 24-hour emission values. To assess diurnal emission patterns, sampling was conducted over 24-hours on three dates during the ice-free season at Pond 1 in 2005. Sampling took place every two hours between 1000 and 0800 the following day. Measurements of greenhouse gases over 24-hours occurred on August 12, 2005 at the DCW. Five chambers were sampled, two in the open water and

three in the riparian area. Sampling took place every two hours between 0800 and 0600 the following day. Samples were taken at intervals of 0, 8, 16, 24, 40, and 60 minutes.

4.2.9 Stacking vs. Small Chambers

Flux measurements made from small chambers placed between emergent plants may underestimate total emissions if gas is emitted from the vegetation itself (Chanton et al., 1993). A transect was established with both small and stacking chambers to assess the possible effect of this emission pathway. This was done to determine if there were differences in gas flux from stacking chambers with intact riparian vegetation and small chambers placed in the riparian area with vegetation trimmed. Gases were sampled bi-weekly from June 9, 2005 to October 11, 2005 at the DCW. Six chambers were used in total, of which three were small PVC-chambers with a headspace volume of 1.62 L covering a surface area of 0.03 m^2. Vegetation inside the chamber was trimmed periodically. The remaining three chambers were made of three stackable pieces of PVC pipe. Stacking chambers had a headspace volume of 14.02 L, covered a surface area of 0.03 m^2, and were 46 cm above the soil surface. Vegetation within the stacking chambers was unaltered. Gas samples were taken at intervals of 0, 8, 16, 24, 40, and 60 minutes.

4.2.10 Gas Analysis

Concentration of CO_2 in gas samples from Pond 1 was determined using a Varian CP 3800 gas chromatograph (GC) using a thermal conductivity detector (TCD) (Varian Canada Inc. Mississauga, ON). The analytical column was a 1.83-m x 3.18-mm i.d., 80/100 mesh Porapak QS. The carrier gas was He with a flow rate of 30 mL

min^{-1}. Concentration of CH_4 was determined with a flame ionization detector (FID) (Varian Canada Inc, Mississauga, ON). The analytical column was a 1.83-m x 3.18-mm i.d., 80/100 mesh Porapak QS. The carrier gas was He with a flow rate of 30 mL min^{-1}. Samples (2.5 mL) were drawn using a CombiPAL™ autosampler (CTC Analytics AG, Switzerland) from a 12-mL Exetainer™. System calibration was obtained using standard gases (Praxair Gases, Edmonton, AB) composed of 385 μL L^{-1} CO_2, and 1.46 μL L^{-1} CH_4. Data processing was completed using Varian Star ™ Chromatography Workstation (ver. 6.2) software.

Greenhouse gas concentrations for samples from the DCW were determined using a Varian CP 3800 GC (Varian Canada Inc. Mississauga, ON) housed at the University of Manitoba. Concentration of CO_2 was determined using a TCD (Varian Canada Inc. Mississauga, ON). Concentration of CH_4 was determined with a FID (Varian Canada Inc, Mississauga, ON). The analytical column was a 200-cm x 0.3175-cm, 80/100 mesh Porapak QS, and 50-cm x 0.3175-cm, 80/100 Hayesep N.

Minimum detectable concentration differences and curve fitting for calculation of flux were done following the procedures discussed in Phipps et al. (2006) (Chapter 3).

Methane can be emitted through ebullition or "bubble" events. Gas builds in the sediment pore space to a point of supersaturation and is then released as a bubble (Tremblay et al., 2005). Chamber based methods of measuring greenhouse gases are designed to determine diffusive gas emissions over a period of time and consequently are not the appropriate method to measure instantaneous bubble events. To determine diffusive CH_4 flux, bubbles had to be defined and identified. Methane bubbles were defined as an increase in concentration of ≥ 3.5 μL L^{-1} (i.e., greater than 2 times the atmospheric concentration of CH_4) between time steps and an increase in concentration

of all subsequent time steps of < 3.5 μL L^{-1}. When a CH_4 bubble was identified as a t_0 or t_{60} point then that point was dropped and the linear equation of the three remaining points was used to calculate flux. If the CH_4 bubble occurred in the middle of a run then the average slope of the line before and after the bubble was used to determine flux (following Matthews et al. 2003).

4.2.11 Cumulative Emissions

Interpolation of daily fluxes between sampling dates was used to determine the cumulative emissions for the sampling period. Interpolation between sampling dates followed Yates (2006), where the mean flux for a gas on a particular sampling date was multiplied by the time interval (days) between sampling dates. To determine the cumulative estimate, results were summed over the sampling period.

Carbon dioxide equivalents were calculated by multiplying CH_4 values by 23 for a 100 year time horizon (IPCC, 2001).

4.2.12 Statistical Analysis

Statistical analysis was completed using SPSS (ver 14.0). Carbon dioxide and CH_4 flux data was not normally distributed. Data was log-transformed and still did not approximate a normal distribution, and therefore non-parametric statistics were used. To test for significant differences between daytime and nighttime fluxes of both gases a Mann-Whitney U test was performed at the 0.05 significance level. Spearman rank correlation analysis was used to determine if relationships exist between daily greenhouse gas flux and environmental variables measured (i.e., windspeed, air and

water temperature, pH, redox potential, conductivity, turbidity, percent oxygen saturation).

4.3 Results

4.3.1 Environmental Variables

The 2004 and 2005 seasons at Pond 1 were particularly wet, exceeding the 30 year precipitation normal. Cumulative precipitation during the 2004 season was 485 mm and 450 mm during the 2005 season. The month of June was especially wet in both years: 165 and 216 mm in 2004 and 2005, respectively. The long-term average cumulative precipitation for April to October is 281 mm (including snowfall). Average temperature from April to October was 9.9 ºC, slightly below the seasonal normal (Environment Canada, 2004).

Cumulative precipitation from April to October as measured at the Brandon Airport was 463 mm, exceeded the climate normal by 80 mm. The ice-free season in Brandon in 2005 was slightly warmer than the 30-year climate normal with an average temperature of 12.2 ºC from April to October (Environment Canada, 2004).

4.3.2 Nutrients

Total nitrogen (TN) and total phosphorous (TP) concentrations were 4.39 mg L^{-1} (±1.69 STD; n=5) and 0.60 mg L^{-1} (±0.83 STD; n=6), respectively in Pond 1 in 2004. Nutrient concentrations in Pond 1 decreased from 2004 to 2005 (1.63 mg L^{-1} TN ±0.32 STD; n=3 and 0.30 mg L^{-1} TP ±0.17 STD; n=3). A macro-nutrient molar ratio of 106C:16N:1P has been established for marine phytoplankton; TN:TP ratios below or above this ratio can result in nutrient limitations (Redfield et al., 1963). Total

phosphorous concentrations in April and June of 2005 were below the minimum detection limit of the lab (0.20 mg L^{-1}). Depending on the actual concentration, Pond 1 may have been P-limited (TN:TP ratio >7:1 by mass) in the spring and N-limited (TN:TP ratio <7:1 by mass) in mid summer.

Nutrient concentrations, TN and TP, increased through the season at the DCW in 2005 and averaged 2.20 (±0.62 STD; n=3) and 0.28 mg L^{-1} (±0.19 STD; n=3), respectively. The TN:TP ratio in May was 21:1 by mass indicating that the DCW was P-limited. By August the wetland had switched to a slight N-limitation with a TN:TP ratio of 6:1 by mass.

4.3.3 Electrical Conductivity, Major Ions, and pH

Water levels in Pond 1 in 2004 were low and had declined to the point that the wetland was separated into three separate water bodies. The wetland was moderately brackish (2,000-5,000 µS cm^{-1}) (Stewart and Kantrud, 1972) with a mean EC of 4526.67 µS cm^{-1} (±847.62 STD; n=3). Conductivity decreased to 830.00 µS cm^{-1} (±205.18 STD; n=3) in 2005 due to the high water levels in 2005, and the wetland was slightly brackish (500-2,000 µS cm^{-1}) (Stewart and Kantrud, 1972).

From 2004 to 2005 the concentration of all major ions decreased in Pond 1, with the exception of HCO_3 which increased slightly from 175.67 (±122.61 STD; n=6) to 194.00 mg L^{-1} (±67.02; n=3). Magnesium (522.50 mg L^{-1} ±147.85 STD; n=6) and sulfate (3136.67 mg L^{-1} ±942.71 STD; n=6) ions dominated Pond 1 in 2004. In the spring of 2005, the rapid rise in water level caused a considerable dilution effect and the wetland was dominated by calcium (72.33 mg L^{-1} ±19.86 STD; n=3) and sulfate (267.00

mg L^{-1} ±58.85 STD; n=3). The mean dissolved organic carbon (DOC) concentration in 2005 was 3.94 mg C L^{-1} (±1.35 STD; n=2).

Seasonal mean pH in 2004 was 8.3 (±0.9 STD; n=21). July and August had the highest mean pH, over 9.0 in both months. pH was lower in 2005 and the seasonal mean pH was 8.0 (±0.6 STD; n=97). It increased through the season from a mean of 7.2 (±0.2 STD; n=26) in July to 8.6 (±0.0 STD; n=11) in October.

The DCW was slightly brackish in 2005 with an EC of 1910.00 µS cm^{-1} (±546.17 STD; n=3) (Stewart and Kantrud, 1972). The DCW was dominated by magnesium and sulfate. Sulfate concentration was 892.67 mg L^{-1} (±315.85 STD; n=3), which is three times the concentration of Pond 1 in 2005. The mean DOC concentration in the DCW was 2.38 mg C L^{-1} (±0.37 STD; n=3).

4.3.4 Macrophyte and Algal Dynamics

Submerged and emergent macrophyte dry-weight was substantially higher in the DCW than Pond 1 in 2005 (Figure 4.1). Pond 1 was dominated by open water in 2005 with sparse emergent vegetation made up of bulrush (*Scirpus spp.*). Submerged macrophytes did not appear until mid-July and percent cover increased in August and was mainly composed of coontail (*Ceratophyllum demersum*). The dry-weight biomass of submerged and emergent macrophytes in August was 111.3 (±25.4 STD; n=3) g m^{-2} and 85.0 (±125.2 STD; n=3) g m^{-2}, respectively.

Open water at the DCW was surrounded by a dense ring of cattails (*Typha spp.*). Giant water moss (*Fontinalis spp.*) was the dominant submerged macrophyte, and ivy-leaved duckweed (*Lemna trisulca*) was also present. Submerged macrophyte dry-weight in August was 2168.8 (±1322.9 STD; n=3) g m^{-2}. Emergent macrophyte dry-

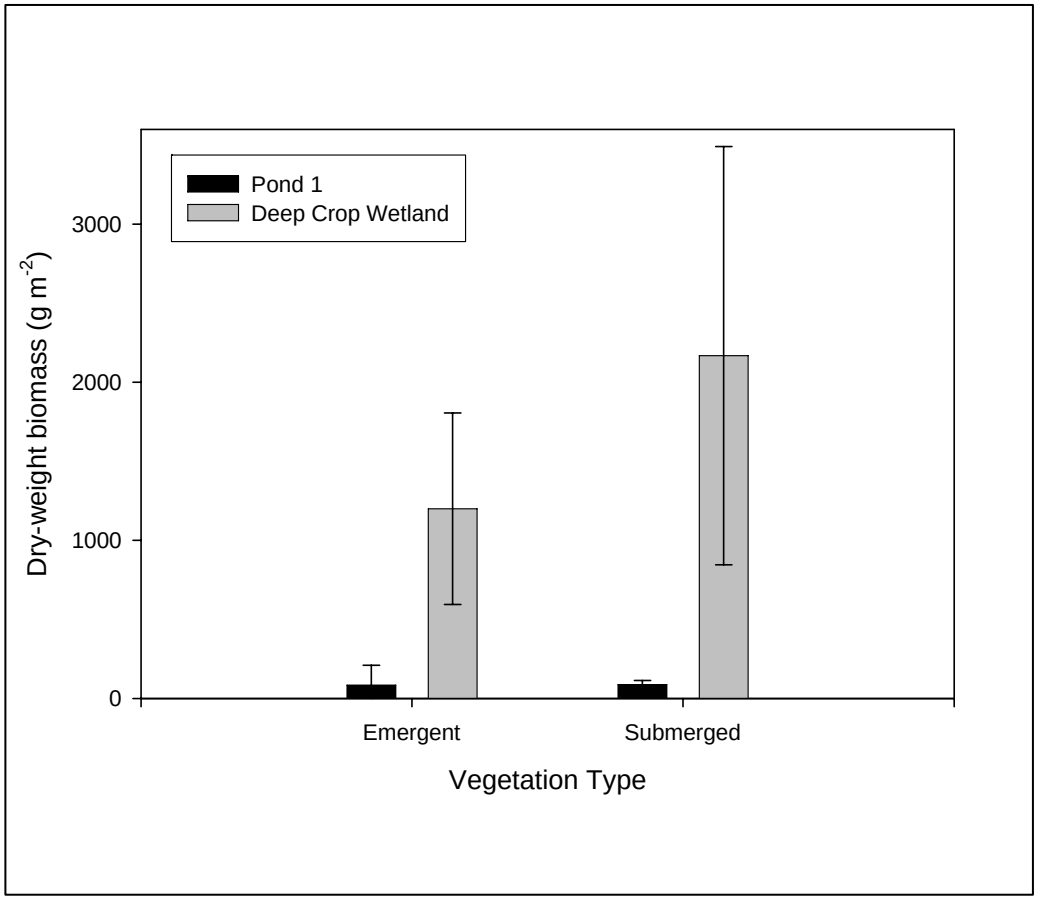

Figure 4.1 Dry-weight biomass of submerged and emergent macrophytes in August 2005 at Pond 1 and the Deep Crop Wetland. Error bars represent the standard deviation.

weight was 1200.2 (±605.6 STD; n=3) g m^{-2}, 15-times greater than that at Pond 1 (Figure 4.1).

Seasonal mean phytoplankton biomass during the ice-free season in Pond 1 was 4.5 µg L^{-1} (±4.0 STD; n=23) (Figure 4.2). Phytoplankton biomass peaked on June 8 at 17.6 µg L^{-1}, followed by a rapid decline or "clear water phase". Phytoplankton biomass remained low until August 4 when it peaked again at 12.8 µg L^{-1}, and then gradually declined throughout the remainder of the season.

Seasonal mean phytoplankton biomass in the DCW was higher than Pond 1 in 2005 (87.3 µg L^{-1} ±107 STD; n=20). Phytoplankton biomass was moderate (< 16 µg L^{-1}) until late July when it increased until late September, peaking at 369.6 µg L^{-1} (Figure 4.2). Phytoplankton biomass remained high until the end of the sampling season in mid-October.

Seasonal mean periphyton biomass was 781.4 µg cm^{-2} (±943.7 STD; n=20) in Pond 1 in 2005 (Figure 4.2). Periphyton biomass in Pond 1 was greatest from mid June to mid July after which it rapidly declined and remained low until the end of the season. Upper sections of periphyton rods had mean biomass concentrations greater than biomass concentrations on mid and lower rod segments.

Seasonal mean periphyton biomass was 575.2 µg cm^{-2} (±353.5 STD; n=19) in the DCW in 2005 (Figure 4.2). Upper sections of the periphyton rod had biomass concentrations higher than the mid and lower rod segments. Periphyton biomass gradually increased from the start of the season until late September after which it declined.

Metaphyton was present on 18 of 23 sampling dates in Pond 1 in 2005. Seasonal mean metaphyton biomass was 3972.6 µg cm^{-2} (±4129.6 STD; n=18) (Figure 4.2).

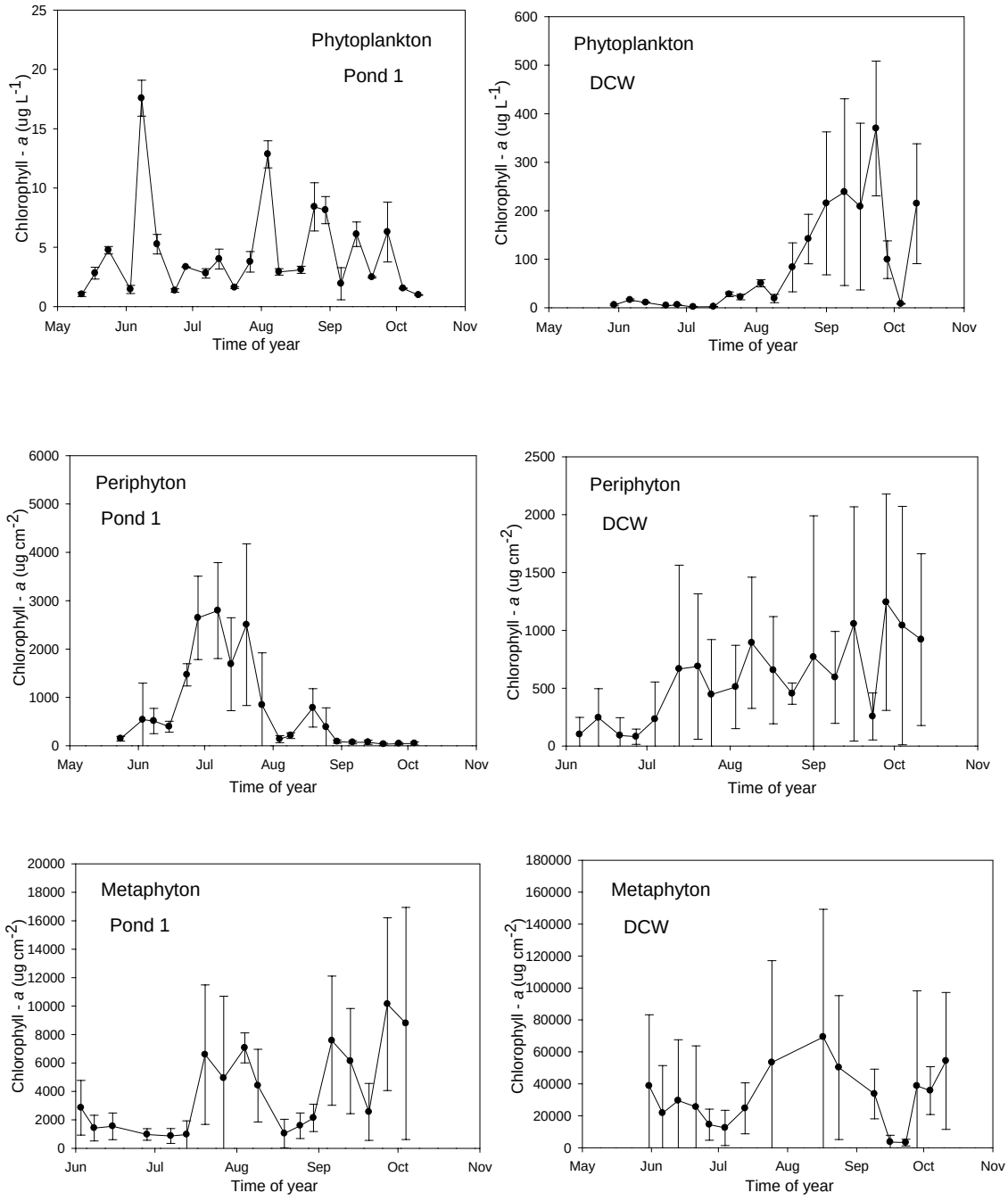

Figure 4.2 Seasonal algal biomass in Pond 1 and the Deep Crop Wetland (DCW) in 2005. Error bars represent the standard deviation. (Note change in scale of y axis).

Metaphyton biomass was low until late July. Metaphyton biomass peaked at the end of September at 10 131.8 µg cm^{-2}.

Metaphyton was present at the DCW on 16 of 20 sampling dates. Metaphyton biomass was high throughout the season and peaked in mid August at 69 318.4 µg cm^{-2} (Figure 4.2). Seasonal mean metaphyton biomass was 31 806.3 µg cm^{-2} (±37 265.7 STD; n=16), which is seven-times higher than seasonal mean metaphyton biomass in Pond 1.

4.3.5 Diurnal Patterns of Greenhouse Gas Emissions

Methane and CO_2 exhibited a diurnal pattern on all three 24-hour sampling dates at Pond 1. Daytime emissions (0600 to 1600 h) were significantly greater than nighttime emissions (1800 to 0400 h) (p=0.05) (Table 4.1). The nighttime emissions were divided by the daytime emissions for each 24-hour sampling date and the mean was taken as the correction factor. When calculating the cumulative emissions the correction factor was used to account for the lower CH_4 and CO_2 fluxes from the open water during the nighttime period, nighttime flux was equal to daytime flux multiplied by 0.4958 and 0.4706, respectively.

Table 4.1 Mean daytime (0600h to 1800h) and nighttime (1800h to 0600h) methane and carbon dioxide emissions from Pond 1 and the Deep Crop Wetland. Standard deviations are in brackets (n=6).

Date	0600 to 1800	1800 to 0600	0600 to 1800	1800 to 0600
	μmol CH_4 m^{-2} d^{-1}		mmol CO_2 m^{-2} d^{-1}	
		Pond 1		
May 31	85.4 (236.9)	46.7 (114.9)	12.0 (39.7)	2.5 (62.5)
Jul 5	2032.9 (6279.5)	1383.0 (5577.7)	53.2 (32.4)	36.4 (23.2)
Aug 11	1222.2 (4725.1)	318.4 (174.7)	28.4 (30.2)	14.9 (27.3)
		Deep Crop Wetland open water		
Aug 12	158.7 (48.4)	106.4 (45.2)	64.0 (26.3)	65.5 (33.6)
		Deep Crop Wetland riparian		
Aug 12	9.2 (16.8)	5.9 (47.4)	142.1 (101.7)	147.6 (61.9)

4.3.6 Seasonal Methane Emissions

Methane emission from the open water of Pond 1 in 2004 displayed a seasonal pattern. Fluxes were generally higher in July and early August and lowest in September and October. Fluxes ranged from -251.55 to 191.55 μmol CH_4 m^{-2} d^{-1} (Figure 4.3a). Negative flux values observed in September and October 2004 in the open water of Pond 1 indicated that the wetland acted as a sink for CH_4 at this time. A seasonal pattern for CH_4 emissions from the riparian area was not as evident but generally fluxes were lower later in the season. That being said, highest CH_4 flux from the riparian area occurred on the 7th of October. Methane flux ranged from -80.35 to 148.65 μmol CH_4 m^{-2} d^{-1} (Figure 4.3b).

Methane emissions from the open water of Pond 1 in 2005 displayed a seasonal trend with emissions peaking on July 5 (Figure 4.3c). Methane emissions here ranged from -469.10 to 3776.08 μmol CH_4 m^{-2} d^{-1}. Fluxes were low from April to July and from mid-August to the end of the sampling season.

A seasonal pattern in CH_4 emissions from the open water at the DCW was also evident (Figure 4.3d). Mean daily emissions were low until mid-September when they peaked at 110.47 μmol CH_4 m^{-2} d^{-1}. Daily CH_4 flux ranged from -13.64 to 110.47 μmol CH_4 m^{-2} d^{-1}. Methane flux from the riparian area at the DCW in 2005 ranged from -4.51 to 40.23 μmol CH_4 m^{-2} d^{-1} (Figure 4.3e). Methane flux peaked on June 28th and declined until the end of the sampling season.

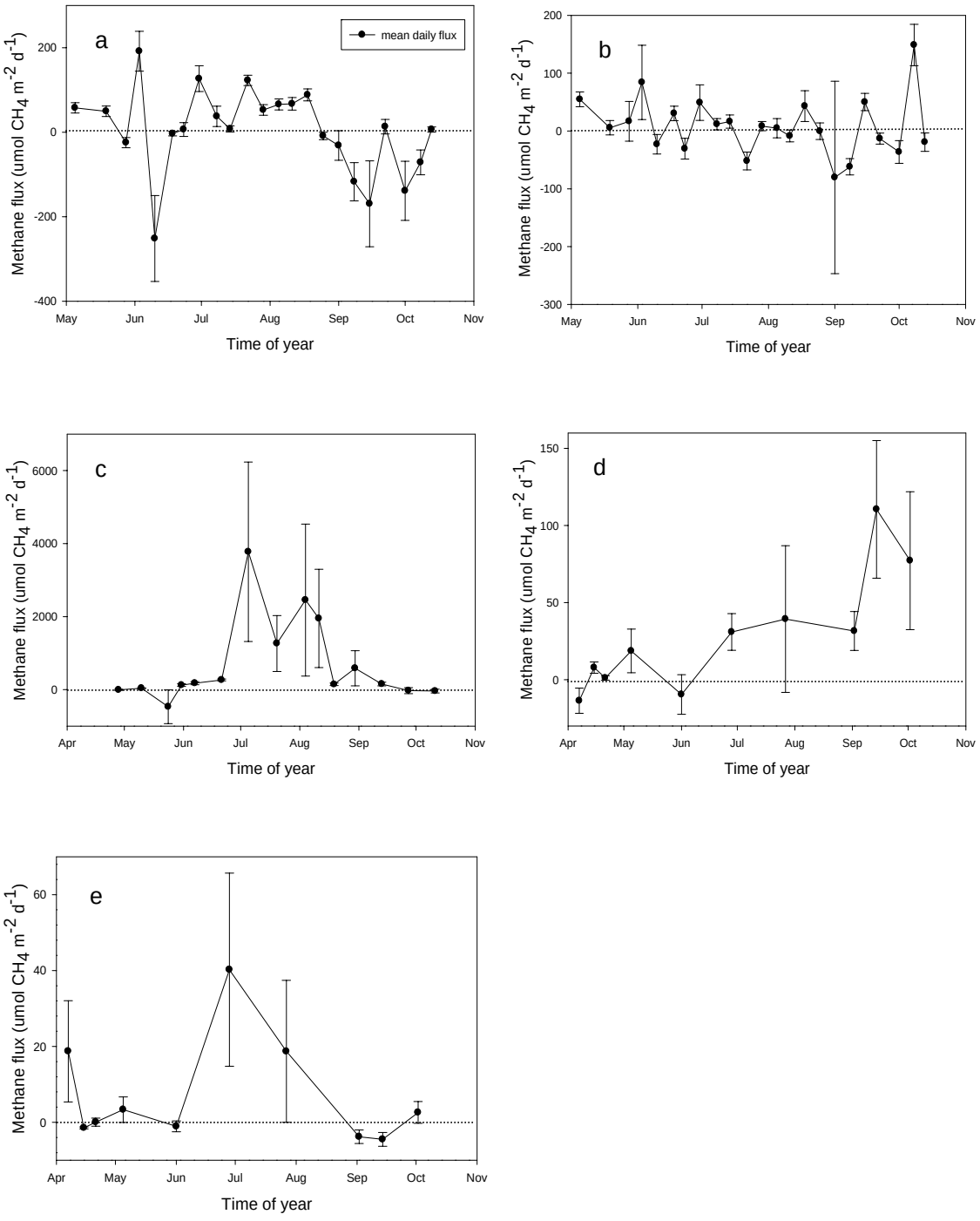

Figure 4.3 Seasonal variation in methane flux from a) the open water of Pond 1 in 2004, b) the riparian area of Pond 1 in 2004, c) the open water of Pond 1 in 2005, d) the open water of the Deep Crop Wetland 2005 and e) the riparian area of the Deep Crop Wetland in 2005. Error bars represent the standard error of the mean. (Note the change in scale of the y axis).

Cumulative CH_4 emissions from the open water of Pond 1 in 2004 were 0.92 mmol CH_4 m^{-2} 170.5 d^{-1} (0.34 g $CO_{2\ eq}$ m^{-2} 170.5 d^{-1}) and 1.60 mmol CH_4 m^{-2} 170.5 d^{-1} (0.59 g $CO_{2\ eq}$ m^{-2} 170.5 d^{-1}) from the riparian area. Cumulative emissions from the open water of Pond 1 in 2005 were corrected for diurnal variation in emissions. Cumulative emissions for the 2005 season were 94.40 mmol CH_4 m^{-2} 179 d^{-1} (34.90 g $CO_{2\ eq}$ m^{-2} 179 d^{-1}) from Pond 1.

Cumulative emissions for the open water at the DCW were low in 2005. Cumulative emissions from the open water were 4.61 mmol CH_4 m^{-2} 191 d^{-1} (1.70 g CO^2_{eq} m^{-2} 191 d^{-1}), 20-times lower than emissions calculated for Pond 1 in the same year. Methane emissions from the riparian area were also very low in 2005. At 1.79 mmol CH_4 m^{-2} 191 d^{-1} (0.66 g CO^2_{eq} m^{-2} 191 d^{-1}), these emissions were similar to cumulative emissions from the riparian area of Pond 1 in 2004.

4.3.7 Seasonal Carbon Dioxide Emissions

Carbon dioxide emissions from Pond 1 displayed a seasonal pattern (Figure 4.4a). Emissions remained low (< 50 mmol CO_2 m^{-2} d^{-1}) until early June at which time emissions peaked at 95.42 mmol CO_2 m^{-2} d^{-1}, but then started to gradually decline. By late August Pond 1 acted as a CO_2 sink. Fluxes remained negative until the end of the sampling season. Carbon dioxide flux ranged from -96.42 to 95.42 mmol CO_2 m^{-2} d^{-1}.

Carbon dioxide emissions from the open water at the DCW also showed a seasonal pattern with emissions peaking on July 27 (Figure 4.4b). Carbon dioxide flux

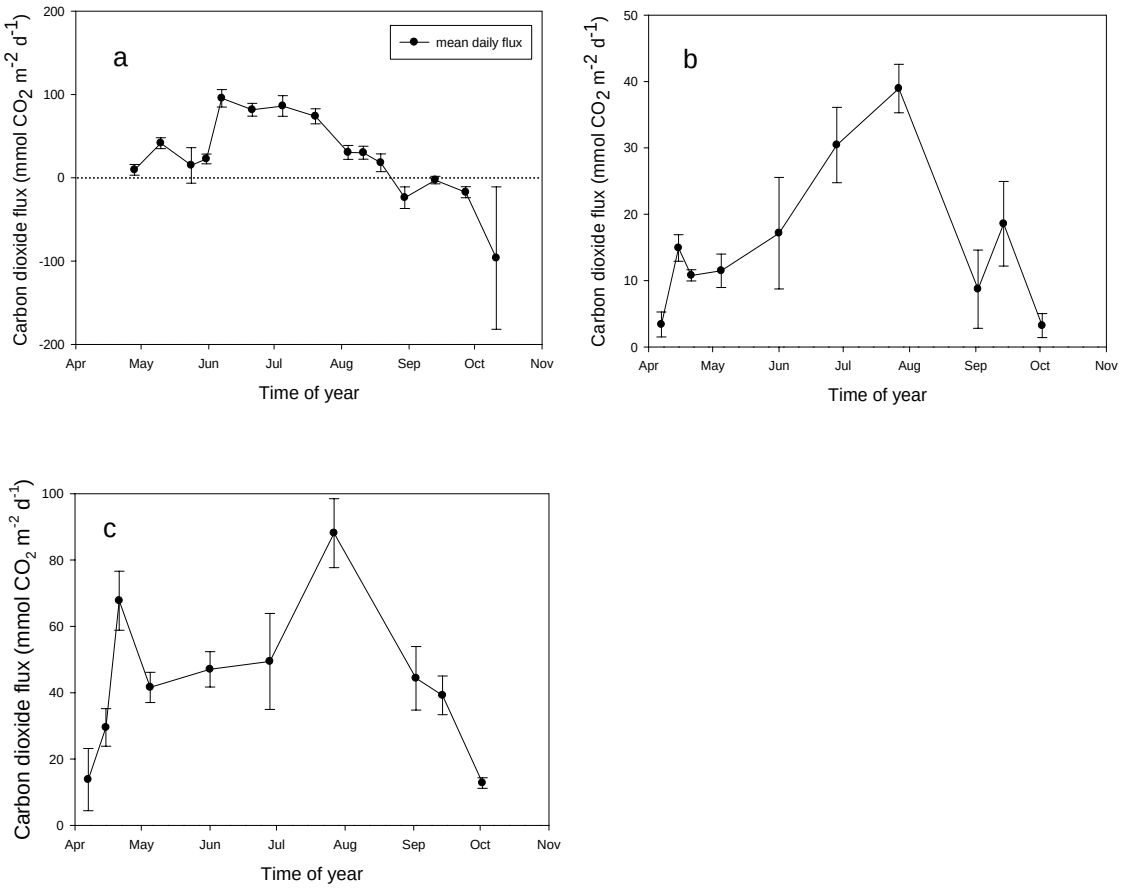

Figure 4.4 Seasonal variation in carbon dioxide flux from a) the open water of Pond 1 in 2005, b) the open water of the Deep Crop Wetland in 2005 and c) the riparian area of the Deep Crop Wetland in 2005. Error bars represent standard error of the mean. (Note the change in the scale of the y axis).

from the open water ranged from 3.21 to 38.94 mmol CO_2 m^{-2} d^{-1}. Carbon dioxide emissions from the riparian area were consistently higher than from the open water. Carbon dioxide flux from the riparian area ranged from 12.79 to 88.09 mmol CO_2 m^{-2} d^{-1}, with highest fluxes occurring in late July (Figure 4.4c).

Cumulative CO_2 emissions from the open water were corrected for the diurnal variation in emissions. Cumulative CO_2 emissions from the open water of Pond 1 in 2005 were 3135.30 mmol CO_2 m^{-2} 179 d^{-1} (138.12 g CO_2 m^{-2} 179 d^{-1}). Cumulative emissions from the DCW were 2664.58 mmol CO_2 m^{-2} 191 d^{-1} (117.38 g CO_2 m^{-2} 191 d^{-1}), similar to those found at Pond 1 in 2005. Cumulative emissions from the riparian area were 3.5 times greater than from the open water: 9312.54 mmol CO_2 m^{-2} 191 d^{-1} (410.24 g CO_2 m^{-2} 191 d^{-1}).

4.3.8 Stacking vs. Small Chambers

The seasonal cumulative emission calculated using small chambers may be in error if significant emissions occur through plants. Methane emissions from the stacking chambers with intact vegetation ranged from -752.10 to 1420.15 µmol CH_4 m^{-2} d^{-1} (Figure 4.5). Methane emissions from the paired small chambers with trimmed vegetation showed a similar pattern with highest and lowest mean fluxes occurring on the same sampling dates. Cumulative CH_4 emissions from the stacking chambers and paired small chambers were similar, 13.96 and 10.55 mmol CH_4 m^{-2} 137.5 d^{-1}, respectively, even though the means for the sampling dates were different.

Carbon dioxide emissions from the stacking chambers with intact vegetation were consistently higher than from the paired small chambers with trimmed vegetation (Figure 4.5).

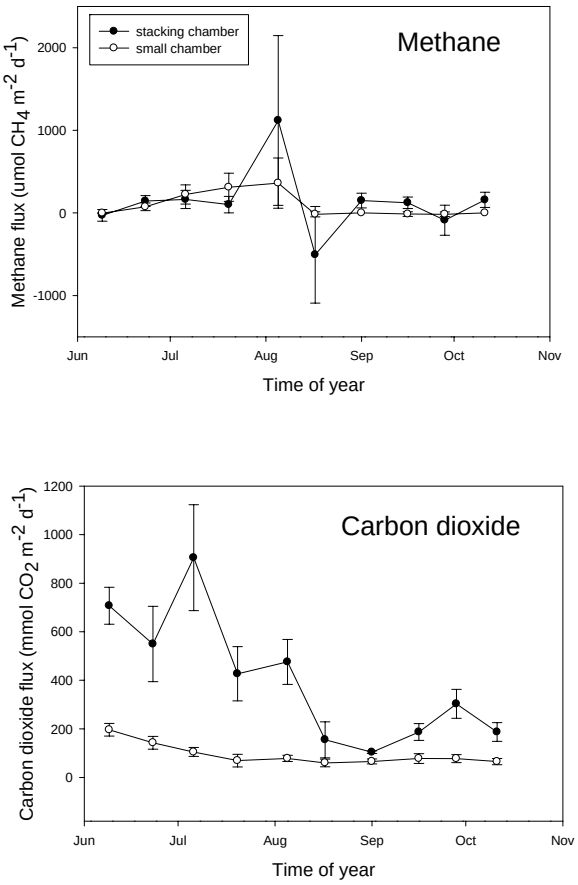

Figure 4.5 Methane and carbon dioxide flux from the stacking and small chambers at the Deep Crop Wetland in 2005. Error bars represent the standard error of the mean. (Note the change in scale of the y axis.)

Cumulative emissions from the stacking chambers with intact vegetation were 55 011 mmol CO_2 m^{-2} 137.5 d^{-1} compared to 12 897 mmol CO_2 m^{-2} 137.5 d^{-1} from the paired small chambers with trimmed vegetation.

4.3.9 Correlation Analysis

Spearman rank correlations were used to determine if relationships exist between environmental variables measured (i.e., windspeed, air and water temperature, pH, redox potential, conductivity, turbidity, percent oxygen saturation) and daily greenhouse gas flux from the open water of Pond 1 in 2004 and 2005. Environmental variables were only measured from July 14 to September 13 at the DCW in 2005 while the majority of gas sampling dates took place prior to this time; therefore correlation analysis was not undertaken for that data set.

Water temperature was highly and significantly correlated to air temperature (r_s=0.884, $p<0.01$; Figure 4.6a) in 2004. Methane flux in 2005 was moderately and significantly correlated to pH (r_s=0.481 $p<0.05$; Figure 4.6b), water temperature (r_s=0.669, $p<0.01$; Figure 4.6c), and air temperature (r_s=0.508, $p<0.05$; Figure 4.6d).

In 2005, CH_4 flux was significantly correlated to pH (r_s=-0.900, $p<0.01$; Figure 4.7a), water temperature (r_s=0.800, $p<0.01$; Figure 4.7b), air temperature (r_s=0.732, $p<0.01$; Figure 4.7c), and wind speed (r_s=-0.561, $p<0.05$; Figure 4.7d).

In 2005, significant correlations were found between CO_2 flux and pH (r_s=-0.950, $p<0.01$; Figure 4.8a), water temperature (r_s=0.667, $p<0.05$; Figure 4.8b), and percent saturation of dissolved oxygen (r_s=-0.857, $p<0.05$; Figure 4.8c). Water temperature was significantly correlated to air temperature (r_s=0.750, $p<0.05$; Figure 4.8d).

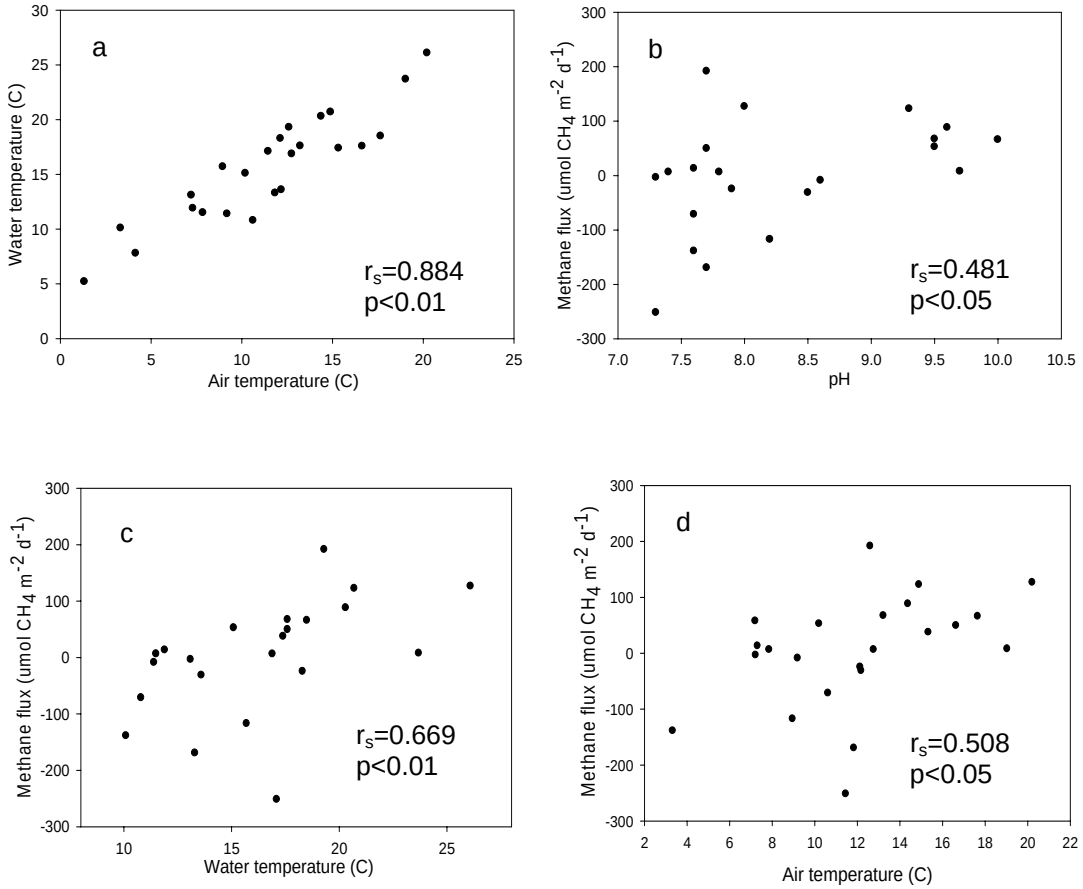

Figure 4.6 Scatterplots of a) air temperature vs water temperature, b) pH vs methane flux, c) water temperature vs methane flux and d) air temperature vs methane flux in Pond 1 in 2004.

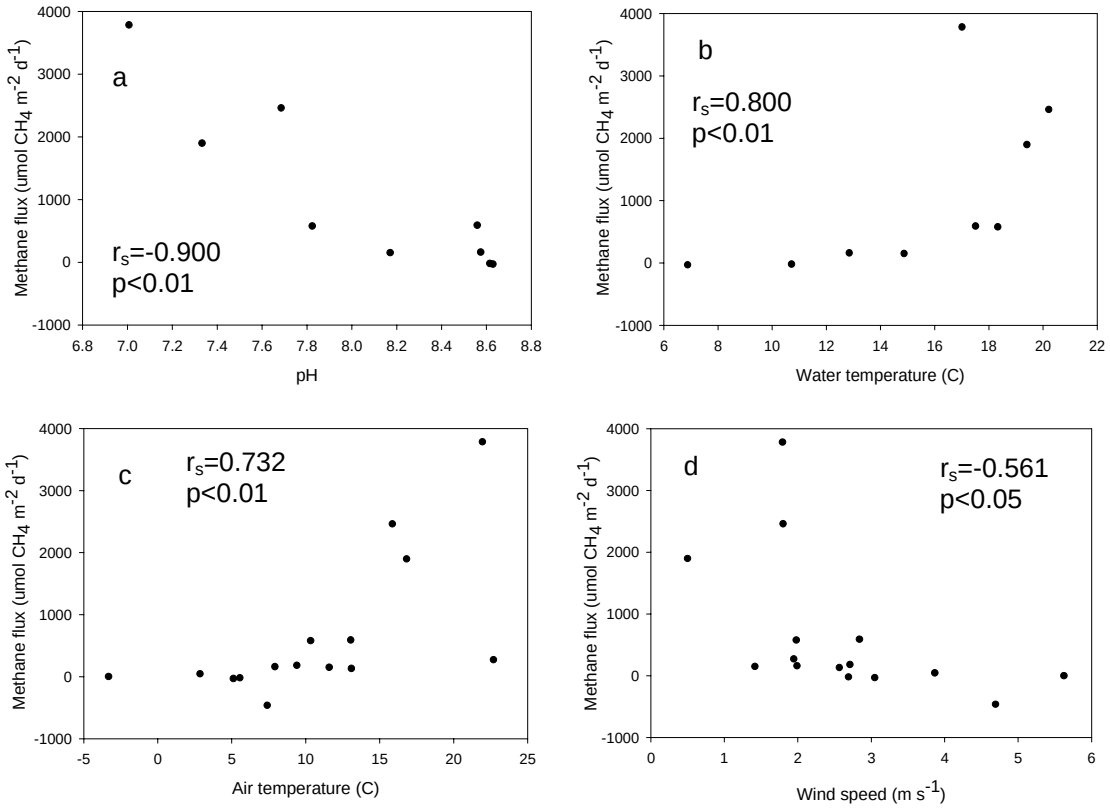

Figure 4.7 Scatterplots of a) pH vs methane flux, b) water temperature vs methane flux, c) air temperature vs methane flux and d) wind speed vs methane flux in Pond 1 in 2005.

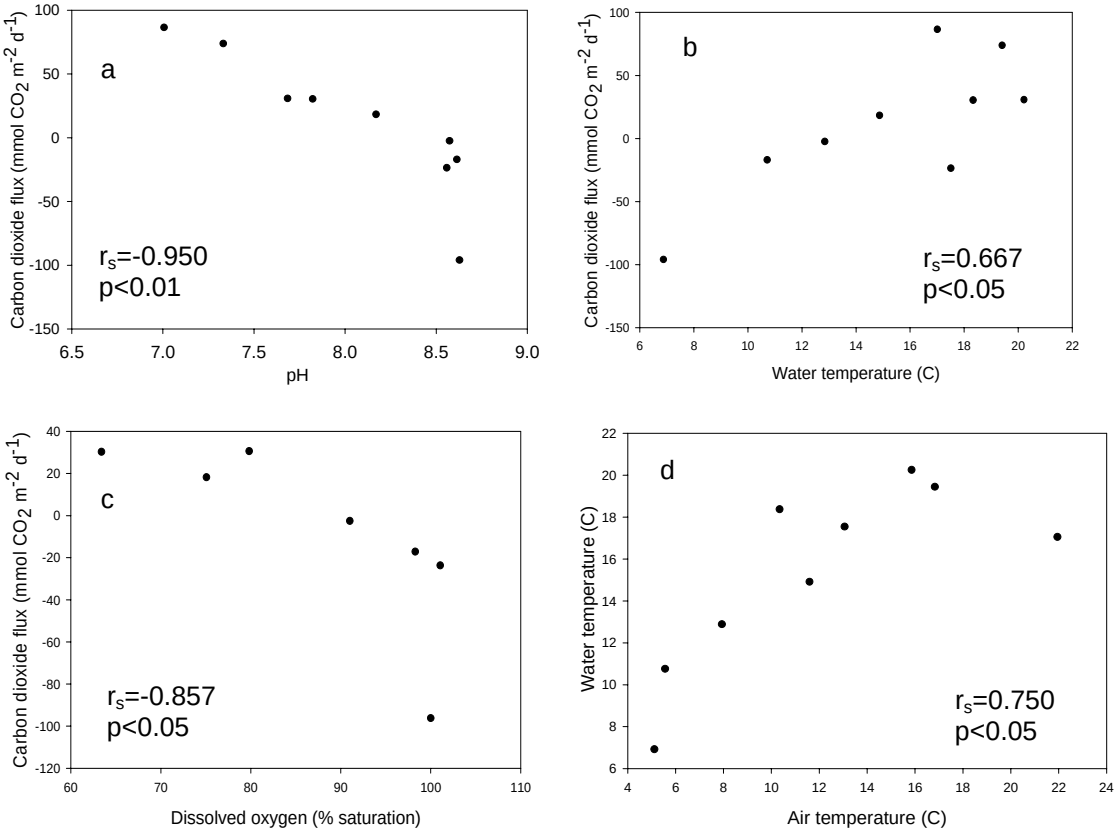

Figure 4.8 Scatterplots of a) pH vs carbon dioxide flux, b) water temperature vs carbon dioxide flux, c) percent oxygen saturation vs carbon dioxide flux and d) air temperature vs water temperature in Pond 1 in 2005.

Spearman rank correlations were used to determine if there were correlations between the biomass of the algal assemblages (as measured by Chl-*a*) and daily greenhouse gas flux in 2005. At Pond 1, CH_4 flux was not significantly correlated algal biomass. CO_2 flux was significantly correlated to periphyton biomass (r_s=0.741, $p<0.01$). Periphyton biomass was inversely correlated to pH (r_s=-0.905, $p<0.01$). Correlations between phytoplankton and metaphyton and pH were not significant.

4.4 Discussion

4.4.1 Overview

The results of this study allow greenhouse gas emissions from wetlands under two strongly contrasting situations to be assessed. The first contrast is water chemistry and water levels in Pond 1 following the major increase in pond volume after snowmelt in 2005 compared to 2004. Fluctuation in wetland water levels gave rise to large changes in water chemistry and changes in wetland biology and greenhouse gas emissions from these wetlands. Evapoconcentration of ions and sulfate in particular following drought and dilution of ions following deluge may be a major factor in controlling greenhouse gas emissions from prairie wetlands. The second situation is the strong contrast in biological productivity between Pond 1 and the DCW in 2005.

The approach used to assess greenhouse gas emissions and biological properties was a mensurative design, where emissions under prevailing environmental conditions were measured and no treatments were imposed. Mensurative designs are of value primarily as hypothesis-generating studies that occur relatively early in the development of a particular field of enquiry. Hence, the emphasis in the discussion is on documenting the rates of the processes measured and on suggesting linkages between the measured

properties. These linkages can then be more thoroughly evaluated in subsequent manipulative designs.

4.4.2 Effects of Wetland Biology on CO_2 Emissions: Pond 1 and the DCW in 2005

Despite the substantial differences in wetland biology between Pond 1 and the DCW, the cumulative CO_2 flux from the two wetlands was relatively similar in 2005. Cumulative CO_2 emissions from Pond 1 and the DCW in 2005 were 3135 and 2665 mmol CO_2 m^{-2} $season^{-1}$, respectively. Carbon dioxide emissions from Pond 1 were highest from mid-June to the end of July. This was the time of lowest phytoplankton biomass and may be attributed to zooplankton grazing. Zooplankton grazing of phytoplankton has been linked to the stimulation of bacterial production (Jeppesen et al., 1997; Waiser and Robarts, 2004), and potential periods of heterotrophy even in productive prairie wetlands that are dominated by net autotrophy during the season (Waiser and Robarts, 2004). In a study of 20 temperate lakes del Giorgio et al. (1999) found that plankton (bacteria, microzooplankton, macrozooplankton) metabolism was a significant source of CO_2 from unproductive lakes. Carbon dioxide losses from bacterial production during the period of low phytoplankton biomass may be responsible for the relatively higher CO_2 fluxes. This is speculative as neither bacterial production nor zooplankton biomass was measured in this study.

Xing et al. (2005) found that periods of time when the lake was acting as a sink for CO_2 corresponded to periods of maximum NPP and Chl – *a* in an autotrophic subtropical lake. No significant correlations were found between CO_2 flux and phytoplankton or metaphyton biomass in this study. Periphyton biomass was positively and significantly correlated to CO_2 flux in Pond 1 in 2005, although a negative

relationship would have been expected. Periphyton is prone to cycles of accumulation and loss due to sloughing (Graham and Wilcox, 2000), potentially providing organic substrates to the water column.

Xing et al. (2005) found a negative relationship between CO_2 flux and air temperature and they suggest this indicated that algal activity and not mineralization of organic matter was related to CO_2 flux. In this study, air temperature and water temperature were highly correlated and CO_2 flux increased with increasing water temperature and this may suggest a link between CO_2 flux and organic matter mineralization.

Carbon dioxide flux was inversely correlated to pH and Pond 1 was acting as a source of CO_2 when pH < 8.4 and a sink for CO_2 when pH > 8.4 (Figure 4.8a). pH in prairie wetland systems can change dramatically from day to night and over the course of the season as H^+ is consumed during photosynthesis and released during respiration (Wetzel, 1983). Tremblay et al. (2005) found that mean gross CO_2 flux was highest and significantly different when pH < 7.9 and lowest when pH ≥ 7.9. The negative correlation between periphyton biomass and pH suggests that periphyton photosynthesis alone is not responsible for the changes in pH but that some other factor or combination of factors is governing pH in this system and there is an interaction between these biotic factors and CO_2 flux. This reinforces Walter and Heimann's (2000) comment that factors (environmental variables and biotic factors) are not independent of each other, rather they may exert stronger controls at different times throughout the season.

Unlike Pond 1, the DCW did not act as a sink for CO_2 in 2005. Carbon dioxide flux from the DCW steadily increased until the end of July, and phytoplankton biomass

was lowest during this period. Relationships between CO_2 flux and algal biomass were not evident.

Lack of correlation between algal biomass and CO_2 flux could be a result of using a concentration rather than a productivity measurement (i.e., a rate of C fixed). Chlorophyll-*a* is a useful and accurate measure of algal biomass and it is also widely used and hence allows for comparison among studies. The drawback of this method is that it is a measurement at a single point in time. Frequent sampling throughout the season allows for a better understanding of the dynamic nature of algal biomass but if used as a surrogate for primary production it will underestimate the actual amount of carbon fixed as algae can turnover quite rapidly. Regardless of this, Pond 1 and the DCW had strikingly different algal biomass and relatively similar CO_2 emissions.

4.4.3 Water Level and Water Chemistry Effects: Pond 1 in 2004 and 2005

Wetland water levels will have an effect on the water chemistry, which in turn influence the biological activity of the wetland in terms of algae and aquatic macrophytes (Robinson et al., 1997a). The increase in water level in Pond 1 from 2004 to 2005 was reflected in the chemistry of the wetland. There was an overall dilution effect on solutes in the wetland and concentration of all ions decreased from 2004 to 2005 with the exception of HCO_3 which increased in 2005. Seasonal mean concentrations of TN and TP were at least twice as great in 2004 as they were in 2005 and the concentration of sulfate was 12-times higher in 2004 than in 2005.

As oxygen is consumed in sediments and the water column through heterotrophic respiration, a sequence of reactions takes place as lower redox potentials are achieved. When low redox potentials are reached (< -220 mV), sulfate reduction takes place

whereby sulfate acts as an alternative electron acceptor in the oxidation of organic matter (Schlesinger, 1997). Below the zone of sulfate reduction in the sediments is a zone of methanogenesis. Sulfate-reducing bacteria and methanogenic bacteria are competitors for the same organic substrates and the sulfate-reducing bacteria are more efficient in the uptake of H_2, resulting in little overlap between the zones of sulfate reduction and methanogenesis (Holmer and Storkholm, 2001). This results in lower amounts of CH_4 production in aquatic systems with high concentrations of sulfate.

4.4.4 Effects of Water Chemistry on CH_4 Emissions

In this study, CH_4 emissions were negligible in the presence of high concentrations of sulfate, and the concentration of all ions was most likely governed by the inputs of water. The high concentration of sulfate and the relationship between sulfate-reducing bacteria and low CH_4 production is most likely responsible for differences in CH_4 emissions in Pond 1 between 2004 and 2005. Pond 1 in 2004 had the highest sulfate concentration followed by the DCW in 2005 and Pond 1 in 2005. At what concentration sulfate can be present and CH_4 flux can still occur in prairie wetlands is not known and cannot be determined from this study. If sulfate is limiting to sulfate-reducing bacteria then methanogenic bacteria may be able to successfully compete for hydrogen and acetate (Lovley et al., 1982); if sulfate is not limiting to sulfate-reducing bacteria then CH_4 should not be produced (Lovley and Klug, 1983). This limitation of sulfate on CH_4 flux was less apparent in 2005 in Pond 1 following the major increase in water level that occurred after snowmelt in the spring of 2005. Methane was highest in Pond 1 in 2005 on days when the water temperature was warm and the wind speed was low (< 2 m s^{-1}).

4.4.5 Seasonal Algal Dynamics and their Relationship to CH_4 Emissions: Pond 1 and the DCW in 2005

A major focus of this thesis was to assess the seasonal patterns of algae and of CH_4 and to determine if there was any correlation between them. Algal biomass generally follows a seasonal pattern starting with a spring bloom when temperature starts to rise and nutrients become available in the water column (Crumpton, 1989), often followed by a clear water phase once zooplankton grazers start to feed on the algae (Lampert et al., 1986). It is a combination of the top down (predation) and bottom-up (resource) control that shapes the seasonal succession of algal biomass (Carpenter et al., 1985) in individual wetlands. There has been no information to date on the possible linkages between carbon fixation into and release from the algal biomass and the seasonal pattern of CH_4 emissions from prairie wetlands.

At Pond 1 in 2005 phytoplankton biomass peaked at the beginning of June which may have represented the spring bloom (Figure 4.2). Following this peak in biomass there was a rapid decline in phytoplankton biomass that persisted until early August. This sustained decrease in phytoplankton biomass may have been due to intense grazing of phytoplankton by zooplankton until the zooplankton became food-limited and phytoplankton biomass could recover or were replaced with larger bodied algae (Lampert et al., 1986).

At the Deep Crop Wetland there was no spring bloom evident and phytoplankton biomass remained low until early August. A P-limitation (TN:TP ratio of 21:1 by mass) may have contributed to the low phytoplankton biomass early in the season, or it may just be that the spring bloom was missed because algal sampling did not start until May 30. Other studies in prairie wetlands have seen similar patterns of

mid-summer and fall maxima occurring with no evidence of a spring bloom in wetlands with high productivity (Crumpton, 1989; Waiser and Robarts 2004).

In Pond 1, periphyton biomass was low at the beginning of the season and did not start to increase until phytoplankton biomass decreased in mid June. Periphyton biomass in the DCW was lower than in Pond 1 and this may be due to shading effects by emergent macrophytes. The immobile nature of periphyton makes them prone to grazing and light limitations caused by the dense cattail ring. For example, photosynthetically available radiation reaching the periphytic community was reduced up to 85% in a cattail stand in the Florida Everglades (Grimshaw et al., 1997). When the acrylic rods were installed in the DCW they were placed just outside the dense cattail ring which may have contributed to the shading effect.

Although metaphyton blooms were not common in Pond 1, metaphyton biomass started to increase when periphyton biomass starts to decline (July 15). Due to the size of the wetland and lack of emergent vegetation, conditions may have been sub-optimal for metaphyton as there is little refuge from wind and wave action in this wetland.

Large metaphyton blooms were common in the DCW and the seasonal metaphyton biomass was seven-times higher than in Pond 1. Areas of the DCW were probably well sheltered by the dense cattail stand, providing refuge for metaphyton. Robinson et al. (1997b) observed metaphyton at a maximum in July and persisting until late August. This was not the case at the DCW where metaphyton biomass peaked at the end of the season; however, there was a smaller peak in mid-July that persisted until mid-August in which metaphyton may have been sequestering nutrients (Turner et al., 1995). McDougal et al. (1997) speculated that the greatest loss of N and P from the water column was through uptake by metaphyton. Senescence of the initial metaphyton

mat in early to mid-August may have contributed nutrients to the water column, resulting in increases in phytoplankton biomass. Dense metaphyton mats may have altered the under-water light environment decreasing the transmission of light (Turner et al., 1995; McDougal et al., 1997) and further inhibiting the phytoplankton biomass until senescence of the initial metaphyton mat.

No significant correlations were found between periphyton, phytoplankton or metaphyton biomass and CH_4 flux at Pond 1 in 2005, although periphyton biomass did follow a similar pattern to CH_4 flux. The negative correlation between CH_4 flux and pH and lack of correlation between the three algal assemblages measured and CH_4 flux could be a result of oxygen saturation of the water column during the day due to high rates of photosynthetic activity and an increase in CH_4 oxidation. Tremblay et al. (2005) found that mean gross CH_4 flux across their whole Canadian data set was significantly higher at $pH < 7.2$.

Relationships between primary production (Whiting and Chanton, 1993; Aselmann and Crutzen, 1989; Xing et al., 2005) and CH_4 flux have demonstrated that higher productivity tends towards higher CH_4 emissions. This would suggest that the higher algal and macrophyte biomass of the DCW should correspond to high CH_4 flux, and that Pond 1 should have low CH_4 flux to correspond to lower productivity. The seasonal mean phytoplankton biomass in the DCW was 19-times higher than in Pond 1, but CH_4 emissions from Pond 1 were 20-times higher than from the DCW. Relationships between CH_4 flux and primary production may only exist when the wetland is not sulfate dominant. The dominance of sulfate may have pre-empted any relationships between CH_4 flux and biological activity in 2004 in Pond 1 and the DCW in 2005.

Lack of correlation between CH_4 flux and algal biomass may also be a result of the limitation of the technique used. Algal biomass as determined by the concentration of Chl-*a* provides a measure at a single point in time and does not reflect the high turnover rate of the algae. A measure of productivity (rate of C fixed) and CH_4 flux (rate of gas emissions) over the same time period may have resulted in stronger correlations. Bearing this in mind, it might be expected that a "lag time" effect would be present with higher CH_4 flux occurring a length of time after senescence of the algae.

4.4.6 Comparison of CO_2 and CH_4 Fluxes in Prairie Wetlands and other Wetland Types

Overall the fluxes of CO_2 and CH_4 from the open water and riparian area are well within the range of fluxes measured from other sources such as peatlands and reservoirs (Chimner and Cooper, 2003; Dalva et al., 2001; Matthews et al., 2003; Tremblay et al., 2005; Rask et al., 2002). Seasonal mean fluxes from this study were below 25 mmol CO_2 m^{-2} d^{-1} for both wetlands. The ranges in CO_2 flux from Pond 1 and the DCW were much lower than found in a study by Chimner and Cooper (2003), where CO_2 emissions from a Colorado fen were between 40 to 950 mmol CO_2 m^{-2} d^{-1}. Carbon dioxide fluxes were also on the low end of the range reported by Matthews et al. (2003) of 24 to 137 mmol CO_2 m^{-2} d^{-1} in an Ontario reservoir. As well, CO_2 fluxes in this study were below the mean flux found in two years of study in a Nova Scotia bog where seasonal mean emissions were 116 mmol CO_2 m^{-2} d^{-1} and 73 mmol CO_2 m^{-2} d^{-1} (Dalva et al., 2001). In an extensive study on Canadian boreal aquatic ecosystems between 1993 and 2003, over 2500 diffusive fluxes were calculated and mean CO_2 emissions from these lakes and reservoirs was 23 mmol CO_2 m^{-2} d^{-1} (Tremblay et al., 2005).

Methane flux from Pond 1 and the DCW was well within the range reported by Matthews et al. (2003) of -2056 to 9657 μmol CH_4 m^{-2} d^{-1} and well below the yearly emissions of 38 to 2250 mmol CH_4 m^{-2} y^{-1} (dependent on position within the fen) reported by Rask et al. (2002) from a minerotrophic fen in Saskatchewan.

4.5 Conclusions

The two wetlands in this study were net sources of greenhouse gases. The dominant greenhouse gas in 2005 was CO_2. When wetlands hold water on a more permanent basis and sulfate is the dominant ion it is likely that the environment is unfavorable for the production of CH_4. Low sulfate concentrations may increase the potential for CH_4 emissions. Cumulative CH_4 emissions when converted to CO_2 equivalents ($CO_{2\ eq}$) from the open water of Pond 1 in 2004 and the DCW in 2005 are less than 1 g $CO_{2\ eq}$ m^{-2} d^{-1} and from the open water of Pond 1 in 2005 are 34.9 g $CO_{2\ eq}$ m^{-2} d^{-1}, and are generally below the total emissions in $CO_{2\ eq}$ reported by Tremblay et al. (2005) for lakes, rivers, and reservoirs across Canada which ranged from 1.2 to 39.5 g $CO_{2\ eq}$ m^{-2} d^{-1}.

Fluctuations in wetland water levels give rise to large changes in water chemistry and resulted in changes in wetland biology and greenhouse gas emissions from these two prairie wetlands. Evapoconcentration of ions and sulfate in particular following drought and dilution of ions following deluge may be a major factor in controlling CH_4 from prairie wetlands. Relationships do exist between CO_2 flux and environmental and biotic variables as seen in the high correlations with pH. Methane flux also exhibits strong relationships with environmental and biotic variables under conditions of low sulfate concentrations. Significant relationships with pH demonstrate interactions with the

biological activity of the wetland, but which aspect of the biology was not evident in this study. Carbon dioxide emissions were the largest contributor to total greenhouse gases in 2005 and these wetlands were much lower CH_4 emitters than emissions from peatlands and reservoirs. Studies of prairie wetlands over a wide range of productivities, wetland permanence classes and water chemistries would provide a more complete assessment as to the role that prairie wetlands play in the global greenhouse gas budget and the factors controlling those emissions.

5.0 SYNTHESIS AND CONCLUSION

5.1 Contribution of Open Water Prairie Wetlands to Greenhouse Gas Emissions

The two wetlands in this study were sources of greenhouse gases (Table 5.1). Only N_2O and CH_4 were measured in 2004. After conversion to $CO_{2\ eq}$ it can be seen that the contribution to the total greenhouse gas emissions from N_2O was greater than CH_4 from the open water of Pond 1 in 2004 (Table 5.2). In 2005 the dominant greenhouse gas (in $CO_{2\ eq}$) emitted from these wetlands was CO_2 followed by CH_4 and N_2O.

When wetlands hold water on a more permanent basis and sulfate is the dominant ion, it is likely that the environment is unfavorable for the production of CH_4 and N_2O. Low sulfate concentrations may increase the potential for CH_4 emissions. Temporary or more ephemeral wetlands that are prone to drying through the season may provide more favorable conditions for N_2O emissions. Wetlands that do not experience dry-down during the summer season are unlikely to have the necessary combination of oxygen, carbon, and nitrogen availability to produce significant N_2O emissions. Ephemeral wetlands at the St. Denis site have shown high N_2O flux events during the period of dry-down of the wetland in 2005, but this was not evident at all wetlands studied (Yates, 2006). These small ephemeral wetlands were located in the upland, were freshwater wetlands and were also higher emitters of CH_4 in 2005 (Pennock, unpublished data, 2006).

Table 5.1 Summary of cumulative emissions at Pond 1 and the Deep Crop Wetland.

Year	period (days)[1]	Methane mmol CH_4 m^{-2} y^{-1}	Carbon dioxide mmol CO_2 m^{-2} y^{-1}	Nitrous oxide g N_2O-N ha^{-1} y^{-1}
		Pond 1 Open Water		
2004	170.5 CH_4 194 N_2O	0.92	-	147.49
		Pond 1 Riparian Area		
2004	170.5 CH_4 194 N_2O	1.60	-	203.57
		Pond 1 Open Water		
2005	179	94.40	3135.30	-131.92
		Deep Crop Wetland Open Water		
2005	191	4.61	2664.58	10.46
		Deep Crop Wetland Riparian Area		
2005	191	1.79	9312.54	144.43

[1] Period is the number of days the mean daily flux is interpolated over to estimate the cumulative flux for the sampling season.

Table 5.2 Cumulative emissions for Pond 1 and the Deep Crop Wetland in carbon dioxide equivalents.

Year	period (days)[1]	Methane	Carbon dioxide	Nitrous oxide	Total
		g $CO_{2\ eq}$ m^{-2} y^{-1}	g CO_2 m^{-2} y^{-1}	g $CO_{2\ eq}$ m^{-2} y^{-1}	in $CO_{2\ eq}$
			Pond 1 Open Water		
2004	170.5 CH_4 194 N_2O	0.34	-	6.86	7.20
			Pond 1 Riparian Area		
2004	170.5 CH_4 194 N_2O	0. 59	-	9.47	10.06
			Pond 1 Open Water		
2005	179	34.90	138.12	-6.14	166.88
			Deep Crop Wetland Open Water		
2005	191	1.70	117.38	0.48	119.44
			Deep Crop Wetland Riparian Area		
2005	191	0.66	410.24	6.72	417.62

[1] Period is the number of days the mean daily flux is interpolated over to estimate the cumulative flux of the sampling season.
[2] CO_2 equivalents are the cumulative emissions multiplied by the global warming potential of 23 for CH_4 and 296 for N_2O for a 100 year time horizon (IPCC, 2001).

5.2 Conversion of Wetlands to Agricultural Land

Conversion of wetlands to agriculture may have a profound effect on greenhouse gas emissions from the wetlands. Pond 1 and the DCW are both located within hummocky till landscapes of the prairie pothole region (PPR). This region is dominated by agricultural landuse, resulting in a high potential for wetland drainage and tillage (Mitsch and Gosselink, 1993). Wetlands located in gently sloping terrain (2 to 5%) as is the DCW have a higher number of tilled wetlands per quarter-section than other slope classes (Phipps et al., 2005 unpublished data). In the more strongly to moderately sloping terrain (10 to 15%) it is likely that the smaller wetlands (< 200 m^2) are targeted for tillage, due to ease of tillage. In the more gently sloping terrain (2 to 5%), the mean area of the largest tilled wetland can reach 840 m^2 and in very gently sloping terrain (0.5 to 2%) can reach 1615 m^2 (Phipps et al., 2005 unpublished data).

Implications of wetland landuse conversion on greenhouse gas emissions were not directly measured in this study. Presumably converted wetlands would no longer act as sinks for CO_2 or N_2O as was seen during periods of time during the summer in Pond 1 in 2005. Conversion of wetlands to agricultural land may also result in a loss of soil organic carbon (SOC) of over 80 Mg ha^{-1} (Bedard-Haughn et al., 2006). Potential for the wetland to dry-down may increase with landuse conversion and dependent on the environmental conditions in a given year, N_2O emission events could be significant.

5.3 Conclusion

Pond 1 and the DCW were net sources of greenhouse gases in both years of study. These two wetlands, however, contributed less greenhouse gas than other aquatic systems reported in the literature. This study was necessary to quantify greenhouse gas

emissions from these two open water prairie wetlands and to try and establish links with the biological activity of the wetlands. The lack of strong relationships between greenhouse gases and biological parameters measured is an indicator that there is a component of these systems that was not measured or that the strong relationships found in other studies do not hold true for prairie wetlands. This study also demonstrated the importance of climate as a variable governing the water chemistry of the aquatic system. The structure and function of prairie wetlands is unique and should not be inferred from the knowledge of lakes, rivers, reservoirs or peatlands. An effort should be made to further study these aquatic systems as they are an important component of the PPR and are continually being lost and degraded without quantitative knowledge of effects.

Further research on greenhouse gas emissions from prairie wetlands should focus on an emissions inventory from wetlands of different trophic levels, salinities, water chemistries, and wetland permanence classes. Researchers from other studies at the St. Denis site have shown that different types of wetlands within the same geographical region have very different dynamics in relation to greenhouse gas emissions (Pennock, unpublished data, 2006; Yates, 2006). Furthermore, these studies should also include components of zooplankton and bacterial biomass to determine the importance and interaction of each with algal dynamics in eutrophic aquatic ecosystems and to strengthen the knowledge of the relationship with periods of net heterotrophy and the potential for these periods to produce CO_2, as this was the dominant gas in Pond 1 and the DCW in 2005. A focused study on the rates of primary production and greenhouse gas emissions from prairie wetlands will assist in understanding the relationship between the two factors in eutrophic prairie wetlands. It is extremely important that relationships in these wetlands are identified and understood in order to guide future research as these

systems are unique in their structure and function and are an integral component of the Prairie Pothole Region.

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