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Identifying potential carbon flux responses to
shifting hydroecological and climatic regimes in
the Peace-Athabasca Delta

By
Caleb W. Light
B.Sc. Geography, Wilfrid Laurier University, 2007

Thesis
Submitted to the Department of Geography and Environmental Studies
in partial fulfilment of the requirements
for the Master of Science
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2010

Abstract

The CO₂ flux response of organic carbon stored in lake sediments and littoral peat contained in sensitive, northern wetlands may contribute to accelerating atmospheric CO₂ concentrations. Temperature and moisture conditions are important variables that affect the rate and quantity of CO₂ released to the atmosphere from organic matter stored in lake sediments and peat. Antecedent hydroecological conditions also influence the direction and magnitude of CO₂ fluxes to the atmosphere in a changing environment. To better understand and characterize the role of antecedent conditions on CO₂ fluxes, this study combines paleolimnological reconstructions with laboratory incubations of littoral peat and lake sediment from two ponds in the Peace - Athabasca Delta (PAD) in Alberta to (1) investigate the role that past and present hydrological conditions plays on the amount and lability of stored organic carbon to oxidation and respiration potentials and (2) evaluate potential production of CO₂ in light of anticipated future hydroecological conditions.

Lake sediment geochemical records from a currently closed-drainage site (PAD 1) provide evidence for a three-phase hydrological history spanning the last ~600 years, consistent with other independently identified climatic intervals in the PAD. Bulk organic carbon and nitrogen elemental and isotopic analyses of lake sediment organic matter and reconstruction of lake water $\delta^{18}\text{O}$ from cellulose oxygen isotope analyses reveal periods of hydrological connectivity to Lake Athabasca during the Little Ice Age (LIA) high-stand. Low $\delta^{13}\text{C}_{\text{org}}$, high C/N and variable but elevated $\delta^{18}\text{O}_{\text{w}}$ values from the beginning of the record to ~1600 CE, align with the Medieval Period (MP), when lower water levels characterized the central interior of the PAD and this site would have been a closed-drainage basin. A shift to higher $\delta^{13}\text{C}_{\text{org}}$, lower and constant C/N and lower

$\delta^{13}C_{org}$ values occur during the LIA, suggesting that elevated Lake Athabasca water levels would have been capable of inundating this basin during this time. This is further supported by minimum $\delta^{13}C_{org}$ values at -1700, when maximum discharge occurred from the Rocky Mountain glacial headwaters. A shift to lower $\delta^{13}C_{org}$, declining C/N and variable but increasing $\delta^{15}N_{org}$ values define the 20th century, reflecting a decline in water levels and the development of closed-drainage conditions at PAD 1.

Lake sediment organic matter profiles of three sediment cores from PAD 31 in the southern, Athabasca-sector of the delta provide evidence for increases in the frequency of overland flood events due to the natural upstream bifurcation of the Embarras River (Embarras Breakthrough, 1982). High $\delta^{13}C_{org}$ values indicate periodic hydrological connection with Lake Athabasca water at the peak of the LIA, while lower $\delta^{13}C_{org}$ values and increasing bulk organic content indicate the development of closed-drainage conditions following water level declines into the 20th century. An inflection of organic content to lower values and higher bulk densities indicate the increasing flood frequency following the 1982 Embarras Breakthrough event.

Laboratory incubations measuring CO₂ production potentials from selected lake sediment and peat depth intervals reveal site, substrate and stratigraphic differences in potential CO₂ production. Mean, depth-integrated CO₂ production rates are greatest during warm, moist treatments. Production of CO₂ from PAD 31 peat substrates is greater than from PAD 1 peat, while PAD 1 sediments produce more CO₂ during both moist and saturated treatments. Stratigraphic-dependent CO₂ production reveals that sediment and peat deposited during the LIA at PAD 1 potentially produce less CO₂ than

MP or 20¹ century intervals. Intervals characterized by increased flooding at PAD 31 (following the 1982 Embarras Breakthrough) deposit peat and sediment that produces greater amounts of CO₂ compared to earlier, less flood-dominated stratigraphic intervals. PAD 31 peat and sediment substrates are more sensitive to changes in temperature and moisture than those obtained from PAD 1. Near-surface substrates also exhibit the least temperature sensitivity of CO₂ production at each site. These results suggest that more flood-prone, frequently flooded sites (PAD 31) produce and store organic matter in peat and lake sediment that may contribute greater amounts of CO₂ to the atmosphere than closed-drainage sites (PAD 1). Stratigraphic differences in CO₂ production also emphasize the importance of considering antecedent hydrological conditions when evaluating potential CO₂ fluxes from northern wetland environments.

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Table of Contents

Abstract.....	i
Acknowledgements.....	iv
Table of Contents.....	v
List of Tables.....	vii
List of Figures.....	viii
Chapter 1. Introduction.....	1
1.1 Atmospheric CO ₂ and global climate change.....	1
1.2 Significance of northern wetlands to the global carbon cycle.....	4
1.3 The Peace - Athabasca Delta, Alberta.....	6
Climate.....	7
Overview of river and basin hydrology of the PAD.....	7
Vegetation characteristics of the PAD.....	9
Past, present and future directions of hydrological change in the PAD.....	11
1.4 Study rationale and research objectives.....	12
Theoretical approach and research design.....	12
Objectives and research questions.....	14
Site selection rationale.....	15
1.5 Study Site Descriptions.....	16
PAD 1 site description.....	16
PAD 31 site description.....	16
Chapter 2. Theory and Methods.....	18
2.1 Littoral peat and lake sediment coring.....	18
2.2 Paleohydrological reconstructions.....	21
Loss-On-Ignition and radiometric (²¹⁰ Pb, ¹³⁷ Cs) analyses.....	21
Bulk organic carbon and nitrogen elemental and stable isotope composition; cellulose oxygen isotope composition.....	24
Peat core physical and chemical analyses.....	27
•2.3 Laboratory flask incubation experiment design.....	27
Chapter 3. Paleohydrological reconstructions for PAD 1 and PAD 31.....	31
3.1 PAD 1 Sediment core chronology.....	31
3.2 PAD 1 elemental and stable isotope stratigraphy.....	33
Organic matter stratigraphy.....	33
Elemental carbon and nitrogen stratigraphy.....	33
Carbon and nitrogen isotope stratigraphy.....	33
Cellulose-inferred lake water oxygen isotope stratigraphy.....	34
3.3 Evidence for variable hydrological conditions related to Lake Athabasca at PAD 1.....	36
3.4 PAD 31 Elemental and stable isotope stratigraphy.....	40
Organic matter stratigraphy.....	40
3.5 PAD 31 three-phase paleohydrological record over the past -400 years.....	44
3.6 Controls on organic matter deposition at PAD 1 and PAD 31 over the past 600 years.....	45
Chapter 4. Potential CO ₂ fluxes from the Peace - Athabasca Delta.....	50
4.1 Introduction.....	50

4.2	Peat and lake sediment physical and chemical analysis results.....	55
	Physical and chemical properties of peat and lake sediment from PAD 1.....	55
	Physical and chemical properties of peat and lake sediment from PAD 31.....	59
	Lake sediment and peat soil characteristics and substrate quality.....	65
4.3	Peat and lake sediment laboratory incubation results.....	67
	Grouped, mean depth-integrated CO ₂ fluxes.....	67
	CO ₂ production at different stratigraphic depths.....	69
	PAD 1 CO ₂ fluxes from major hydrological intervals spanning the last	
	-600 years.....	72
	The Embarras Breakthrough and PAD 31 CO ₂ production.....	73
	Respiration and oxidation quotients (Q ₁₀) from peat and sediment	
	substrates.....	76
4.4	Discussion.....	79
Chapter 5.	Conclusions and Recommendations.....	85
5.1	Findings summary.....	85
5.2	Recommendations for future research.....	89
Reference List.....		91
Appendix A:	²¹⁰ Pb, ¹³⁷ Cs and ^{2,4} Bi Activity in PAD 1 CIO.....	99
Appendix B:	PAD 1 Organic Carbon and Nitrogen Elemental and Stable Isotope	
	Geochemistry.....	101
Appendix C:	Cellulose Oxygen Isotope Analysis.....	105
Appendix D:	CO ₂ flux measurements.....	108

List of Tables

Table 1: PAD 1 peat and sediment core depths, categories and hydro-intervals of selected sections used for incubation treatments.....	63
Table 2: Selected depth intervals, categories and hydro-intervals of PAD 31 peat and lake sediment selected for laboratory incubation treatments.....	64
Table 3: Mean elemental and isotopic carbon and nitrogen composition, and physical properties (mean %OM, B.D.) of peat and sediment depth intervals obtained from a. PAD 1 and b. PAD 31.....	66
Table 4: Depth-integrated, mean Q_{10} values for PAD 1 and PAD 31 (a.) peat and (b.) lake sediment during each moisture treatment. Error estimates are one standard error (S.E.) about the mean.....	76
Table 5: Mean Q_{10} values for peat and lake sediment substrates at each study site, according to depth categories. Error estimates are one standard error (S.E.) about the mean.....	77
Table 6: Temperature sensitivity quotients (Q_{10}) for potential CO ₂ production in PAD 1 from peat and sediment substrates deposited during hydrologically distinct intervals.....	78
Table 7: Potential respiration/oxidation Q_{10} values for PAD 31 peat (a.) and lake sediment (b.) substrates under all moisture regimes grouped according to major hydrological intervals identified in the sediment and peat stratigraphic record.....	79

List of Figures

Figure 1: Location of the Peace - Athabasca Delta (PAD), Alberta. Study sites PAD 1 and PAD 31 are indicated.....	10
Figure 2: Schematic hydrographs for rivers supplying the PAD with water spanning the last 10 centuries, including the Medieval Period, Little Ice Age and 20 ^l century intervals. Anticipated directional change expected to occur under future climate conditions is shown in the black dashed line (from Wolfe et al. 2008a).....	12
Figure 3: Surface water level changes at both PAD 1 (solid circles) and PAD 31 (open circles) from late May to mid-August, 2007. Water level changes are relative to the surface of the water at the time of instrument installation.....	17
Figure 4: Location of PAD 1 sediment and peat cores collected during the 2007 field season. A schematic diagram of major vegetation zones including <i>Salix spp.</i> , <i>Carex spp.</i> , and <i>Typha spp.</i> is also shown.....	20
Figure 5: PAD 31 sediment and peat core locations collected in the summer of 2007. Sediment and peat cores were collected along a pond bottom through littoral zone gradient. Major littoral vegetation zones are displayed schematically including <i>Salix spp.</i> , <i>Carex spp.</i> , and <i>Typha spp.</i>	21
Figure 6: (a) Total ²¹⁰ Pb and ¹³⁷ Cs activity through the entire core profile (includes measured and interpolated values) and the supported (background) ²¹⁰ Pb. Background ²¹⁰ Pb values (average ²¹⁰ Pb activity from 18-47cm depth) are reached at 18 cm depth, (b) PAD 1 C10 core chronology based on CRS modelling extrapolated beyond where background ²¹⁰ Pb values are reached. Extrapolated basal date of the core is 1423 AD.....	32
Figure 7. Geochemical stratigraphy for the PAD 1 C10 sediment core, including % organic matter (a.), elemental C _{org} and N (b.), C-N ratio (a), carbon and nitrogen isotope composition (d. and e.), and cellulose-inferred lake water oxygen isotope composition (5 ‰ _w) in (f.) with a 3-point running mean (solid line). Contemporary ¹⁸ O surface water value ranges are also shown for Lake Athabasca and PAD 1.....	35
Figure 8: ¹³ C composition of dissolved inorganic carbon (DIC) measured from water samples during three field campaigns from May, 2007 through to May, 2008 in the PAD. Closed and restricted drainage sites are coloured black, open water bodies and rivers are grey [from S. Lyons, MSc in progress, Biology, University of Waterloo].....	38
Figure 9: PAD 31 geochemical stratigraphy from cores collected in 2007 (cores CI, MI and NI) and 2001 (core KB-5) [Wolfe et al., 2008b]. The 1982 stratigraphic horizon identifies the Embarras Breakthrough event. The onset of the LI A (-1900) and the basal date of the KB-5 core (-1963) are also identified.....	43

Figure 10: Key strati graphic units for PAD 1 and PAD 31 identified using organic matter (%OM) and $5^{13}C_{org}$ values over the past 600 and 350 years, respectively.....	49
Figure 11: Organic content (%OM) and dry bulk density (BD in g-cm ³) of peat cores collected from PAD 1 in summer, 2007. Cores span distance and vegetation gradients including willow fringe furthest from the shoreline (CP3,CP4 and CP5), intermediate grass areas (CP1 and CP7) and nearest to the shore cattail zones (CP2 and CP6). See Figure 4 for peat core sampling locations.....	57
Figure 12: Sediment organic content (%OM) and dry bulk density (BD, in g-cm ³) of PAD 1 sediment cores collected along the central (C10, CI), mid (MI) and near-shore (NI) sites in the summer, 2007, used for the incubation treatments and for paleohydrological reconstructions. Time intervals spanning the 20th century, LIA and MP are also shown by dashed lines based on the chronology established for sediment core C10.....	58
Figure 13: Organic matter and dry bulk density of peat cores taken from PAD 31 in the summer of 2007. Location of the cores spans a distance and vegetation gradient towards the current shoreline, including willow fringe (CP8 and CP5), intermediate grass (CP3, CP4 and CP7) and cattail (CP1 and CP6). Lines indicate when %OM begins to decline, indicating the beginning of the onset of increased river influence and flood frequency after an upstream geomorphic event in 1982 (Embarras Breakthrough).....	61
Figure 14: Organic matter and dry bulk density from sediment cores collected in the summer, 2007 from PAD 31 spanning a pond-depth gradient from the centre (CI) to the mid-basin (MI) and near-shore (NI) areas. Organic content, elemental C, N and cellulose inferred $5^{18}O_w$ composition is also shown from a sediment core obtained in 2001. Horizontal lines indicate the base of core C10, the end of the LIA and the 1982 Embarras Breakthrough.....	62
Figure 15: Grouped depth-integrated CO ₂ production rates for PAD 1 and PAD 31 under all simulated moisture and temperature conditions. Gray bars indicate the warm temperature (20°C) while black bars indicate the cool temperature (4°C) treatments. Error bars represent one standard error (S.E.) of the grouped mean flux values.....	68
Figure 16: Mean CO ₂ fluxes grouped by depth category (near-surface, mid and deep sections) for incubated samples during each moisture (dry, moist and saturated) and temperature (warm and cool) treatment. Incubated samples are separated according to substrate type (peat and sediment). Error bars indicate ± 1 standard error (SE).....	71
Figure 17: Potential CO ₂ production from peat and lake sediment substrates at PAD 1, grouped into major hydrological intervals spanning the last -600 years including the Medieval Period (MP), Little Ice Age (LIA) and the 20 th century.....	72
Figure 18: CO ₂ production potentials (mg CO ₂ g ⁻¹ day ⁻¹) from peat and sediment substrates deposited during hydrological intervals at PAD 31 including prior to and following increased river influence after the Embarras Breakthrough	

event in 1982 and during the LIA for each simulated moisture and temperature treatment. Error bars represent one standard error (S.E.) about the mean75

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Chapter 1. Introduction

1.1 Atmospheric CO₂ and global climate change

Global climate changes are linked to increases in the amount of greenhouse gases (GHGs) found in the Earth's atmosphere [IPCC, 2007]. Fossil fuel combustion (domestic and industrial) and land use change are the largest contributors to changing concentrations of GHGs in the atmosphere. Arctic temperatures have increased at nearly twice the global average rate over the last century, suggesting that high-latitude areas are more sensitive to climate changes initiated by rising atmospheric GHGs [IPCC, 2007]. Global climate models predict continuing changes to the Earth's climate, most importantly warmer atmospheric temperatures. As a result, ocean surface levels, precipitation and evapotranspiration patterns, and soil-atmosphere carbon exchanges are expected to be altered [IPCC, 2007]. The complete effects of climate change on the environment remain largely uncertain, but the likelihood of accelerated carbon cycling patterns and positive feedback processes is high. Thus, there is a need to better evaluate the possible changes in carbon cycling pathways that can occur in sensitive, high-latitude biomes.

Gradual increases in the atmospheric carbon dioxide (CO₂) concentration from ~280 ppm in pre-industrial periods to approximately 380 ppm presently has occurred largely as a result of human activities like fossil-fuel burning, deforestation, and land use change [IPCC, 2007]. Consequently, the Earth's surface temperatures have increased by 0.74 °C (4.9%) since 1850 as a result of the accumulation of greenhouse gases in the atmosphere, and are expected to increase by another 1.1 to 6.4°C (7.3% to 42%) by the end of the century [IPCC, 2007]. The major GHGs found in the atmosphere include water vapour,

carbon dioxide (CO₂), methane (CH₄) and nitrous oxide (N₂O). However, due to high reactivity of water vapour and its short residence time in the atmosphere, CO₂, CH₄ and N₂O are considered the main forcings of climate change. Concentrations of CO₂, CH₄ and N₂O have changed rapidly in response to land use changes and fossil fuel combustion over the 20th century. GHG warming potentials are 1, 23, and 296, respectively, for CO₂, CH₄ and N₂O [IPCC, 2007]. While CH₄ and N₂O have greater radiative forcing potentials, CO₂ contributions to temperature changes are most dominant and are responsible for close to 60% of total increases in radiative forcing [IPCC, 2007].

Changes in Earth's surface temperatures have the potential to alter or even enhance ecosystem carbon (C) fluxes. This is significant because of the positive feedback mechanisms involving soil organic material, atmospheric temperatures and CO₂ composition. CO₂ efflux from soil organic material at any point in time is determined by a number of factors; most importantly, the amount and quality of available substrate, temperature, and the moisture conditions that control the decomposer activity [Kirschbaum, 2006]. It is commonly accepted that warmer temperatures accelerate organic material decomposition, oxidation and remineralization, leading to a build up of CO₂ in the atmosphere. Despite this widely accepted relationship, large spatial and temporal variations in the direction and magnitude of CO₂ fluxes from organic soils continue to be reported over similar temperature changes [Kirschbaum, 2006]. This soil - atmosphere CO₂ feedback process remains particularly uncertain in the western boreal forest biome of North America [Foote and Krogman, 2006]. The high spatial and temporal variability of CO₂ fluxes from organic substrates in temperature sensitive

biomes demands further quantification of the controls on the soil - atmosphere CO₂ exchange.

The rising concentration of CO₂ in Earth's atmosphere can be partially linked to changes in the rates of soil organic matter respiration. The close to 75×10^{15} g C yr⁻¹ flux from soil respiration to the atmosphere is highly influenced by the thermal regime of the climate and will likely increase given increasing temperatures and changing moisture conditions in the Earth's climate [Schlesinger and Andrews, 2000]. Since soil carbon respiration rates are limited in most cases by organic C supply and consequently increase or decrease with changes in net primary production, some authors suggest mid-latitude and tropical areas will experience the greatest losses in soil carbon with increases in temperature [e.g., Trumbore et al., 1996]. However, the cold, water-logged conditions of tundra and boreal biomes support an accumulation of labile fractions of organic carbon that can be easily decomposed under a warmer climate [Chapman and Thurlow, 1998]. Soil respiration rates are limited by temperature and moisture conditions in these areas and cause a net accumulation of organic matter as a result [Schlesinger and Andrews, 2000]. Tundra and boreal soil respiration rates are more sensitive to changes in temperature and moisture conditions than other soil types, due to the cool and saturated conditions that led to their development. Changes in moisture conditions (water table levels) can lead to an increase in decomposition rates via sustained aerobic conditions [Moore and Knowles, 1989]. Thus, the high predicted temperature changes in boreal and tundra regions will likely influence the potential losses of C from soils, since these areas store the greatest amount of labile soil organic matter [Schlesinger and Andrews, 2000].

1.2 Significance of northern wetlands to the global carbon cycle

Over 25% of the global terrestrial carbon pool is contained within the boreal biome [IPCC, 2000], and 27% of the world boreal biome is contained within nearly one-fifth of Canada's land mass [Benoy et al., 2007]. Reviews of boreal carbon stocks estimate that 113 Pg (61%>) of the boreal carbon stock occurs in peatlands (bogs and fens) [Bhatti et al., 2002]. These estimates however, do not include the storage of lacustrine and other wetland sediments since few estimates are available. Benoy et al. [2007] estimates that 146 Pg or 66.7% of total carbon stocks in Canada's boreal biome occur in water-covered lands (lakes, wetlands and peatlands). Approximately 30% of the total boreal forest in Canada is occupied by water-covered lands, meaning that two-thirds of the boreal carbon pool is concentrated in one-third of the total biome area. Accumulation rates in peatlands across the boreal biome (25 Tg C year⁻¹) indicate a net transfer of carbon from the atmosphere, consistent with the known functioning of peatlands (and other water-covered lands) as sites of carbon sequestration and storage [Gorham, 1991; Roulet, 2000].

Wetlands are waterlogged due to poor drainage and a water table that is at or near the surface permanently or seasonally [National Research Council Canada, 1998]. These conditions favour the accumulation of organic detritus as organic peat [National Research Council Canada, 1998]. Boreal peatlands are dominated by mosses, sedges, and other hydrophytic vegetation [National Research Council Canada, 1998]. Since the onset of boreal peatland development at the beginning of the Holocene with the retreat of the Laurentide Ice Sheet, an estimated 0.076×10^{15} g CO₂ has been sequestered from the atmosphere via photosynthesis, while 0.032×10^{15} g CH₄ has been contributed to the atmosphere through anaerobic decomposition of organic matter [Gorham, 1991; Vitt et

al, 2000]. Reductions in the ability of northern wetlands to function as a carbon sink has occurred with the ongoing loss of these wetlands through anthropogenic and natural influences. In addition, the extensive soil carbon deposits remain sensitive to changes in moisture conditions, which can cause losses of soil carbon during enhanced aeration and disturbance under a different future climate [Bridgham et al., 2006]. Thus, the significance of northern wetlands in the carbon budget demands a need for a better understanding of climatic and hydrological controls on carbon feedback processes, including production, sedimentation and preservation in lake sediments and peat soils, as well as potential contributions of CO₂ to the atmosphere under changing hydroclimatic regimes [Bridgham et al., 2006].

Aquatic wetlands are wetlands that are dominated by shallow standing water, lakes and ponds [Benoy et al., 2007]. Carbon enters aquatic wetlands through two major pathways. The first pathway is through invasion of CO₂ during periods of high productivity or when CO₂ concentrations in the overlying water are reduced to levels below that of the atmosphere. The second pathway is through hydrologic and fluvial processes that transport particulate and dissolved forms of carbon from terrestrial sources. The carbon that is incorporated into and stored in lakes and ponds is more permanent than that stored in peat because of persistently saturated (anoxic) conditions [Molot and Dillon, 1996].

A global estimate of the transfer of CO₂ from inland aquatic systems to the atmosphere is 0.75 Pg C yr⁻¹ [Cole et al., 2007]. This rate is much greater than the rate at which carbon is buried in these systems, suggesting that the CO₂ loss from the decomposition of organic matter results from the oxidation of a substantial fraction of the

terrestrial organic load inland waters receive [Cole et al, 2007]. Boreal lake sediments are estimated by Kortelainen et al. [2004] to contain 19-27 Pg of carbon. However, a much larger estimate of 120 Pg was calculated from Canadian datasets and is nearly twice the carbon found in boreal plant biomass (64 Pg) [Molot and Dillon, 1996]. Despite the large variability in estimates of lake burial and sequestration capacity, boreal lakes are an important part of the total carbon stored in watersheds at the regional scale [Cole et al., 2007]. A global estimate of the fraction of carbon transported from terrestrial sources and stored or exported by aquatic systems is 1.03 Pg y^{-1} [Cole et al., 2007].

Canada's northern wetlands and lakes are clearly significant in the global carbon budget. Many of these lakes and wetlands that act as sinks for carbon lie within the Boreal - Subarctic transition zone, the total fluxes which are estimated to be 87 Tg C yr^{-1} (including forests and peatlands) [Bhatti et al., 2003]. Surface water uptake (or sediment accumulation) in the same study ranges from 5.0 to 8.5 Tg C yr^{-1} . Comparatively, Campbell et al. [2000] estimates that Holocene lake sediments in Alberta sequester $15 \text{ g C m}^{-2} \text{ yr}^{-1}$, or 2.3 Pg C over the entire Holocene. Wetlands and lakes in the boreal forest are known, and widely accepted as sites that function to sequester and store carbon, a substantial portion of which is transported from terrestrial regions to surface waters during watershed processes [Gorham, 1991; Roulet, 2000].

1.3 The Peace -Athabasca Delta, Alberta

The Peace - Athabasca Delta (PAD) ($59^{\circ}\text{N } 112^{\circ}\text{W}$) (Figure 1) is a significant northern wetland and the largest alluvial-wetland habitat in the region surrounded by a low density of wetland habitat [Peace-Athabasca Delta Technical Studies (PADTS), 1996]. This

large (3900 km²) inland freshwater deltaic wetland is situated at the confluence of the Peace, Athabasca and Birch Rivers in northern Alberta, Canada. The western arm of Lake Athabasca receives inflow from the north-ward flowing Athabasca River, and water exits the lake northward through the Riviere des Rochers, Quatre Fourches and Revillon Coupe, which all connect with the Peace River to form the Slave River. Three distinct deltaic regions exist including the more active Athabasca to the south (-1970 km), where fluvial geomorphologic processes are more active compared to the Birch to the west (-170 km) and the relict Peace to the north (—1680 km).

Climate

The PAD is located within the Boreal Plain ecoregion and in a zone of discontinuous permafrost [Ecoregions Working Group, 1989]. The climate is characterized by relatively long, cold winters and short warm summers typical of northern, continental sub-humid mid-boreal environments [Devito et al., 2005]. Mean annual air temperature is -1.9 °C, with mean July and January air temperatures being 16.7 °C and -23.2 °C, respectively [1971-2000 climate normals; Environment Canada Weather Station at Fort Chipewyan, Alberta]. Average precipitation is -390 mm annually, with approximately 59% falling as rain through the May to September period.

Overview of river and basin hydrology of the PAD

The PAD (Figure 1) receives water from the Athabasca River, which flows into Lake Athabasca from the south. The Birch River flows from the west into Lake Mamawi; which is connected to Lake Athabasca near its outflow down the Quatre Forches. The Peace River flows to the north of the PAD and joins the Riviere des Rochers to form the Slave River, which continues to flow northward. Elevated (perched) basins, small lakes

and ponds that are hydrologically isolated from the main flow system are found surrounding the main lakes and rivers throughout the PAD. Water levels in perched basins and channel networks are generally highest during the spring melt period and into the early summer but decline in response to evaporation through the summer months. Through the fall and winter period, water levels are the lowest. When water levels in the Peace River are higher than those of Lake Athabasca (mainly spring ice-jam flood events), flow reversals can occur where water flows southward from the Peace River through the Quatre Forches or the Riviere des Rochers into Lake Athabasca.

The Peace River is regulated by impoundment at the W.A.C. Bennett Dam, constructed in 1968 and formed the Williston Lake reservoir. Construction of the dam and the subsequent draw-down of water levels in the Peace River sparked concern over permanent and irreversible hydroecological change downstream in the PAD [Peace-Athabasca Delta Project Group (PADPG), 1973]. Recent studies suggest that although temporary declines in discharge of the Peace River during infilling of the Williston Reservoir at the Bennett Dam did result in measurable changes downstream in the PAD, subsequent changes observed in the delta are driven largely by regional climate and hydrological conditions [Timoney et al., 1997; Timoney, 2002; Wolfe et al., 2005; Wolfe et al., 2006].

The numerous, individual basins in the PAD possess water balances that reflect the relative importance of each of the water budget components, including precipitation, snowmelt, overbank flooding and evaporation. The delta's landscape is characterized by >1000 perched basins that range from being continuously connected to periodically connected, or entirely disconnected from the main river network [Peters et al., 2006b].

Hydrologically-connected basins share continuous channel connection to the main flow network, while restricted- and closed-drainage types are only periodically inundated by river waters during peak flow or ice jam conditions. Closed-drainage basins are different from restricted-drainage since these basins predominantly receive inputs of water from atmospheric sources and are less susceptible to inputs of river water during overland flooding events. Groundwater inputs and exports to individual basins have been shown to be negligible as a result of the low local relief, relict permafrost, and low permeability of the silty-clay deposits from Glacial Lake McConnell [Peters et al., 2006a].

Vegetation characteristics of the PAD

Variable hydrological conditions with fluctuating water levels allow swamp, marsh, fen and bog wetland communities to persist within the PAD [Peters et al., 2006a]. An abundance of emergent and submergent herbaceous vegetation, ranging from semi-floating aquatic plants to sedges and grasses, are found in the PAD [Prowse and Conly, 2000]. Vegetation that dominates grassland lowlands in each of the deltas are sedge (*Carex antherodes*) and reed (*Calamagrostis spp.*) grasses [Prowse and Conly, 2002]. The shallow water bodies are dominated by pondweed (*Potamogeton spp.*), duckweed (*Lemna spp.*), bladderwort (*Utricularia vulgaris L.*), coontail (*Leratophyllum demersium L.*) and water horsetail (*Equisetum fluviataile*) that typically dominate the edges of water courses [Timoney, 2002]. Elevated areas surrounding water bodies and inland areas are dominated by willow (*Salix spp.*), poplar (*Populus L.*), spruce (*Picea spp.*), and white birch (*BetulaL.*).

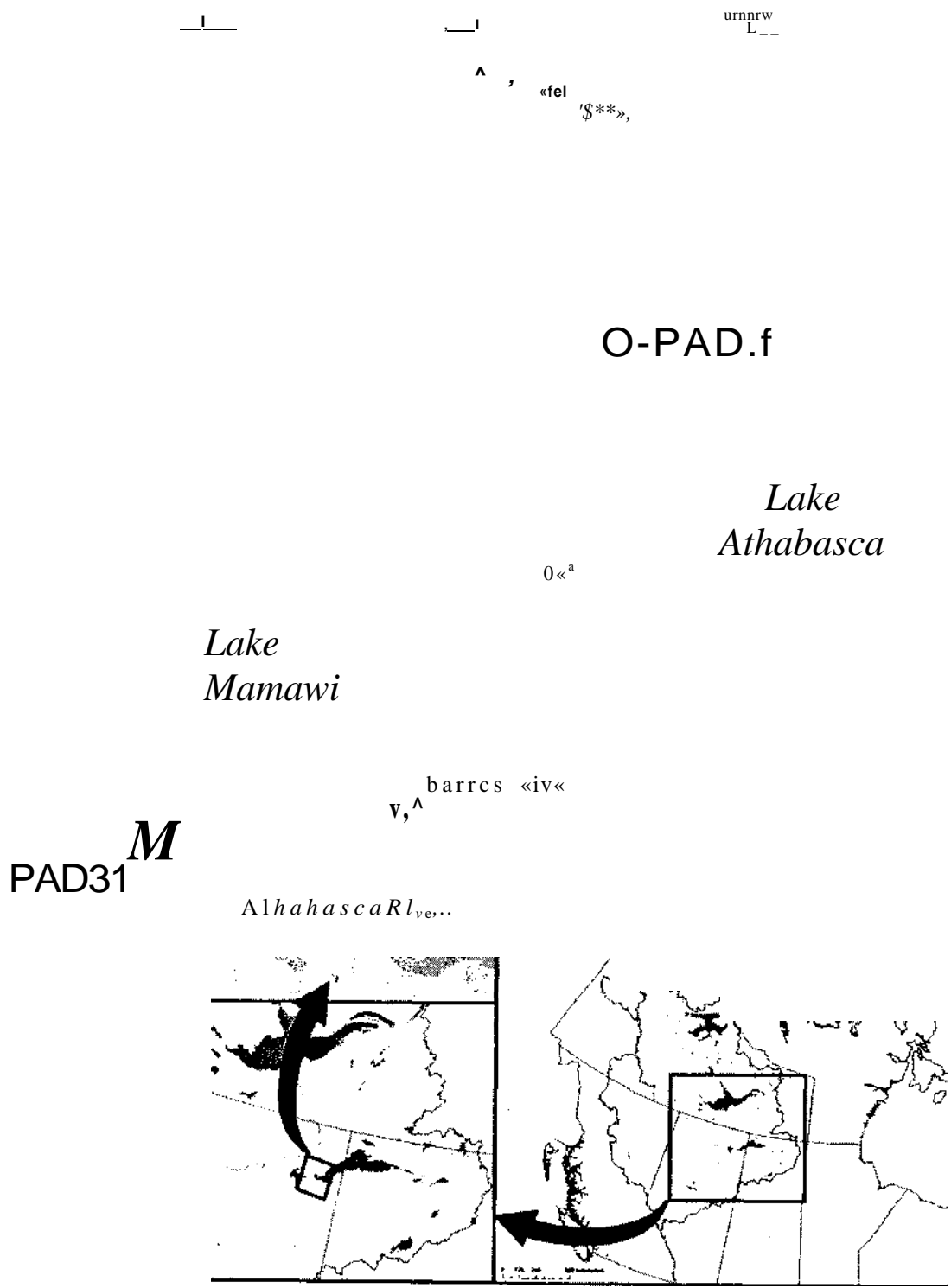


Figure 1: Location of the Peace - Athabasca Delta (PAD), Alberta. Study sites PAD 1 and PAD 31 are indicated.

Past, present and future directions of hydrological change in the PAD

Like many regions of western North America, the PAD has experienced shifts in hydrological regimes in response to prevailing climate conditions. A recent rapidly declining glacial water source in the headwaters of the Athabasca and Peace rivers combined with intensifying industrial development upstream threaten the sustainability and integrity of the PAD as an aquatic ecosystem [Schindler and Donnahue, 2006]. Historical water levels and hydrological conditions in the PAD over the last few centuries have been characterized by a three phase climate history, which includes the "Medieval" (AD -1000 - 1600), followed by the Little Ice Age (LIA) (AD -1600 to -1900) and the 20th century [Wolfe et al., 2008a; Edwards et al., 2008]. Schematic hydrographs derived from paleohydrological records in the PAD [Wolfe et al., 2008a] shown in Figure 2 indicate that the Medieval Period, characterized by generally warmer conditions causing early and rapid melt of alpine snow pack, had a higher frequency of ice-jam flooding. Summer river discharge and Lake Athabasca water levels were not sustained through the summer and fall months as a result of warmer conditions. A transition to a period of colder temperatures (i.e. the LIA), accompanied by an expansion in headwater glaciers, and a slow delayed spring thaw reduced spring ice jam flood frequency while sustaining high summer discharge and Lake Athabasca water levels. The 20th century hydrograph has been characterized by low flood frequency and magnitude as a result of declining water contributions from headwater glaciers and snowpacks and generally warming conditions. A return to Medieval Period-like conditions is unlikely since snow and glacial melt water sources are diminishing, a trend that is expected to continue [Schindler and Donnahue, 2006; Wolfe et al., 2008a; Edwards et al., 2008]. The recent period is

unlike any other time interval over the past millennium. The anticipated hydrograph for the PAD is to be characterized by flashy, low river discharge and low water levels, especially when considering the projected rapid climatic changes and increased industrial usage of water resources for economic development upstream of the PAD.

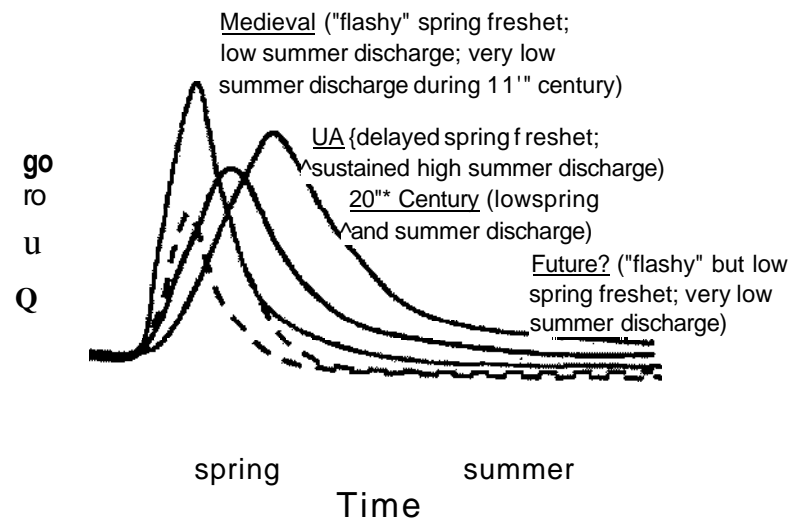


Figure 2: Schematic hydrographs for rivers supplying the PAD with water spanning the last 10 centuries, including the Medieval Period, Little Ice Age and 20th century intervals. Anticipated directional change expected to occur under future climate conditions is shown in the black dashed line (from Wolfe et al. 2008a)

1.4 Study rationale and research objectives

Theoretical approach and research design

The importance of boreal water-covered lands functioning as sites for atmospheric carbon storage is widely known and accepted [Roulet, 2000; Bridgham et al., 2006; Frohking et al., 2006; Tarnocai, 2006; Benoy et al., 2007]. Better characterizing the potential response of these sites to climatic and hydrological changes is needed to address consequences of increased climate variability and land use change. Studies evaluating potential carbon losses under changing environmental conditions typically consider only the anticipated environmental conditions. Few studies consider the possible impact that

antecedent and current environmental conditions play on determining the magnitude and direction of trace gas fluxes from organic (including peat and lacustrine sediment) substrates [Updegraff et al., 1998]. Chronological effects on substrate responses to environmental changes often limit the ability to accurately predict the response to changing conditions [Updegraff et al., 1998]. Lake sediments contain paleohydrological archives that can be used to inform the potential response of stored organic matter to changes in hydroecological conditions. Understanding these antecedent hydrological conditions is an important consideration when evaluating carbon fluxes spatially and temporally.

To address uncertainties associated with the response of carbon dynamics to changes in the hydroclimatic regime, this research project combines information obtained from paleohydrological archives and in-vitro laboratory incubation treatments that simulate CO₂ production potentials. The main hypothesis of this research is that paleohydrological information will help characterize the CO₂ response and functioning of organic lake sediment and peat contained in northern wetlands like the PAD.

The spatially and temporally variable hydrological regimes in perched basins of the PAD provide an opportunity to investigate how variable hydrological and climatic conditions affect potential CO₂ fluxes to the atmosphere. For example, the concentration, quality and lability of lacustrine sediment and peat organic matter is the result of a suite of hydrological processes that occur over long time periods. The results of these processes are retained in lake sediments, providing information pertaining to the source and history of the organic substrates. Therefore, paleohydrological reconstructions from perched basins in the PAD can be used to assess the types of hydrological conditions that

have existed in the past, and to inform the direction and magnitude of anticipated changes. This study will help to evaluate whether an understanding of the past changes occurring in northern wetlands is important to include when assessing the potential changes to carbon exchange between peat, lake sediments and the atmosphere.

Objectives and research questions

The major objective of this study is to characterize how changes in the hydrological conditions of lakes in the PAD, a significant northern wetland, influence the sustainability of carbon stores in organic lake sediment and littoral peat deposits. This study will address two specific research questions that will evaluate how the spatial and temporal differences in the hydrology of perched basins influence the amount, lability, and sustainability of organic matter in lake sediments and littoral peat deposits. The research questions are:

- (1) What influence does antecedent and contemporary hydrological conditions have on the amount and lability of stored organic carbon to CO₂ production potentials?
- (2) How will potential CO₂ emissions respond to anticipated hydroecological conditions in the PAD?

These research questions are designed to investigate the impact of past, present and potential hydrologic and climatic changes on the functioning of the PAD, as a significant northern wetland, with respect to its carbon dynamics. These questions also address concerns about the potential changes to the magnitude and direction of carbon fluxes resulting from directional change in climate and river discharge that are expected to create increasingly drier conditions.

Site selection rationale

To satisfy the objectives of this project and to address the research questions, two study basins were selected, which have contrasting contemporary water balances [Wolfe et al., 2007b]. One site is selected on the basis of contemporary, closed-drainage conditions with a water balance dominated by precipitation and evaporation. The second site is currently highly influenced by river waters and its water balance is dominated by frequent inundations of river water. Carbon fluxes may be linked to both the past and present hydrological regimes, and provides an opportunity to investigate the relative roles that water balance differences have on carbon respiration and oxidation potentials.

The northern, Peace sector of the delta is a relict deltaic landscape that contains numerous perched basins largely disconnected from the main river network. PAD 1 lies within this sector and is a typical closed-drainage basin. Conversely, PAD 31 is in the more active, southern Athabasca sector and is a restricted-drainage basin frequently influenced by river waters during overland flooding events. The paleohydrological variability of these basins is also thought to be different. The hydrological history of PAD 31 is known, having become increasingly influenced by river water following an upstream geomorphic event in 1982 [Hall et al., 2004; Wolfe et al., 2008b]. The historical water balance of PAD 1 is unknown and determining this is a major objective of this project. The differences between these sites allows for the investigation of the influence of hydrological connectivity and antecedent conditions on the amount and sustainability of carbon stored in organic sediment and littoral deposits.

1.5 Study Site Descriptions

PAD 1 site description

PAD 1 (Figure 1) is a shallow (~1.5 m maximum depth) lake dominated by emergent and submerged vegetation. Only during major ice-jam induced flood events is this basin thought to receive riverine inputs of water. The water balance of this basin consists of inputs from precipitation including snowmelt (P) and river floodwater (Rp) and outputs from exclusively evaporation (E). The water balance equation is:

$$\text{Water balance} = P + R_F - E \quad (1)$$

Water level changes over the open water season of 2007 (Figure 3) demonstrate that changes in water level responds sensitively to precipitation and evaporation events. Between early spring and late summer, mean daily water level declined approximately 30 mm (Figure 3). Points of inflection (increase) indicate the inputs of precipitation during rain events. This short-term seasonal water level record highlights that this basin is typical of a closed-drainage basin.

PAD 31 site description

The second study site, PAD 31 ("Johnny Cabin Pond") (Figure 1), is a shallow (-1.2 m maximum depth) freshwater slightly alkaline lake, dominated by extensive submerged and emergent macrophyte growth. The present water balance is characterized by a 'restricted' to periodically 'open-drainage' type [Wolfe et al., 2007a; Wolfe et al., 2008b]. Inputs of water include precipitation and snowmelt (P) and river water from overbank flooding (Rp) during both spring freshet periods and flooding during periods of elevated flow along Mamawi Creek (RE). Outputs include evaporation (E) and possible exports of water outflow (O) during periodic connectivity to the local discharge network. The water balance can be expressed as:

$$\text{Water balance} = P + R_F + R_E - E - 0 \quad (2)$$

Seasonal changes in mean daily surface water level for 2007 are shown in Figure 3. The water level declined ~30mm from late May through August. Sharp rises in water level during early spring indicate inundation of river water during peak flow events along Mamawi Creek.

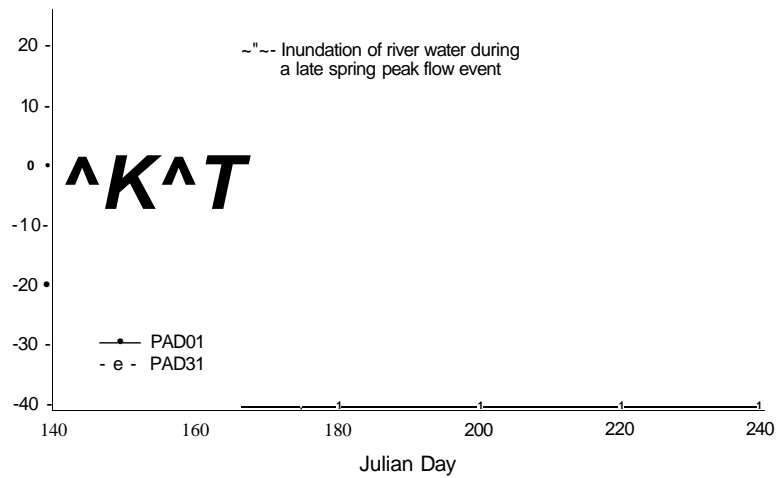


Figure 3: Surface water level changes at both PAD 1 (solid circles) and PAD 31 (open circles) from late May to mid-August, 2007. Water level changes are relative to the surface of the water at the time of instrument installation.

Chapter 2. Theory and Methods

A variety of field and laboratory methods have been used to evaluate the paleohydrological conditions at both PAD 31 and PAD 1 and to simulate potential CO₂ emissions. Both lake sediment and peat cores were collected for analysis.

Paleolimnological reconstructions employ several elemental and isotopic analyses of lacustrine sediment organic matter. Climate and hydrological simulations in the laboratory are designed to assess the potential production of CO₂ from organic matter stored in the lake sediments and paludal peat deposits.

2.1 Littoral peat and lake sediment coring

Three lake sediment cores (20 - 47 cm long) were collected along a transect from the central to the near-shore for both PAD 1 (Figure 4) and PAD 31 (Figure 5) in the summer of 2007. A gravity coring device was used because it preserves the sediment - water interface necessary for paleolimnological reconstructions [Glew, 1988; 1989]. Sediment cores were obtained at each basin from a centrally-located site (C), near-shore site (N) and an intermediate-site (M) and sectioned into 0.5 cm intervals at the field station prior to transport back to the laboratory. Replicate sediment cores were taken to provide sufficient material for paleolimnological analyses, including radiometric (²¹⁰Pb and ¹³⁷Cs) dating, organic carbon (C_{org}, ¹³C_{org}) and nitrogen (N, ¹⁵N) elemental and isotopic composition and cellulose oxygen isotope composition (¹⁸O_{cc,ii}) to infer lake-water ¹⁸O composition (¹⁸O_{i,w}). Intervals of lake sediment from all three locations were selected for laboratory incubations designed to measure CO₂ production.

Peat cores were collected from locations representative of dominant vegetation zones through a littoral zone transect. The dominant terrestrial vegetation species included

Typha spp., *Carex spp.*, and *Salix spp.* Using a Wardenaar peat coring platform, a total of 7 peat cores at PAD 1 and 8 peat cores at PAD 31 were obtained. Cores were extracted from a *Typha spp.* fringe, 5 m inland from the *Typha spp.* fringe, 5 m from the *Salix sp.* fringe, and 5, m inside the *Salix spp.* Fringe (Figure 4, Figure 5). Peat cores were packaged and sealed to prevent moisture loss for transport. In the laboratory each core was frozen, split lengthwise, visually described, photographed and sectioned into 2 cm intervals for analysis. Approximately 3 litres of pond water was collected from each pond for subsequent use in the incubation experiments.

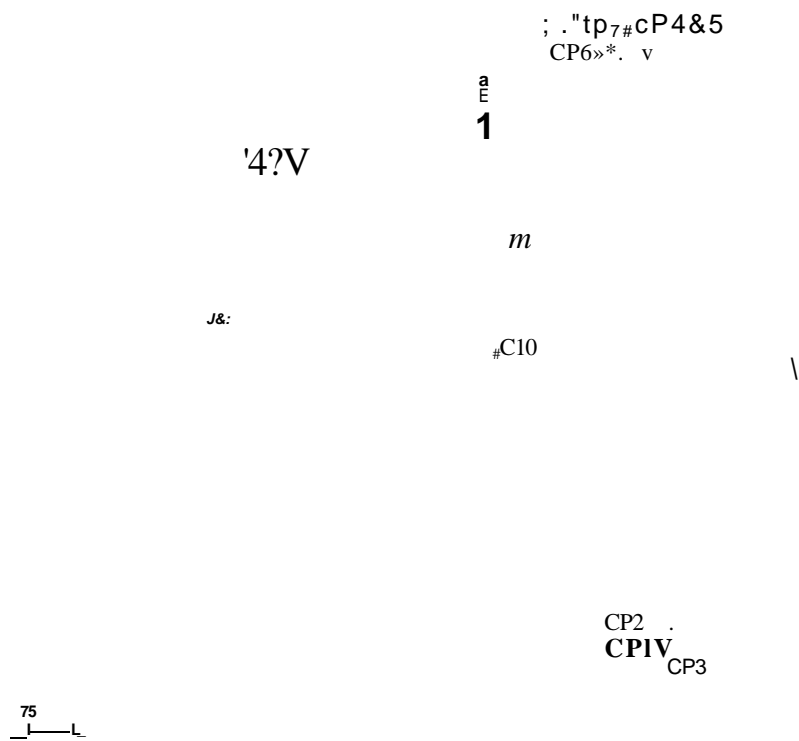


Figure 4: Location of PAD 1 sediment and peat cores collected during the 2007 field season. A schematic diagram of major vegetation zones including *Salix spp.*, *Carex spp.*, and *Typha spp.* is also shown.

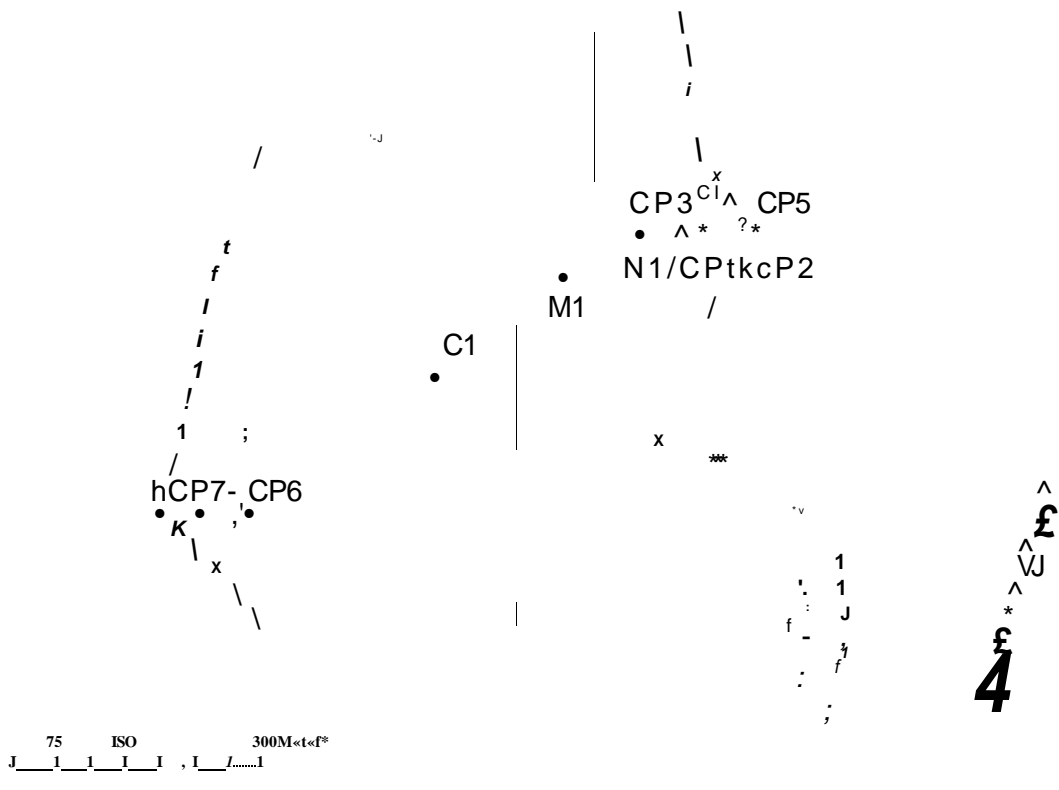


Figure 5: PAD 31 sediment and peat core locations collected in the summer of 2007. Sediment and peat cores were collected along a pond bottom through littoral zone gradient. Major littoral vegetation zones are displayed schematically including *Salix spp.*, *Carex spp.*, and *Typha spp.*

2.2 Paleo hydro logical reconstructions

Loss-On-Ignition and radiometric (^{210}Pb , ^{137}Cs) analyses

Dry bulk density (BD) and organic matter (OM) content of the sediment were used to characterize the physical properties of the samples. Sub-samples of lake sediment were used to gravimetrically determine moisture, organic and inorganic (including CaCO_3) fractions. BD was determined by:

$$\text{Dry Bulk Density} = \frac{\text{Weight of oven dry sample (g) at } 90^{\circ}\text{C}}{\text{Volume of sample (cm}^3\text{)}} \quad (3)$$

Loss-on-ignition following Dean [1974] and Heiri et al. [2001] was used to determine the organic fraction of the samples. Sub-samples of sediment were placed in a crucible, weighed, and then placed in a muffle furnace at 550°C for 1 hour. Mass differences were used to estimate the organic fraction of the sample by:

$$\% \text{ Loss - On - Ignition} = \frac{W_{cso} - W_c}{W_{cso} - W_c} \quad (4)$$

where W_c is the weight of the crucible (g), W_{cso} is the weight of the oven-dried sediment in the crucible (g), and W_{csi} is the weight of the remaining (inorganic) sediment and crucible (g). The same procedure was repeated for a temperature of 950°C to estimate mineral content of the samples.

Reliable chronological reconstructions of lake sediment cores are necessary for interpreting paleoenvironmental records effectively [Appleby, 2001]. The naturally occurring radioactive isotope of lead (^{210}Pb) can be used to generate recent (past -150 years) sediment chronologies. ^{210}Pb is part of the Uranium decay series. Uranium-238

^{238}U ^{238}U

decays via a number of species to Radium-226 (^{226}Ra). ^{226}Ra decays at the soil-atmosphere interface to produce Radon-222 (^{222}Rn) gas and eventually decays further to

^{210}Pb . This ^{210}Pb is deposited onto water bodies and their catchments and is incorporated

into the sediments. The decay of ^{222}Rn to ^{210}Pb in-situ after material has been eroded and

deposited in the water body is the supported ^{210}Pb fraction and is assumed to be in

equilibrium with ^{226}Ra . Excess ^{210}Pb deposited by wet/dry atmospheric fallout or by

deposition from the catchment constitutes unsupported ^{210}Pb . Since the half-life of ^{210}Pb

is 22.29 years, this provides information on which to model the age-depth relationships of

the lake sediments. Most ^{210}Pb -inferred chronologies use a Constant Rate of Supply (CRS) model, which has been shown to be the most appropriate for paleolimnological applications [Appleby, 2001]. This model assumes there has been a constant rate of supply of ^{210}Pb to the surface and that the sedimentation rate has varied through time.

The artificial radionuclide ^{137}Cs is also commonly used as an independent stratigraphic marker on which to model recent sediment chronologies. The source of this artificial radionuclide is from testing of high-yield nuclear weapons beginning in November, 1952. Steady increases in nuclear testing until the 1963 Test Ban Treaty produced enough debris in the atmosphere and subsequent fallout of ^{137}Cs (including other artificial radionuclides like ^{90}Sr and $^{239,240,241}\text{Pu}$) onto the Earth's surface [Appleby, 2001]. Peaks

117

in ^{137}Cs activity can indicate the 1963 sediment depth. Less commonly observed is a peak in ^{137}Cs associated with Chernobyl accident 26th of April, 1983 [Appleby, 2001].

Samples from the PAD 1 centrally-located sediment core (C10) were analyzed for ^{210}Pb and ^{137}Cs at the University of Waterloo WATER laboratory to develop sediment chronologies. 1 to 3 g sub-samples were analyzed every 1 cm by gamma spectrometry for 48 hours. The constant rate of supply (CRS) model was used to generate the geochronology of PAD 1 C10. Loss-on-ignition was performed on the middle (M1) and near-shore (N1) sediment cores to correlate stratigraphic records among the cores.

All sediment core samples from PAD 31 were analyzed for loss-on-ignition. This was done to identify stratigraphic markers of organic content needed to correlate depths with other cores obtained previously and dated using ^{210}Pb [Wolfe et al., 2008b].

Bulk organic carbon and nitrogen elemental and stable isotope composition; cellulose oxygen isotope composition

Sedimentary organic matter provides an archive of paleoenvironmental indicators. Organic carbon and nitrogen elemental and isotope composition obtained from sedimentary organic matter is typically used to evaluate changes in source and cycling of carbon and nitrogen [Meyers and Lallier-Verges, 1999; Meyers and Teranes, 2001; Leng et al., 2005]. Lacustrine sedimentary organic matter is derived from two general sources: (1) detritus from terrestrial and (2) aquatic plants and single-celled phytoplankton [Meyers, 1997]. The ratio of organic carbon (C) to nitrogen (N) often indicates the relative contribution of allochthonous (terrestrially-derived) to autochthonous (aquatic origin) sources of organic matter to the lake sediment. High C/N values generally indicate a source of organic matter that is allochthonous since terrestrial plants have proportionally higher amounts of carbon-rich structural compounds. C/N values are typically around 20 or more for terrestrially-derived sedimentary organic matter [Meyers and Teranes, 2001]. Autochthonous sources of organic matter in lake sediments typically have lower C/N values since nitrogen that occurs preferentially in proteins and nucleic acids is relatively abundant [Meyers, 1997; Leng et al., 2005]

The stable carbon isotope ratio ($\delta^{13}\text{C}$) measured in sedimentary organic matter is also used as a tool to interpret the paleoenvironment of a lake and its catchment [Leng et al., 2005]. Expressed as a ratio difference from the global standard Vienna Pee-Dee Belemnite (VPDB) in per-mil (‰) notation, the $\delta^{13}\text{C}$ record provides information that reflects within-lake processes if organic matter is autochthonous assuming limited post-depositional changes [Leng et al., 2005]. Algae and macrophytes growing in the water

column utilizing dissolved inorganic carbon (DIC) incorporate the ^{13}C signature by isotopic fractionation of the source DIC [Leng et al., 2005]. Factors controlling the $\delta^{13}\text{C}_{\text{DIC}}$ composition include the source and supply of inorganic carbon (e.g., from runoff), ^{13}C -enrichment from preferential uptake of ^{12}C by phytoplankton during photosynthesis, isotopic exchange with atmospheric CO_2 , and recycling of ^{13}C -depleted carbon from respiration/decay of water column and bottom sediment organic matter [Wolfe et al., 2000]. The $\delta^{13}\text{C}$ values of the lake bottom sediment organic material record the changes in the above processes. Productivity-driven changes in $\delta^{13}\text{C}_{\text{DIC}}$ are typically responsible for down-core variability of $\delta^{13}\text{C}_{\text{org}}$ records, however hydrologically driven changes have also been shown to be important [Wolfe et al., 1999, 2000].

Nitrogen isotope composition of lacustrine sediment organic matter is also used as an indicator of past limnological conditions. The use of ^{15}N in paleolimnological research is less frequently used due to complications associated with the variety of biochemical processes that can contribute to N in sedimentary organic matter [Talbot, 2001]. The heavier ^{15}N is strongly discriminated against during important physical and chemical reactions, with the exception of N_2 fixation by cyanobacteria where negligible fractionation occurs. When N is a limiting nutrient and all DIN is consumed, the N isotopic composition of organic matter reflects the source DIN composition from which it was formed [Talbot, 2001]. Post-depositional diagenetic processes (microbial reworking, decomposition, and mineralization) often have little effect on the ^{15}N composition.

Oxygen stable isotope composition of aquatic plant cellulose can be used to reconstruct the lake water oxygen isotope composition in which it was formed [Edwards

and McAndrews, 1989; Wolfe et al, 2001]. Cellulose is a bio-molecule found in the cell walls of higher and lower plants and is preserved in sediments as amorphous organic matter. During cellulose synthesis in the growing season, oxygen molecules are incorporated into the cellulose molecule and retain the oxygen isotope signature of that lake water through a fractionation factor assumed to be constant, unaffected by temperature or plant species [Wolfe et al., 2001]. Measuring the relative proportion of the stable oxygen isotopes ($^{18}\text{O}:^{16}\text{O}$) in cellulose extracted from lake sediments allows for the reconstruction of the water balance under the conditions that it was formed, assuming aquatic origin.

Sediments from PAD 1 C10 were pre-treated with a 1M HCl solution to remove the inorganic fraction and measured for bulk organic carbon (C%) and nitrogen (N%) content and stable isotopic ratios ($^{13}\text{C}/^{12}\text{C}$, $^{15}\text{N}/^{14}\text{N}$) on the <500 μm fraction using an elemental analyzer interfaced with a continuous flow isotope-ratio mass spectrometer (CF-IRMS) at the University of Waterloo Environmental Isotope Laboratory (UW-EIL). Results are reported in δ -notation in permil (‰) ($\delta = [(R_{\text{sample}}/R_{\text{std}}) - 1] \times 1000$, where $R = ^{13}\text{C}/^{12}\text{C}$ or $^{15}\text{N}/^{14}\text{N}$) in reference to standard Vienna Pee-Dee Belemnite (VPDB) 5^{13}C and AIR 5^{15}N , respectively. Analytical uncertainty is ± 0.1 ‰ for 5^{13}C and 5^{15}N .

Afterwards, samples from PAD 1 C10 were subjected to a stepwise procedure to extract cellulose, similar to that for extracting cellulose from wood powder [Wolfe et al., 2001; Wolfe et al., 2007a]. This includes solvent extraction, bleaching, and alkaline hydrolysis to remove the non-cellulose organic constituents. Iron and manganese oxyhydrides were then removed using hydroxylamine leaching, which was followed by a heavy liquid density separation to further isolate the cellulose from any minerogenic

residue remaining in the sediment sub-samples. Oxygen isotope composition of cellulose was measured using CF-IRMS at the UW-EIL using standard methods [Wolfe et al., 2007a] . Results are reported in ‰ notation representing per mil deviations from Vienna Standard Mean Ocean Water (VSMOW) on a scale normalized such that Standard Light Antarctic Precipitation has a value of -55‰ in $\delta^{18}\text{O}$ [Coplen, 1996]. Analytical uncertainty is $\pm 0.5\%$. A constant cellulose-water oxygen isotope fractionation factor of 1.028 was used to reconstruct lake water $\delta^{18}\text{O}$ [Wolfe et al., 2001].

Peat core physical and chemical analyses

Peat sub-samples of known volume and weight were extracted from each 2 cm section of peat, oven dried at 90 °C for 24 hours, and re-weighed to determine volumetric water content and dry bulk density (BD). Loss-on-ignition analyses were performed as described above (see "Loss-On-Ignition and radiometric (^{210}Pb , ^{137}Cs) analyses"). Separate sub-samples of peat and lake sediment from incubated sections were prepared for bulk organic carbon and nitrogen elemental and isotope analyses, as described previously. However, the samples were homogenized and ground with mortar and pestle rather than sieved. Homogenization of the samples was performed to include the bulk organic fraction in the analyses, rather than exclusively the fine-fraction. Samples were analyzed using CF-IRMS at the UW-EIL, and reported in ‰ notation described above. Analytical uncertainty is 0.05‰.

2.3 Laboratory flask incubation experiment design

Peat and sediment core sections representative of the peat soil and sediment profiles were used in flask incubation experiments designed to measure potential respiration rates from bulk organic matter. The selected samples were representative of stratigraphic

intervals in the sediment and peat profiles with distinct physical properties (eg. high BD, low OM, or low BD, high OM). A full factorial design with triplicate samples from the peat and sediment sections were subjected to two temperature (5°C and 20°C) and three moisture (wet, moist and dry) incubation conditions. These were chosen to represent the range of possible conditions that may potentially occur, or do exist, at the field sites. Approximately 10 g of sediment/peat sub-samples was placed in a 250 ml septum jar fitted with a septum lid to create an air-tight seal. Moisture treatments were distinguished using gravimetric soil moisture composition. For "moist" samples, enough pond water was added to wet the sample without creating a slurry. For "saturated" samples, approximately 10 g of pond water was added to completely cover the sub-sample in the jar. "Dry" incubation samples were oven dried at 60°C for 24 hours prior to the incubation period. Gravimetric soil moisture was determined for each treatment using the formula:

$$\text{Gravimetric soil moisture (u)} = \frac{M_w}{M_{\text{substrate}}} \quad (5)$$

where M_w is the sum of the mass of water contained in the substrate and water added during moisture treatments, and $M_{\text{substrate}}$ is the mass of the bulk, dry substrate.

Headspace gas was sampled for CO₂ concentration using an infrared gas analyzer (IRGA) fixed with needles to penetrate the septum lid. Each sample was allowed to equilibrate for approximately 1 minute before each CO₂ gas reading was taken in parts-per-million (ppm). Gas sample intervals continued every 12th hour for 48 hours. Samples were then vented for 12 hours, re-sealed and sampled every 12^h hour for another 48 hours. A third vent period of 12 hours was followed by sampling every 12^h hour for a

final 48 hours. After venting periods, samples were re-weighed and additional water was added to compensate for any water that had been lost through evaporation during the venting period, except for the "dry" incubation samples. Headspace gas sampling protocol follows methods employed by Hogg et al. [1992], Blodau and Moore [2003], and Petrone et al. [2005]. Samples were also weighed to monitor the moisture status of the samples gravimetrically. Temperature was continuously recorded by thermistors and a data logger (Campbell Scientific Instruments CRIOx). These methods were designed to measure the CO₂ flux from peat and sediment substrates under controlled laboratory conditions.

The change in CO₂ concentration over time allows for a calculation of potential carbon production to the atmosphere, while differences in the rate of change between temperature treatments allow determination of temperature quotient (Q₁₀) values. CO₂ fluxes are expressed as the mean of triplicate samples for every incubation treatment by calculating a linear regression, interpolated between headspace CO₂ concentration and time. The results are expressed as a mass of gas (CO₂) produced per mass of oven dry substrate. The formula used to calculate the CO₂ mass flux is:

$$CO_2 \text{ Flux (R)} = \frac{A \times CF \times MM}{\text{Sample Dry Mass}} \quad (6)$$

where CO₂ Flux is expressed as mg CO₂ g⁻¹day⁻¹, A is the change in CO₂ concentration (ppm) in the headspace of the incubation flask per day, CF is a conversion factor to change ppm CO₂ to mol CO₂, MM is the molar mass of CO₂ (44010 mg mol⁻¹) and the Sample Dry Mass is the mass (g) of the sample incubated absent of moisture.

The Q_{10} value is a dimensionless quantity that describes the temperature dependence of soil respiration. This value is the factor by which the production rate of the products of a reaction (like CO_2 from soil respiration) changes over a 10° temperature interval [Winkler et al, 1996]. The value is calculated using the first order exponential equation:

$$Q_{10} = \left(\frac{R_2}{R_1} \right)^{10 / (T_2 - T_1)} \quad (7)$$

where R_1 and R_2 are CO_2 production rates (fluxes in $\text{mg CO}_2 \text{ g}^{-1} \text{ day}^{-1}$) at two different temperatures, T_1 and T_2 . Temperature independent reactions result in Q_{10} values of 1.0, while values greater than 1.0 indicate that CO_2 production is temperature-sensitive.

Chapter 3. Paleohydrological reconstructions for PAD 1 and PAD 31

Lake sediment core geochemical analyses at PAD 1 and PAD 31 reveal hydrological changes over the past several centuries. These hydrological changes are largely aligned and consistent with independently determined climate intervals [Wolfe et al., 2008a; Edwards et al., 2008]. Other hydrological changes are linked to geomorphic processes that have recently occurred in the Athabasca sector of the delta. These records are useful in assessing the potential CO₂ response of these basins to climate and hydrological change.

3.1 PAD 1 Sediment core chronology

The ²¹⁰Pb activity measured in PAD 1 CIO (Figure 6a) is highly variable throughout the core profile. Maximum activity of 0.1060 Bq·g⁻¹ is recorded in the uppermost sample (0-0.05 cm depth). Activity declines sharply to 0.0364 Bq·g⁻¹ at 10 cm. Below 10 cm, activity remains variable with peaks of 0.0596 Bq·g⁻¹ and 0.0628 Bq·g⁻¹ at 19 cm and 23 cm, respectively. Minimum values (0.0266 Bq·g⁻¹) are reached at 27.5 cm. Less variable but inconsistent activity persists below 18 cm to the bottom of the core. Background ²¹⁰Pb (0.0379 Bq·g⁻¹) was estimated from the mean ²¹⁰Pb activity below 18 cm depth. This depth was chosen on the basis that, with the exception of the two outliers centred at 19 cm and 23 cm, ²¹⁰Pb activity is relatively low compared to measurements above 18 cm. Pb activity initially reaches background values at 8 and 10 cm, but sharply returns to values that are above the background value. This background value is also comparable and in agreement with other lake sediment core ²¹⁰Pb measurements in the PAD [see Wolfe et al., 2005; 2008a]. Linear regression using CRS dates from 11 cm to 18 cm were used to extrapolate the CRS modelled ages below the 18 cm depth (Figure 6 b),

generating a basal date of -1423. The 11 cm to 18 cm interval was chosen since the sedimentation rate appears to be near-constant.

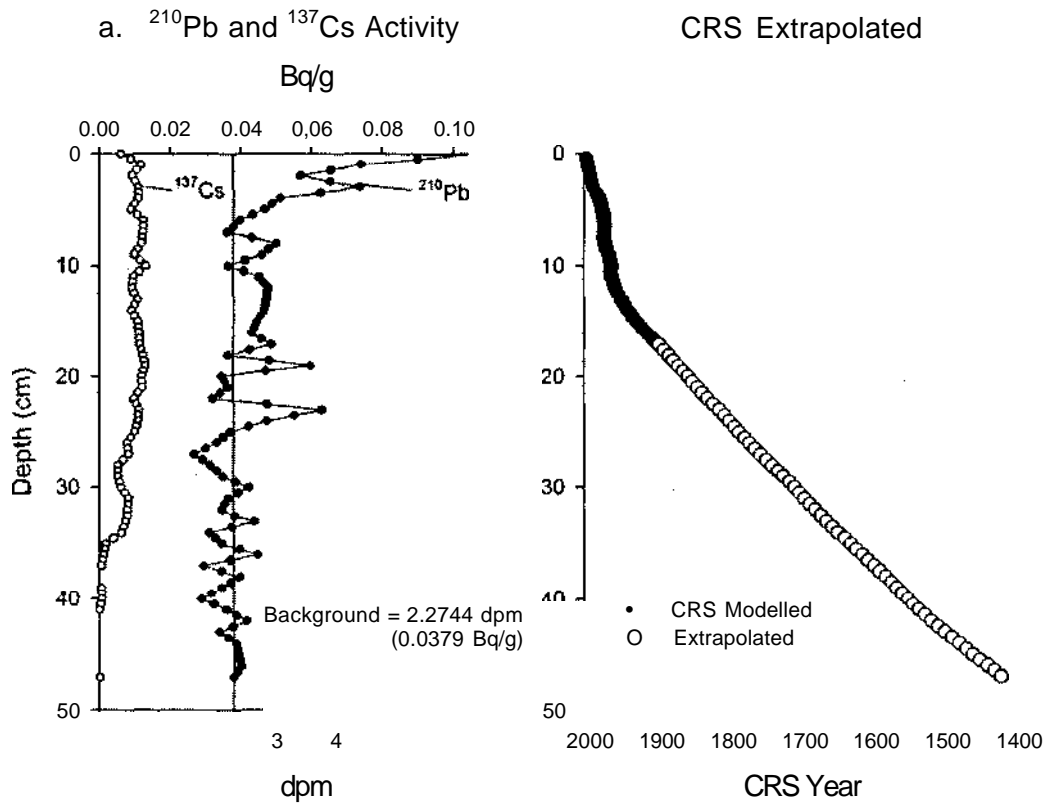


Figure 6: (a) Total ^{210}Pb and ^{137}Cs activity through the entire core profile (includes measured and interpolated values) and the supported (background) ^{210}Pb . Background ^{210}Pb values (average ^{210}Pb activity from 18-47cm depth) are reached at 18 cm depth, (b) PAD 1 C10 core chronology based on CRS modelling extrapolated beyond where background ^{210}Pb values are reached. Extrapolated basal date of the core is 1423 AD.

^{137}Cs activity measured in the PAD 1 C10 sediment core profile narrowly ranges between 0.000 Bq/g at the base of the core to 0.013 Bq/g at 10 cm depth. Activity is nearly uniform throughout the entire profile likely due to post-depositional diffusion of ^{137}Cs , which precludes using ^{137}Cs for developing a sediment chronology.

3.2 PAD 1 elemental and stable isotope stratigraphy

Organic matter stratigraphy

Organic matter (%OM, Figure 7 a.) in PAD 1 C10 ranges from -15% to -37% in the core profile. %OM values are lowest in the oldest sediments (-1423 to -1600) but increase to -25% steadily until -1990. A sharp increase in %OM occurs at 1990 to the top of the core from -25% to -37%.

Elemental carbon and nitrogen stratigraphy

Bulk organic carbon content (%C) increases from 8% to 12% from 1423 to the mid-1500s (Figure 7 b.). %C varies between 10% and 12% until 1800 then increases to 13% by the early 1900s. A sharp increase in %C to -17% occurs from the 1950s to the top of the core. %N follows similar trends observed in %C. Lowest %N values are observed at the base of the core (-0.8%) but increase to 1.2% by -1550. Variable but slightly increasing values to 1.4% occur from the mid-1500s to the mid-1900s. %N values increase sharply to -1.8% in the uppermost portion of the core.

C/N values are low throughout the entire PAD 1 C10 core profile and range from 9 to 11 (Figure 7 c.). C/N values are highest from the bottom of the core to the mid-1600s and then decline from 11 to 9.5. From the mid-1600s to the middle 20th century, C/N' values are constant (-9.5). After 1950, C/N values decline from -9.5 to -9.

Carbon and nitrogen isotope stratigraphy

Organic carbon isotope ($\delta^{13}\text{C}_{\text{org}}$) values narrowly range from -25‰ to -24‰ (Figure 7 d.). Low values of -25‰ occur at the base of the record, then increase to a maximum value of -24‰ at -1580. Constant $\delta^{13}\text{C}_{\text{org}}$ values (-24.5‰) persist from the late 1500s to the mid-1900s. $\delta^{13}\text{C}_{\text{org}}$ values decline and return sharply to a value of -25‰ from the 1950s to the top of the record. $\delta^{15}\text{N}$ values (Figure 7 e.) range from -0.3‰ to 0.6‰, with

the lowest values ($\sim -0.3\text{‰}$) persisting from -1423 to -1600. Between -1600 and -1640, ^{15}N values increase to 0.3‰ . ^{15}N values vary between 0 and 0.4‰ until -1999, and then decline sharply to -0.01‰ at the top of the record.

Cellulose-inferred lake water oxygen isotope stratigraphy

Lake water $\delta^{18}\text{O}$ reconstructed from analysis of lake sediment cellulose ($\delta^{18}\text{O}_{\text{w}}$) in Figure 7 f. has high sample to sample variability. $\delta^{18}\text{O}_{\text{w}}$ averages -19.8‰ , with a maximum value of -15.6‰ and minimum value of -26‰ . From the base of the record, $\delta^{18}\text{O}_{\text{w}}$ values decline from -16‰ to the lowest value of -26‰ at 1740. Based on a three-point running mean, $\delta^{18}\text{O}_{\text{w}}$ values increase after 1740 to -20‰ by the early -1900s. Less variable but slightly more enriched (-21‰ to -17‰) values dominate from -1950s to the top of the core.

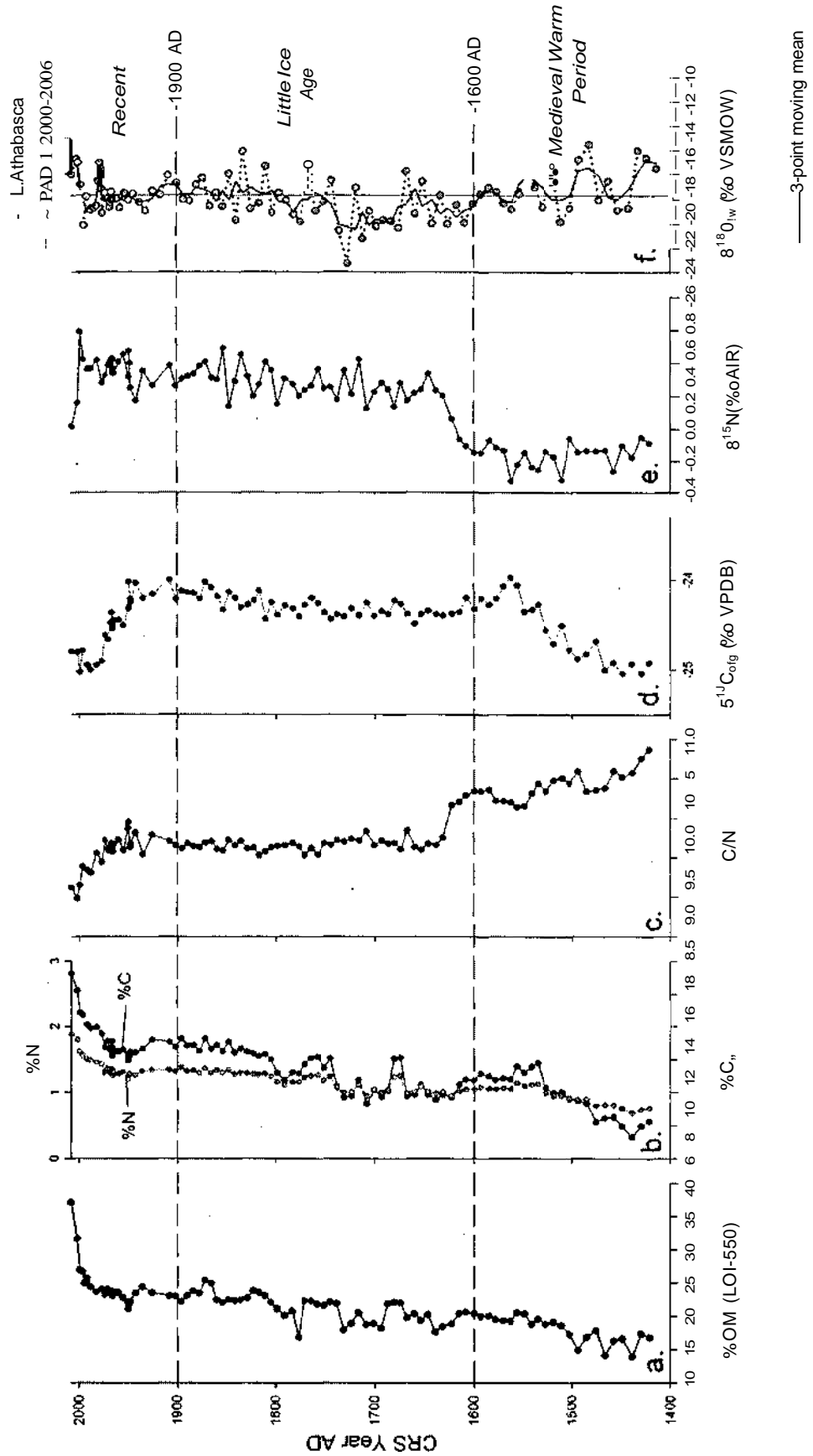


Figure 7. Geochemical stratigraphy for the PAD 1 CIO sediment core, including % organic matter (a), elemental C_{org} and N (b.), C-N ratio (c), carbon and nitrogen isotope composition (d. and e.), and cellulose-inferred lake water oxygen isotope composition ($^{18}\text{O}_{\text{iw}}$) in (f.) with a 3-point running mean (solid line). Contemporary ^{18}O surface water value ranges are also shown for Lake Athabasca and PAD 1.

3.3 Evidence for variable hydrological conditions related to Lake Athabasca at PAD 1

The climate of the PAD during the past 1000 years has shifted through three distinct intervals. Using tree ring 5^{13}C and 8^{18}O data to reconstruct growing season relative humidity (RH_{grs}) and winter temperatures (T_{wjn}), Edwards et al. [2008] identified the following three major climate intervals. High RH_{grs} and T_{wjn} from 1100 - 1250 AD were typical of the Medieval Period (MP). A shift to low RH_{grs} and T_{wjn} occurred during the Little Ice Age (1530 - 1890 AD), where streamflow from the eastern Rocky Mountains was sustained by abundant snowmelt. Lake Athabasca water levels have also been shown to peak from 1600 to 1900 during the LIA [Wolfe et al., 2008a; Sinnatamby et al., 2010; Johnston et al., 2010]. A return to high RH_{grs} and T_{wjn} during the 20th century, similar to the conditions that persisted during the MP, was accompanied by reduced river discharge and a decline in the contribution of glacial snowmelt to streamflow [Wolfe et al., 2008b]. Reduced river discharge and locally drier conditions are typical of the recent 20th century climate interval. The boundaries between these major intervals (1600 and 1900 AD) are shown in Figure 7. Stratigraphic intervals identified in PAD 1 C10 geochemical data broadly align with these independently identified climate intervals in the PAD.

C/N values ranging from 9 to 11 are typical of sediments that are autochthonous in origin [Meyers and Lallier-Verges, 1999; Meyers and Teranes, 2001]. Relatively low C/N values reflect the greater abundance of nitrogen-bearing proteinaceous compounds in algae and other aquatic biota, compared to the carbon-rich and nitrogen-poor structural compounds (lignin, cellulose) found in terrestrial plants [Meyers and Teranes, 2001]. This information is critical in evaluating information found within other analyses from the organic fraction of the lake sediment.

Seasonal changes in the isotopic composition of surface water dissolved inorganic carbon ($\delta^{13}\text{C}_{\text{DIC}}$) obtained from May, 2007 through May, 2008 help identify likely drivers responsible for stratigraphic changes in the $\delta^{13}\text{C}_{\text{org}}$ profile (Figure 8). Decreases in the $\delta^{13}\text{C}_{\text{DIC}}$ in closed- and restricted-drainage basins occur during the growing season (May through August), while open-drainage and river water $\delta^{13}\text{C}_{\text{DIC}}$ increases (Figure 8). This likely indicates a significant contribution of isotopically depleted respired carbon into the water column in closed- and restricted-drainage basins, which would lower the $\delta^{13}\text{C}_{\text{DIC}}$ signature. Periods when basins experience greater connectivity to the open-water network may thus be indicated by increases in sedimentary $\delta^{13}\text{C}_{\text{org}}$ composition. Similarly, decreases in $\delta^{13}\text{C}_{\text{org}}$ values would result from periods of closed- and restricted-drainage conditions where re-utilization of respired organic matter contributes $\delta^{13}\text{C}$ -depleted carbon to the water column.

Interpreting changes in sedimentary $\delta^{13}\text{C}_{\text{org}}$ values as an indication of a shift in the supply of DIC is an unconventional approach, but has been proven useful elsewhere [Wolfe et al., 2000]. Increases in the sedimentary $\delta^{13}\text{C}_{\text{org}}$ values are typically interpreted as reflecting an increase in aquatic productivity [Meyers and Teranes, 2001; Schelske and Hodell, 1995]. This is because during the course of the growing season, preferential consumption of the lighter C isotope (^{12}C) during photochemical reactions leads to enrichment in the remaining $\delta^{13}\text{C}_{\text{DIC}}$ pool. The $\delta^{13}\text{C}_{\text{DIC}}$ values will typically increase as a result of this process. Increases in lake sediment $\delta^{13}\text{C}_{\text{org}}$ values have been shown to be true for large, deep-water Laurentian Great Lakes during periods of enhanced

productivity (eutrophication) following nutrient loading [Schelske and Hodell, 1995; Hodell and Schelske, 1998].

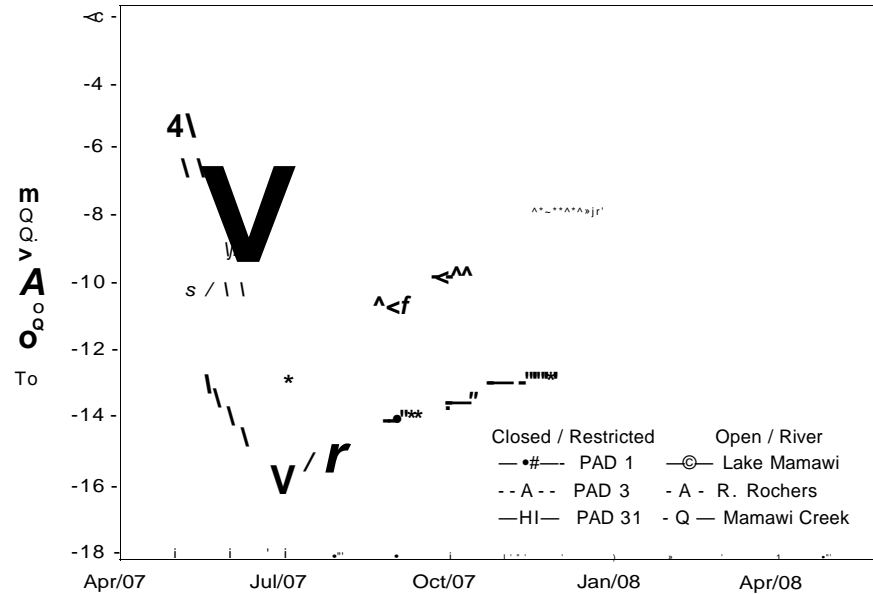


Figure 8:5 $\delta^{13}\text{C}$ composition of dissolved inorganic carbon (DIC) measured from water samples during three field campaigns from May, 2007 through to May, 2008 in the PAD. Closed and restricted drainage sites are coloured black, open water bodies and rivers are grey [from S. Lyons, MSc in progress, Biology, University of Waterloo]).

Patterns in elemental and isotopic C and N stratigraphy and in the $\delta^{18}\text{O}_{\text{w}}$ record align broadly with three major climate intervals known to have influenced water levels in the PAD during the last -600 years. The end of the MP is defined by elevated but declining C/N values and low $\delta^{13}\text{C}_{\text{org}}$ values. Low $\delta^{13}\text{C}_{\text{org}}$ values within this interval indicate that the source of dissolved inorganic carbon (DIC) may largely be supplied by respired sediment organic carbon within the water column under closed-drainage conditions. Infrequent inputs of river water to the basin, and consequently minimal input of enriched $\delta^{13}\text{C}_{\text{DIC}}$ from open and river-like water (Figure 8) during the MP, is reflected by the

depleted sediment organic matter $\delta^{13}\text{C}_{\text{org}}$ values. An increase in $\delta^{13}\text{C}_{\text{org}}$ of approximately ‰ and lower but consistent C/N values occur during the LIA. As mentioned, $\delta^{13}\text{C}_{\text{DIC}}$ values of open-drainage lakes and rivers have been shown to become more enriched through the growing season (Figure 8). Elevated water levels on Lake Athabasca during the LIA would have become the dominant source of water, supplying ^{13}C -enriched DIC through the growing season. Closed-drainage conditions returned in the early 1900s based on a reduction in $\delta^{13}\text{C}_{\text{org}}$ values (~1‰) and a decline in C/N values.

Shifts in the elemental organic carbon ($\%C_{\text{org}}$) and nitrogen ($\%N$) composition of lake sediment are likely the result of a variety of hydrological factors including changes in drainage types (closed- and restricted-drainage). Low but increasing $\%C_{\text{org}}$ values (8% to 12%) during the MP may reflect a period of increasing productivity and preservation of sedimentary organic matter. Sustained, but variable amounts of $\%C_{\text{org}}$ and $\%N$ throughout the LIA resulted from elevated water levels and submergence under an embayment of Lake Athabasca. Recent increases in $\%C_{\text{org}}$ and $\%N$ to maximum values reflect the incomplete diagenesis of lake sediment organic matter and a return to productive, closed-drainage conditions through the 20th century.

Variable, but elevated $\delta^{18}\text{O}_{\text{w}}$ values also support closed-drainage conditions at PAD 1 during the MP, consistent with low water levels reconstructed for Lake Athabasca [Wolfe et al., 2008a]. Subsequent declines in $\delta^{18}\text{O}_{\text{w}}$ values occur during the LIA and reflect a shift towards open-drainage conditions. Minimum $\delta^{18}\text{O}_{\text{w}}$ values indicate increased supply and utilization of ^{18}O -depleted water from enhanced glacial contribution to river discharge. These low $\delta^{18}\text{O}_{\text{w}}$ values indicate that elevated Lake Athabasca water levels

resulting from enhanced glacial contributions to streamflow likely inundated PAD 1. These results are consistent with other evidence for sustained and elevated glacial streamflow during the LIA, supplying Lake Athabasca with isotopically-depleted water at the peak highstand. Minimum $\delta^{18}\text{O}_{\text{w}}$ values occur at a time consistent with maximum discharge from the Rocky Mountain headwaters supplying the delta around -1700 [Edwards et al., 2008]. PAD 1 $\delta^{18}\text{O}_{\text{w}}$ values record the isotopically depleted water supporting elevated Lake Athabasca water levels during the LIA.

Modern $\delta^{18}\text{O}_{\text{w}}$ values for PAD 1 and Lake Athabasca (Figure 7 f) are slightly higher than the recent cellulose-inferred $\delta^{18}\text{O}_{\text{w}}$ values in the uppermost portion of the core. This may result from the utilization of $\delta^{18}\text{O}$ -depleted water, supplied from snowmelt during the spring thaw.

The lake sediment geochemical record at PAD 1 highlights the major hydrologic changes that have occurred in the PAD during the last -600 years. The organic material preserved in the lake sediments, and surrounding paludal deposits has resulted from a variety of hydrological conditions. Additionally, this sediment record emphasises that a number of processes contribute to the information that is incorporated into, and preserved in, sedimentary organic matter. The relatively 'dry' conditions during the MP manifests as low $\%C_{\text{org}}$, $\%N$ and low $\delta^{13}\text{C}_{\text{org}}$ values while the opposite (high $\%C_{\text{org}}$, $\%N$ and $\delta^{13}\text{C}_{\text{org}}$ values) results from persistently 'wet' conditions during the LIA.

3.4 PAD 31 Elemental and stable isotope stratigraphy

Organic matter stratigraphy

Physical and organic matter properties of three sediment cores collected in 2007 from PAD 31 central (CI), mid-basin (MI) and near-shore (NI) locations are shown in Figure

9. Organic matter (% dry mass) in all cores range from -10% to -40%, with shoreline proximal cores (M1, N1) having slightly higher organic matter content. From the bottom of core CI, %OM increases and dry bulk density decreases to values of -40% and -0.3 g cm^{-3} , respectively, to a depth of 12 cm. Sharp declines in %OM and increases in BD occur from 12 cm to 10 cm to values of -10% and -0.5 g cm^{-3} , respectively. Core M1 follows a similar pattern, with the major declines in %OM and increase in BD occurring at 8 cm depth (Figure 9). Core N1 has elevated but constant %OM values (-30%) that increase gradually to -40% until approximately a depth of 6 cm. Sharp declines in %OM and BD to -10% and -0.5 g cm^{-3} , respectively, occur from 6 cm to the top of the core.

Organic matter stratigraphy strongly matches that of other cores collected from PAD 31 in 2001 and analyzed previously. A trend reversal from high to low %OM values identified in other cores collected in 2001 indicates an increase in the flood frequency at PAD 31, as a result of an upstream geomorphic event along the Embarras River that occurred in 1982 [Wolfe et al., 2008b]. Redirection of -40% of flow from the Embarras River into Mamawi Creek resulted in an increased susceptibility of PAD 31 to flooding during high discharge events. This event has been identified in sediment cores collected in 2001, a stratigraphic marker that is also present in the 2007 sediment cores (CI, M1 and N1). Sediment core KB-5 collected in 2001 (Figure 9) has been dated using Pb [Wolfe et al., 2008b]. Using the established 2001 KB-5 ^{210}Pb -chronology, sediment depths that identify the 1982 Embarras Breakthrough are 12, 8 and 6 cm for cores CI, M1 and N1, respectively. The 1900 horizon that indicates the end of the LIA occurs at 11.5 cm depth in KB-5. Using this depth and assuming near-constant sedimentation rates between 1900 and 1982 in all 2007 cores, the 1900 horizon occurs at 18, 14 and 11.5 cm

in cores CI, MI and NI, respectively. Assuming near-constant sedimentation rates is a necessary approach since there are no other obvious stratigraphic indicators that enable cross-core correlations.

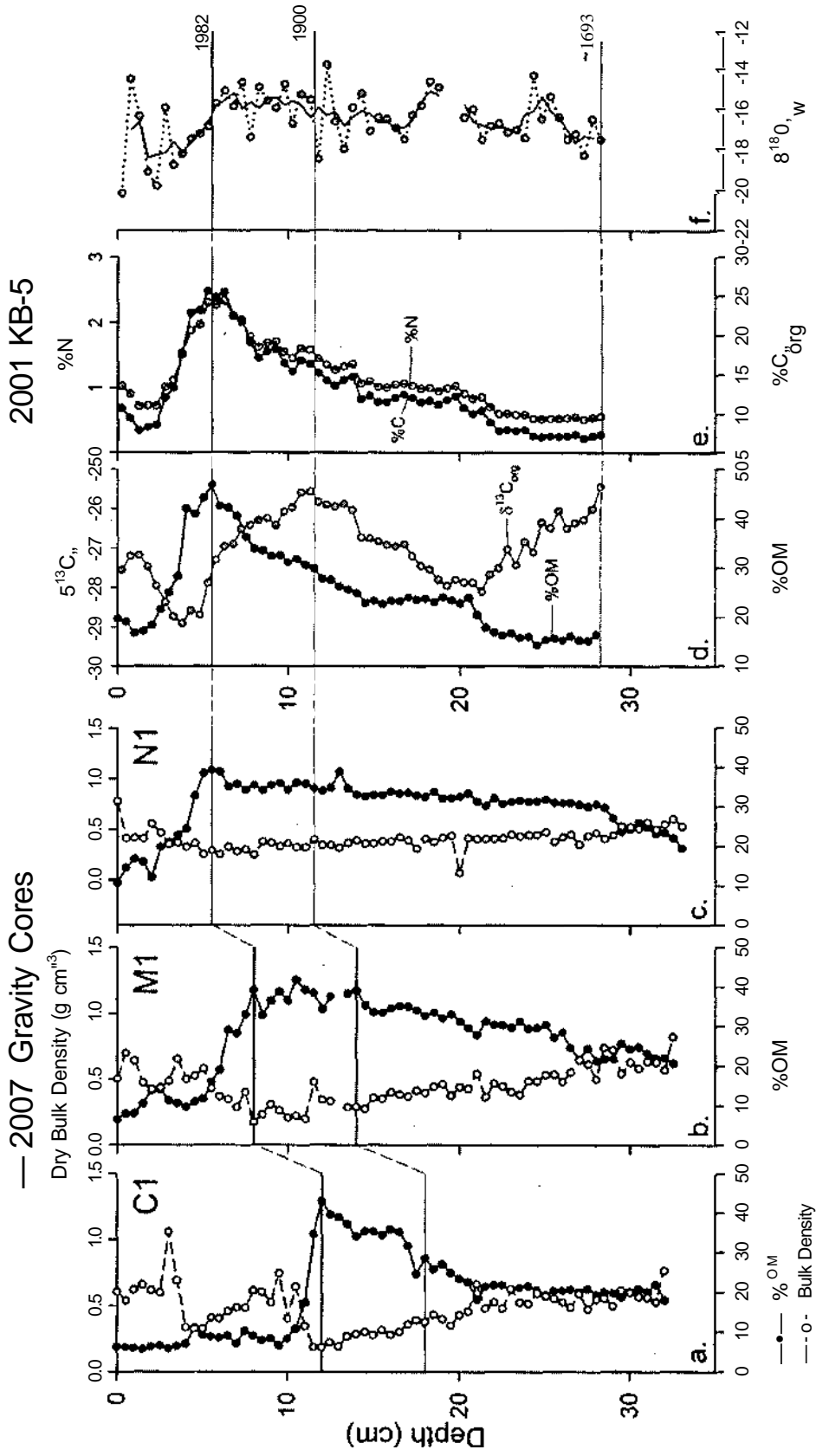


Figure 9: PAD 31 geochemical stratigraphy from cores collected in 2007 (cores C1, M1 and N1) and 2001 (core KB-5) [Wolfe et al., 2008b]. The 1982 stratigraphic horizon identifies the Embarras Breakthrough event. The onset of the LIA (~1900) and the basal date of the KB-5 core (~1693) are also identified.

3.5 PAD 31 three-phase paleohydrological record over the past -400 years

Geochemical stratigraphy from sediment cores collected from PAD 31 provides a three-phase paleohydrological record spanning the last -400 years. Low but increasing organic content, elevated but declining $\delta^{13}\text{C}_{\text{org}}$ values reflect a period during the LIA where PAD 31 likely received water inputs from Lake Athabasca. Lake Athabasca is estimated to have been 2 metres higher during the LIA, which would have inundated PAD 31 [Johnston et al., in press]. Declining $\delta^{13}\text{C}_{\text{org}}$ values that characterize the LIA result from the enhanced supply of ^{13}C -enriched DIC during embayment by Lake Athabasca compared to the reutilization of ^{13}C -depleted respired organic carbon that occurs during closed-drainage conditions. Declines in Lake Athabasca water levels and increasing primary productivity led to enrichment in the CDIC pool nearing the end of the LIA, resulting in increasing $\delta^{13}\text{C}_{\text{org}}$ values. Maximum $\delta^{13}\text{C}_{\text{org}}$ values occur at -1700, consistent with a period of maximum discharge from the Rocky Mountain glacial headwaters and the highest Lake Athabasca water levels. Low $\delta^{18}\text{O}_{\text{w}}$ values that are evident during the LIA (Figure 9 f) likely result from the enhanced supply of ^{18}O -depleted water from glacial melt water, which was responsible for elevating Lake Athabasca water levels [Wolfe et al., 2008a; Sinnatamby et al., 2010; Johnston et al., 2010]. Elevated $\delta^{13}\text{C}_{\text{org}}$ and low $\delta^{18}\text{O}_{\text{w}}$ values in PAD 1 also support the period of maximum discharge and water level rise at -1700.

Increases in %OM, C_{org} , N and $\delta^{18}\text{O}_{\text{w}}$ from 1900 to 1982 indicate a shift towards closed-drainage conditions and a decline in the influence of river and Lake Athabasca water at PAD 31. Enhanced production of organic matter and preservation under closed-drainage conditions persisted through this period. A shift towards lower organic content

and $\delta^{18}\text{O}_{\text{w}}$ values occurs after the Embarras Breakthrough event (1982) that redirected a substantial volume of water from the Embarras River to Mamawi Creek, which borders this basin to the east [Wolfe et al., 2008b]. Following this event, PAD 31 became increasingly susceptible to river water inundation during the spring thaw, ice jam events and periods of high discharge down the Athabasca and Embarras rivers. Subsequent increases in the inputs of inorganic sediment (clays, silts, sands) that accompany flood events diluted the organic content of the uppermost layers of the profile reflected by the low organic content.

These stratigraphic intervals identified in the geochemical stratigraphy from PAD 31 sediment cores span a hydrological history over the past 400 years. Restricted-drainage conditions occurred in the early part of the record (1700 - 1900) during an embayment by Lake Athabasca, then transitioned to closed-drainage conditions in response to declining Lake Athabasca water levels (from -1900 - 1982). An abrupt return to restricted-drainage conditions occurred in 1982 in response to an upstream geomorphic processes that increased the flood frequency at this site.

3.6 Controls on organic matter deposition at PAD 1 and PAD 31 over the past 600 years

Organic matter deposition is controlled by a variety of hydrological and limnological processes. Lake sediment records from PAD 1 and PAD 31 highlight the complex interplay of these process that contribute to the information preserved in lake sediment organic matter, particularly the $\delta^{13}\text{C}_{\text{org}}$ composition. Numerous hydrological and limnological processes control the $\delta^{13}\text{C}$ of ambient DIC, which in turn determines the $\delta^{13}\text{C}$ of lake sediments organic matter. Variations in the $\delta^{13}\text{C}_{\text{org}}$ occur as a result shifts in

the dominance of the various processes that control the $\delta^{13}\text{C}$ of the ambient DIC. The processes that control the $\delta^{13}\text{C}$ of DIC include isotopic exchange with atmospheric CO_2 , ^{13}C -enrichment from catchment runoff weathering of carbonate rocks, ^{13}C -enrichment from the preferential uptake of ^{12}C during photosynthesis, and respiration and recycling of organic matter in the water column and lake bottom sediments. Typically, variations in lake sediment $\delta^{13}\text{C}_{\text{org}}$ values are assumed to be primarily regulated by ^{13}C -enrichment from aquatic productivity [Schelske and Hodell, 1995; Meyers, 1997; Meyers and Teranes, 2001]. However, variations caused by recycling of ^{13}C -depleted organic matter and the weathering of ^{13}C -enriched carbonate rocks are considered less frequently but are equally important as controlling processes [Wolfe et al., 1999; Buhay et al., 2009]. The $\delta^{13}\text{C}$ records from PAD 1 and PAD 31 indicate that several of these processes appear to be at play, and the relative influence of these processes is determined largely by varying hydrological exchange with Lake Athabasca.

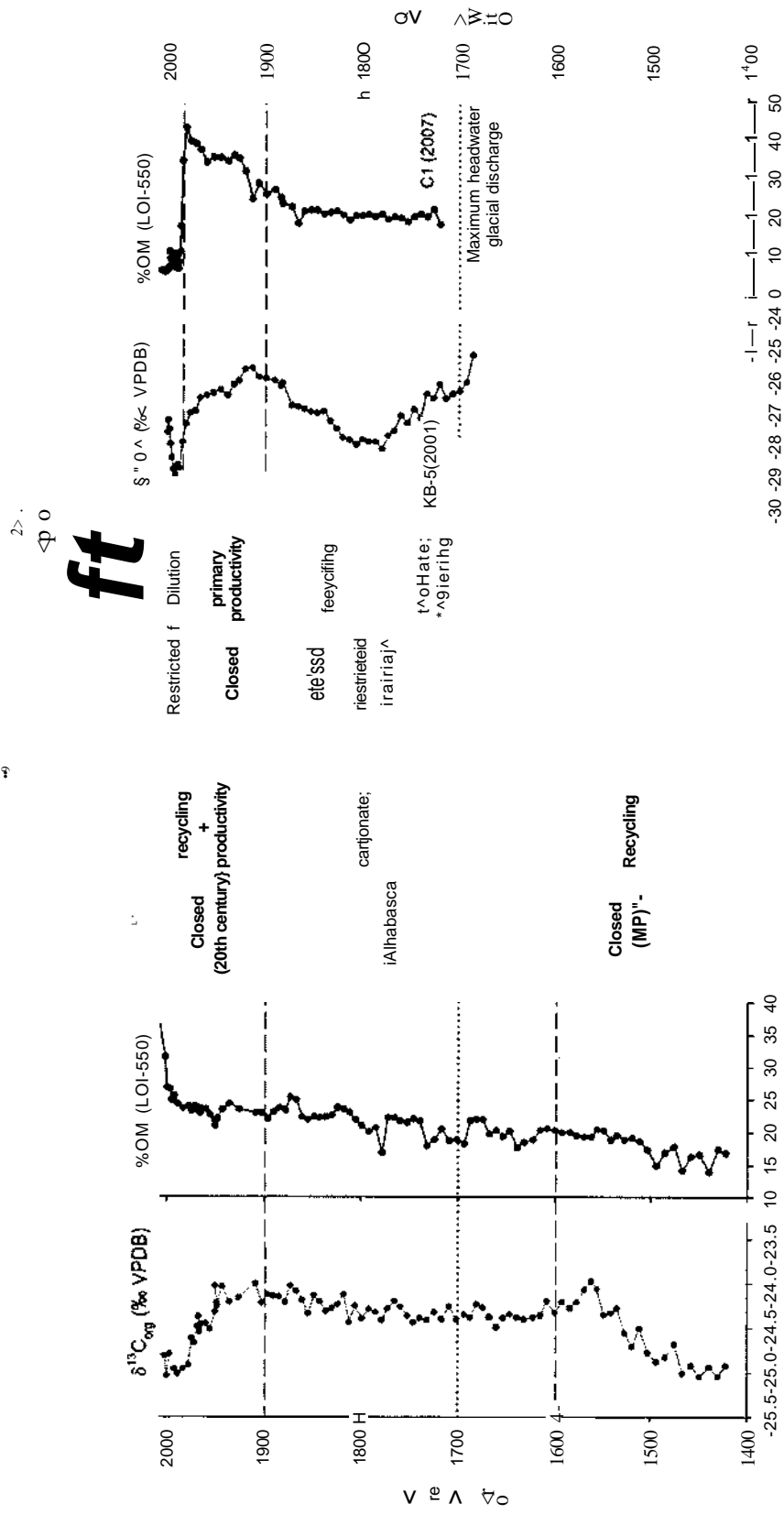
Systematic variations in $\delta^{13}\text{C}_{\text{org}}$ values in the PAD 1 sediment record (Figure 10) reflect the dominance of two processes that occur during and define the Medieval Period, LIA and 20th century hydrological intervals. Low $\delta^{13}\text{C}_{\text{org}}$ indicate enhanced respiration and recycling of organic matter under closed-drainage conditions during the Medieval Period. Similar declines in $\delta^{13}\text{C}_{\text{org}}$ values in contemporary closed-drainage conditions during the late 20th century reflect enhanced recycling and re-utilization of ^{13}C -depleted organic matter. This interpretation is consistent with contemporary $\delta^{13}\text{C}_{\text{DIC}}$ seasonal depletion in closed-drainage basins (Figure 8). Increases in $\delta^{13}\text{C}_{\text{org}}$ values reflect the

input of a ^{13}C -enriched source of DIC under open drainage conditions during the LIA (possibly derived from carbonate weathering).

Variations in the $\delta^{13}\text{C}_{\text{org}}$ record from PAD 31 also reflect the various processes and factors controlling the $\delta^{13}\text{C}$ in organic lake sediments. Increases in $\delta^{13}\text{C}_{\text{org}}$ reflect two processes. The first process is enhanced input of a ^{13}C -enriched source of DIC (-1700) resulting from open-drainage conditions and increased connectivity to Lake Athabasca during the LIA highstand. The second process is increasing $\delta^{13}\text{C}_{\text{org}}$ values due to productivity driven ^{13}C -enrichment from closed-drainage conditions in the 19th and 20th centuries. Declines in the $\delta^{13}\text{C}_{\text{org}}$ values result from the interplay of two processes. Respiration and recycling of organic matter in the water column and lake bottom sediments during closed-drainage conditions (-1800). Recent dilution/flushing of the source DIC as a result of increased flooding frequency and restricted-drainage conditions. The latter processes is further supported by a rapid increase in the $\delta^{13}\text{C}_{\text{org}}$ profile following the 1984 Embarras Breakthrough, indicating enhanced input of ^{13}C -enriched DIC during overland flooding events.

A variety of hydrological and limnological processes control organic matter deposition at PAD 1 and PAD 31. These processes are largely determined by the hydrological status (open, closed and restricted-drainage) of the basins. The $\delta^{13}\text{C}$ values of organic lake sediments from small, perched basins in the PAD reflects the interplay of three major processes: (1) shifts in hydrological connection with Lake Athabasca during the LIA highstand (open-drainage conditions), (2) enhanced respiration and recycling of organic matter under closed-drainage conditions and (3) productivity driven ^{13}C -enrichment and

greater organic matter preservation. The hydrological status of each of these basins control the organic matter stored in these basins. Consequently, the hydrological status may influence the quantity, quality and lability of stored organic matter. This relationship has implications for the potential CO₂ production from organic lake sediments and surrounding paludal deposits under future changing hydroecological regimes, as explored in Chapter 4.



PAD 1

PAD 31

Figure 10: Key stratigraphic units for PAD 1 and PAD 31 identified using organic matter (%OM) and $\delta^{13}C_{org}$ values over the past 600 and 350 years, respectively.

Chapter 4. Potential CO₂ fluxes from the Peace - Athabasca Delta

4.1 Introduction

Northern boreal wetlands, like those found in the PAD, are increasingly threatened by climate variability and increased human development [Schindler and Donnahue, 2006; Schindler, 2001]. These wetlands are responsible for sequestering and storing carbon in accumulating peat and lacustrine sediment organic matter, owed to persistently wet conditions. The response of organic carbon in peat and lacustrine sediment to changing moisture and temperature conditions in the boreal biome is largely unknown [Bridgham et al., 2008]. This is particularly true for the PAD, which is one of Canada's largest inland freshwater wetlands. A directional change in the discharge supplying the PAD with water is contributing to a decline in the abundance of water [Rood et al, 2005; Wolfe et al., 2008a]. Such a decline in water availability combined with temperature increases in northern boreal ecosystems may lead to directional changes in carbon fluxes.

Changes in the hydrology of wetlands in the PAD can lead to positive feedbacks of CO₂ to the atmosphere. These feedback processes result from the enhanced breakdown of stored organic material during changing moisture conditions. Organic soils and sediments in other northern wetlands are known to be sensitive to changes in hydrology that influence trace gas fluxes to the atmosphere. Directional change towards lower water levels and persistently oxic (aerated) conditions can expose previously protected organic lake sediment and peat soils to accelerated organic matter breakdown, and CO₂ emissions. The frequency of drying events that occur in wetland soils is an important element to consider when evaluating the potential contributions of trace gases to the atmosphere.

Wetlands are described and classified fundamentally according to their hydrology. Some wetlands receive significant inputs of surface/ground waters while others receive water (and consequently nutrients) from exclusively atmospheric (precipitation) sources. These differences are apparent in the PAD, where basins have been shown to differ significantly in their water balance [Wolfe et al., 2007b], as discussed previously. Differences in water supply may be responsible for large differences in nutrient availability, soil chemistry, carbon quality and sustainability and trace gas fluxes [e.g., Bridgham et al., 2008]. The latter of these components is important to consider in the PAD, where perched basins and wetlands experience a strong heterogeneity in the relative contribution of components comprising their water balances. The CO₂ flux from organic substrates in these basins are likely to respond differently as a result of the differences in hydrological connectivity and history.

CO₂ efflux from wetland soils and lake sediments to the atmosphere is a function of autotrophic and heterotrophic respiration. Autotrophic respiration is regulated by photosynthesis, temperature, water and nutrient availability [Chapman and Thurlow, 1998]. Heterotrophic respiration is dependent on a variety of controls including soil temperature, oxic (redox) boundaries defined by water table levels, plant community structures and the quality and quantity of decomposable material forming the peat or lake sediment [Bubier et al., 1993; Bubier, 1995; Yavitt et al., 1997; Chapman and Thurlow, 1998]. Near-surface peat layers (acrotelm) initially experience aerobic decomposition that leads to the release of CO₂, but eventually becomes incorporated into the saturated layer of the peat and covered by the water table over time as the peat accumulates [Clymo et al., 1998]. Decomposition proceeds slowly in the water-saturated part of the peat

(catotelm) where the majority of mineralized carbon is released as methane (CH₄).

Exports of carbon from wetlands also occur in dissolved forms (dissolved organic carbon [DOC]) and serves as an important component of the carbon balance [Molot and Dillon, 1996]. DOC exports largely depend on hydrologic throughflow rates and net primary production [Vasander and Kettunen, 2006].

Conventional approaches used to quantify, or estimate, decomposition rates in wetland soils and lake sediments typically rely on either in-situ experimental designs (e.g., closed/open chambers or litter bag placements) or laboratory in-vitro simulations (such as mesocosm or flask incubations). Either of these approaches focuses on quantifying litter mass losses and decay end members (such as CO₂ and CH₄) during respiration and oxidation of organic material. However, environmental effects on the carbon balance are difficult to isolate in field investigations, emphasizing the practicality of utilizing in-vitro incubations of peat soils and lake sediments to estimate respiration and oxidation rates. Despite controlled laboratory environmental conditions, this technique produces variable results when attempting to isolate the effects of changing moisture, temperature and nutrient regimes on potential CO₂ and CH₄ production. One of the shortcomings of this approach has been incorporating the effects that hydrological history has on the potential contribution of CO₂ to the atmosphere [Updegraff et al., 1998]. Furthermore, variable hydroecological conditions are often not considered when attempting to explain the variable results produced by in-vitro experiments.

Carbon storage and turnover rates in peat and lake sediments have been determined in aerobic and anaerobic flask and mesocosm incubation experiments with moisture and temperature manipulations [Hogg et al., 1992; Moore and Dalva, 1997a; Petrone et al.,

2005]. The magnitude and direction of carbon fluxes (as CO₂) have been found to be controlled largely by temperature, volumetric moisture content, availability of oxygen (anaerobism) for aerobic respiration and oxidation of organic material, and the chemical 'quality' of the substrate [Hogg et al., 1992; Bridgham et al., 2006].

Shifts in the climate or land use that alters wetland hydrology, exposing normally flooded peat and sediment to aerobic conditions, provides the potential for the rapid breakdown of organic matter and acceleration of gas-phase carbon fluxes to the atmosphere [Hogg et al., 1992; van Seters and Price, 2001]. Silvola et al. [1996] demonstrated that lowering water tables in boreal wetlands by 1 cm at moderate temperatures (12°C) and in some cases, caused a ~100% increase in CO₂ flux. Further, undisturbed peat samples have been shown to exhibit depth-dependent declines in CO₂ production [Asada et al., 2005], indicating that high substrate quality (availability for microbial consumption and oxidation) is important [Waddington et al., 2001].

Respiration, oxidation and carbon mineralization potentials of organic soils and lacustrine deposits have been determined using aerobic and anaerobic flask incubation experiments [Yavitt et al., 1997; Kettunen et al., 1999]. Simulations of potential carbon exchange often consider the effects of moisture, temperature, aerobic status and nutrient conditions of organic soils (eg. [Waddington et al., 2001; Blodau and Moore, 2003]) and lacustrine deposits while few consider the effects of antecedent conditions (eg Updegraff et al., 1998) or the environmental history of the substrates. Thus, laboratory simulations generally lack the incorporation of hydrological history and the relative influences of moisture, temperature and hydrological history on the potential production of CO₂ from

organic soils, which will be critical to our understanding of the C accumulation rates and the long term sustainability of the carbon stock of a site.

Q₁₀ values serve as an estimate of the temperature dependence of respiration in any substrate, while ignoring other factors that influence microbially-mediated soil respiration [Ise and Moorcroft, 2006]. Higher Q₁₀ values suggest greater sensitivity of soil and sediment organic matter decomposition to temperature increases. Globally, organic matter decomposition sensitivity is Q₁₀ = 1.37 [Ise and Moorcroft, 2006], while other respiration studies provide much greater estimates of soil organic matter temperature sensitivities (mean Q₁₀ = 2.5) [Raich and Schlesinger, 1992]. However, the incorporation of Q₁₀ analysis with quantification of accumulation histories may provide a clearer understanding of how oxidation potential varies within the profile and how stable the entire carbon profile may be in response to any environmental perturbation.

The main objective of this laboratory incubation study was to combine the paleohydrological information available in lake sediment records (Chapter 3) with contemporary in-vitro laboratory measurements of CO₂ production. Distinct hydrological intervals have been identified at both PAD 1 and PAD 31. These hydrological intervals are defined by shifts in hydrological connectivity to the greater drainage network. PAD 1 has been embayed by Lake Athabasca during the Little Ice Age highstand, but has since become increasingly closed-drainage. PAD 31 has also experienced a shift from closed-drainage to restricted-drainage following the onset of increased flooding frequency due to the Embarras Breakthrough event in 1982. It is hypothesized that CO₂ production potentials from organic material from these identified hydrological intervals is related to the conditions under which it was formed and preserved.

4.2 Peat and lake sediment physical and chemical analysis results

Physical and chemical properties of peat and lake sediment from PAD 1

Lake sediment and peat physical and chemical properties were characterized using percent organic matter (%OM), dry Bulk Density (BD), von-Post humification index, elemental and isotopic composition of organic carbon (%C_{org}, $\delta^{13}\text{C}_{\text{org}}$) and nitrogen (%N, $\delta^{15}\text{N}$) on core subsections. Peat BD and %OM of seven cores (CP1 through CP7) from PAD 1 (Figure 11) are variable and range from 0.07 g cm⁻³ - 1.20 g cm⁻³ and 6.65 - 92.32 %OM, respectively. BD increases with depth in all cores except CP1 and CP2, where bulk density declines. %OM declines in peat cores CP2, CP3, CP4 and CP5, while %OM increases with depths in cores CP1, CP6 and CP7. At several stratigraphic horizons, low BD is associated with high %OM (e.g., peat core CP5 has high %OM values from 72 cm to 62 cm, 52 to 50 cm, 44 cm to 14 cm, and 10 cm to the surface which occur in the same depth intervals as lower BD values), except in cores CP2 and CP7.

Physical properties (%OM and BD) of PAD 1 lake sediment cores CI, MI, and NI are shown in Figure 12. %OM in core CI varies from 15% to 37% throughout the core profile. Lowest %OM values (15%) increase to 25% from the bottom of the core steadily to 4 cm. A sharp increase in %OM occurs from a depth of 4 cm to the top of the core to a value of 37%. BD values range from 0.12 g cm⁻³ to 0.69 g cm⁻³ and follow a trend inverse to %OM. Highest BD values (0.69 g cm⁻³) occur at the bottom of the core and then decline slightly to 0.37 g cm⁻³ up to 4 cm. BD declines sharply to 0.12 g cm⁻³ at the top of the core. Core MI %OM values increase from 20% to 24% from the bottom of the core to the top. BD narrowly varies between 0.24 g cm⁻³ to 0.53 g cm⁻³, declining

to minimum values at the top of the core. The near shore sediment core, NI, has higher %OM values than CI and MI sediment cores and varies from 28% to 33%. %OM values are most variable from the bottom of the core to 20 cm, above which values steadily increase to 33% at the top of the core. BD in core NI ranges from 0.15 g cm⁻³ to 0.5 g cm⁻³, declining from the bottom of the core to minimum values at the top of the core.

Age-depth relationships for cores CI, MI and NI were based on the chronology established for sediment core C10 from PAD 1 using radiometric methods (see Loss-On-Ignition and radiometric (²¹⁰Pb, ¹³⁷Cs) analyses, page 21). Systematic changes in physical properties (%OM, BD) observed in core C10 (refer to Loss-On-Ignition and radiometric (²¹⁰Pb, ¹³⁷Cs) analyses, page 21 for description) are absent of striking stratigraphic changes that can be used to correlate sediment cores CI, MI and NI from PAD 1 (Figure 12). Thus, constant sedimentation rates are assumed for cross-core age-depth correlations. The profiles from cores MI and NI spans -232 years, with sediment core basal dates of -1775 and are shown in Figure 12. These extrapolated age-depth relationships in cores CI, MI and NI are used to identify material deposited during the major hydrological intervals over the past -600 years. The selection of intervals to incubate was done prior to the establishment of the PAD 1 sediment core chronology, consequently no sections representative of the MP were selected.

PAD 1 Peat Cores

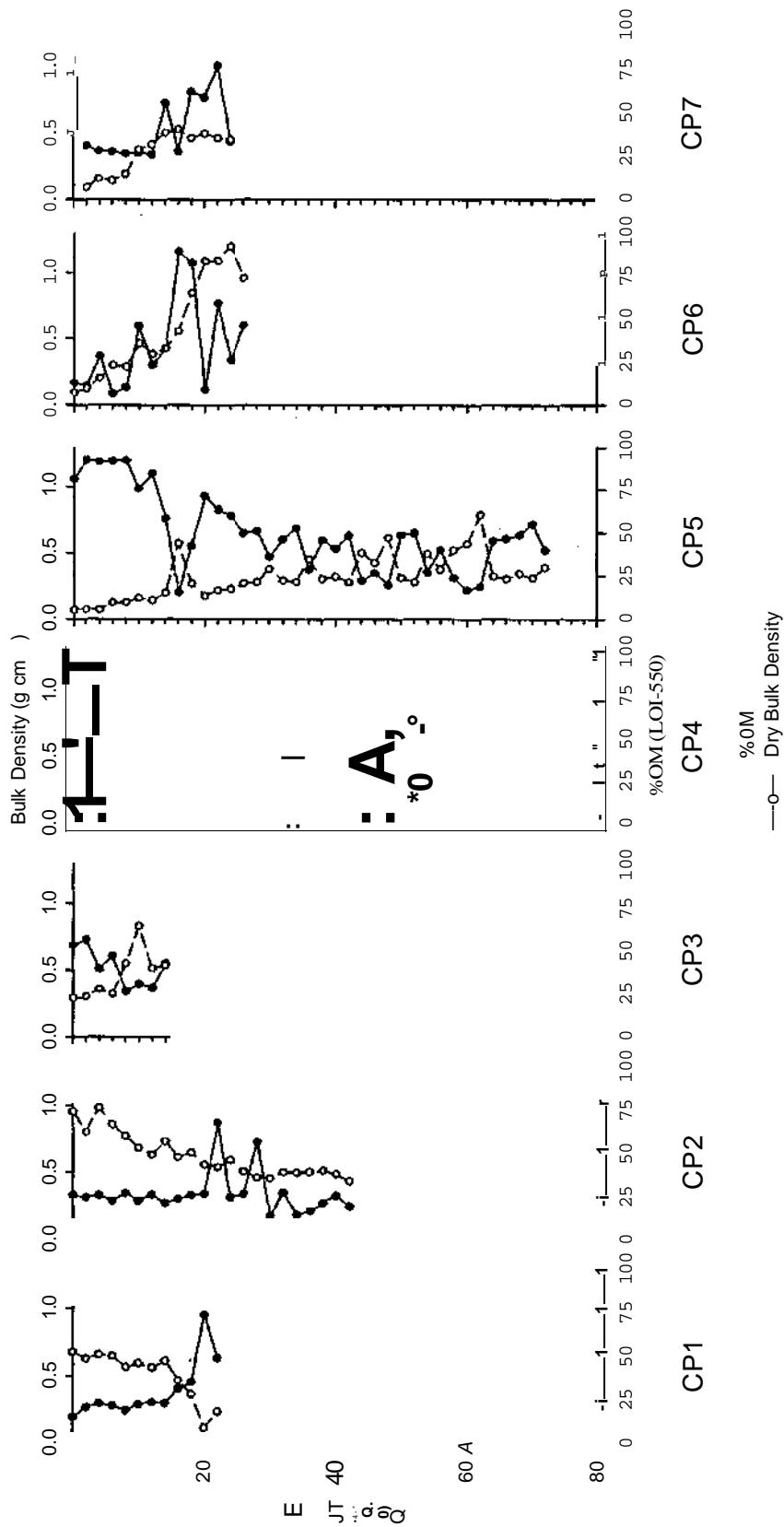
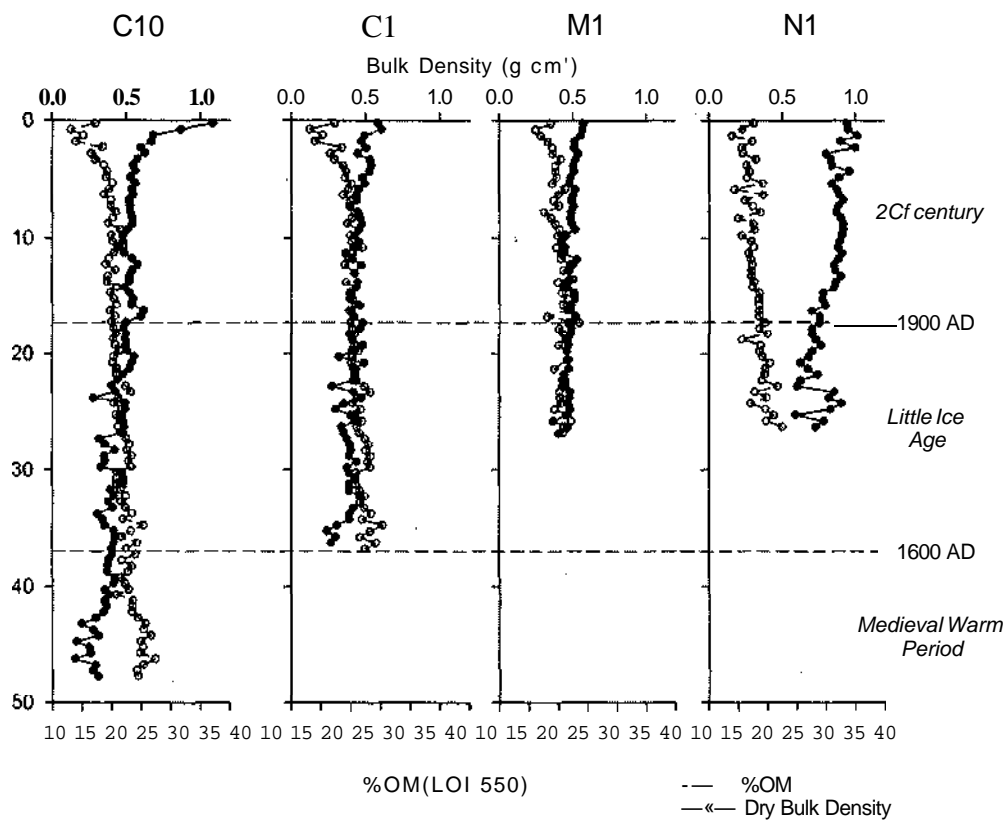


Figure 11: Organic content (%OM) and dry bulk density (BD in g-cm⁻³) of peat cores collected from PAD 1 in summer, 2007. Cores span distance and vegetation gradients including willow fringe furthest from the shoreline (CP3,CP4 and CP5), intermediate grass areas (CP1 and CP7) and nearest to the shore cattail zones (CP2 and CP6). See Figure 4 for peat core sampling locations.

PAD 1 Sediment Cores



12: Sediment organic content (%OM) and dry bulk density (BD, in g-cm⁻³) of PAD 1 sediment cores collected along the central (C10, C1), mid (M1) and near-shore (N1) sites in the summer, 2007, used for the incubation treatments and for paleohydrological reconstructions. Time intervals spanning the 20th century, LIA and MP are also shown by dashed lines based on the chronology established for sediment core C10.

Physical and chemical properties of peat and lake sediment from PAD 31

Dry BD and %OM from PAD 31 peat cores are shown in Figure 13. %OM is variable in all peat cores, and ranges from a minimum of 5.89% to a maximum 75.19%. BD also varies considerably in all cores, and ranges from 0.10 g cm³ to 1.13 g cm³. Variable but distinct increases in %OM occur in all cores from the base of the cores to peaks at depths of 10 cm (CP1), 24 cm (CP3), 22 cm (CP4), 20 cm (CP5), 16 cm (CP6), and 10 cm (CP7). From these %OM peaks, sharp declines to values of ~5% occur to the top of all the cores. BD is also variable, and follows a similar but inverse pattern to the %OM profiles. Declines in BD to the depths indicated previously are followed by variable, but distinct increases to values ~0.5 g cm³. This distinct stratigraphic change in %OM and BD likely indicates the Embarras Breakthrough event.

Physical and organic matter properties from central (CI), mid-basin (M1) and near-shore (N1) have been previously shown (Figure 9) and were described in section 3.4, and are redisplayed in Figure 14. Organic matter (% dry mass) in all cores range from ~20% to ~40%, with shoreline proximal cores (M1, N1) having slightly higher organic matter content. From the bottom of core CI, %OM increases and dry bulk density decreases to values of ~40% and ~0.3 g cm³, respectively, to a depth 12 cm. Sharp declines in %OM and increases in BD occur from 12 cm to 10 cm to values of ~10% and ~0.5 g cm³, respectively. Core M1 follows a similar pattern, with the major declines in %OM and increase in BD occurring at 8 cm depth. Core N1 has elevated but constant %OM values (~30%) that increase gradually to ~40% until approximately 6 cm depth. Sharp declines in %OM and BD to ~10% and ~0.5 g cm³, respectively, occur from 6 cm to the top of the core. This stratigraphic shift in %OM and BD is consistent with the increased sediment

input during increasing frequency of flooding events following the Embarras
Breakthrough.

PAD 31 Peat Cores

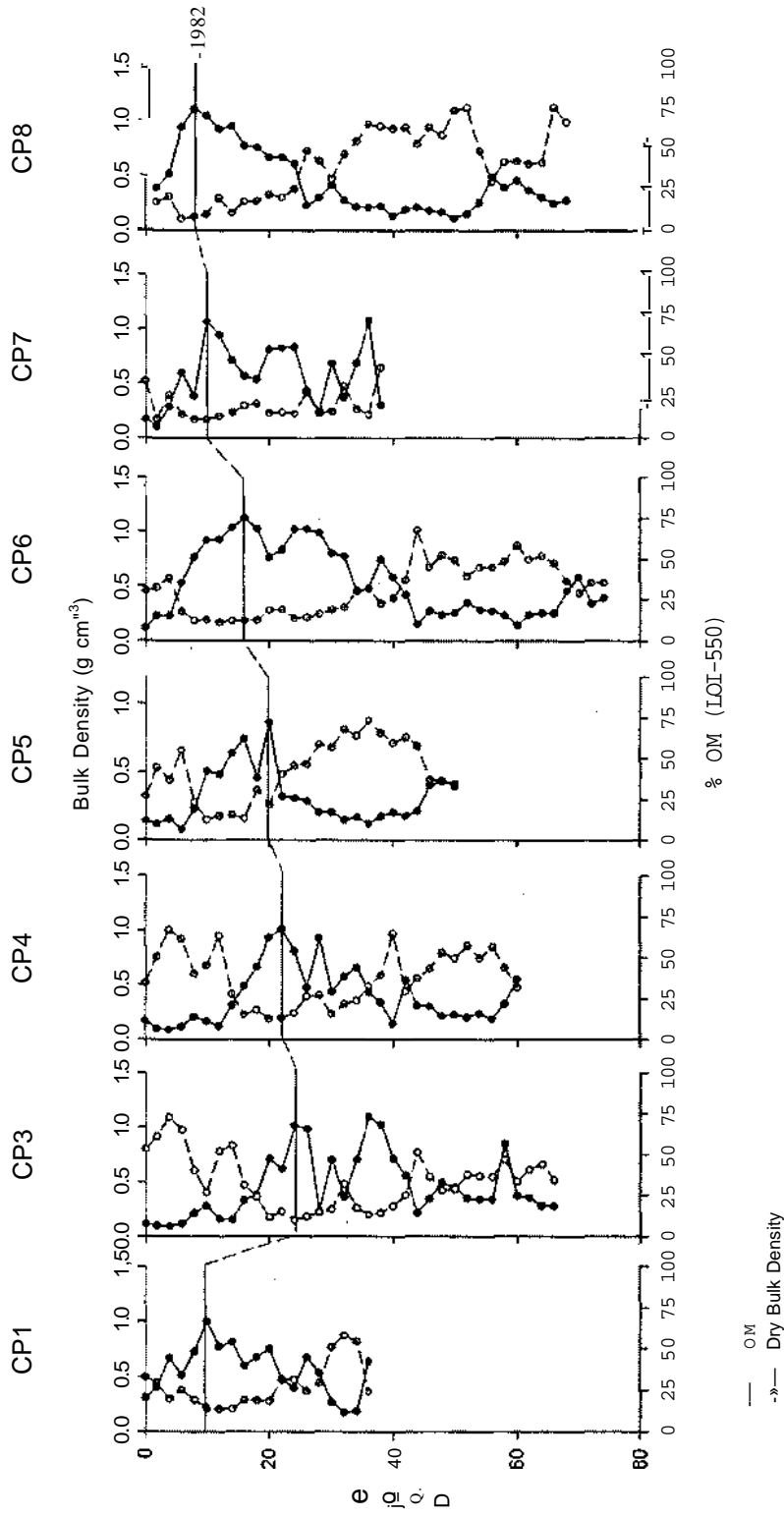


Figure 13: Organic matter and dry bulk density of peat cores taken from PAD 31 in the summer of 2007. Location of the cores spans a distance and vegetation gradient towards the current shoreline, including willow fringe (CP8 and CP5), intermediate grass (CP3, CP4 and CP7) and cattail (CP1 and CP6). Lines indicate when %OM begins to decline, indicating the beginning of the onset of increased river influence and flood frequency after an upstream geomorphic event in 1982 (Embarras Breakthrough).

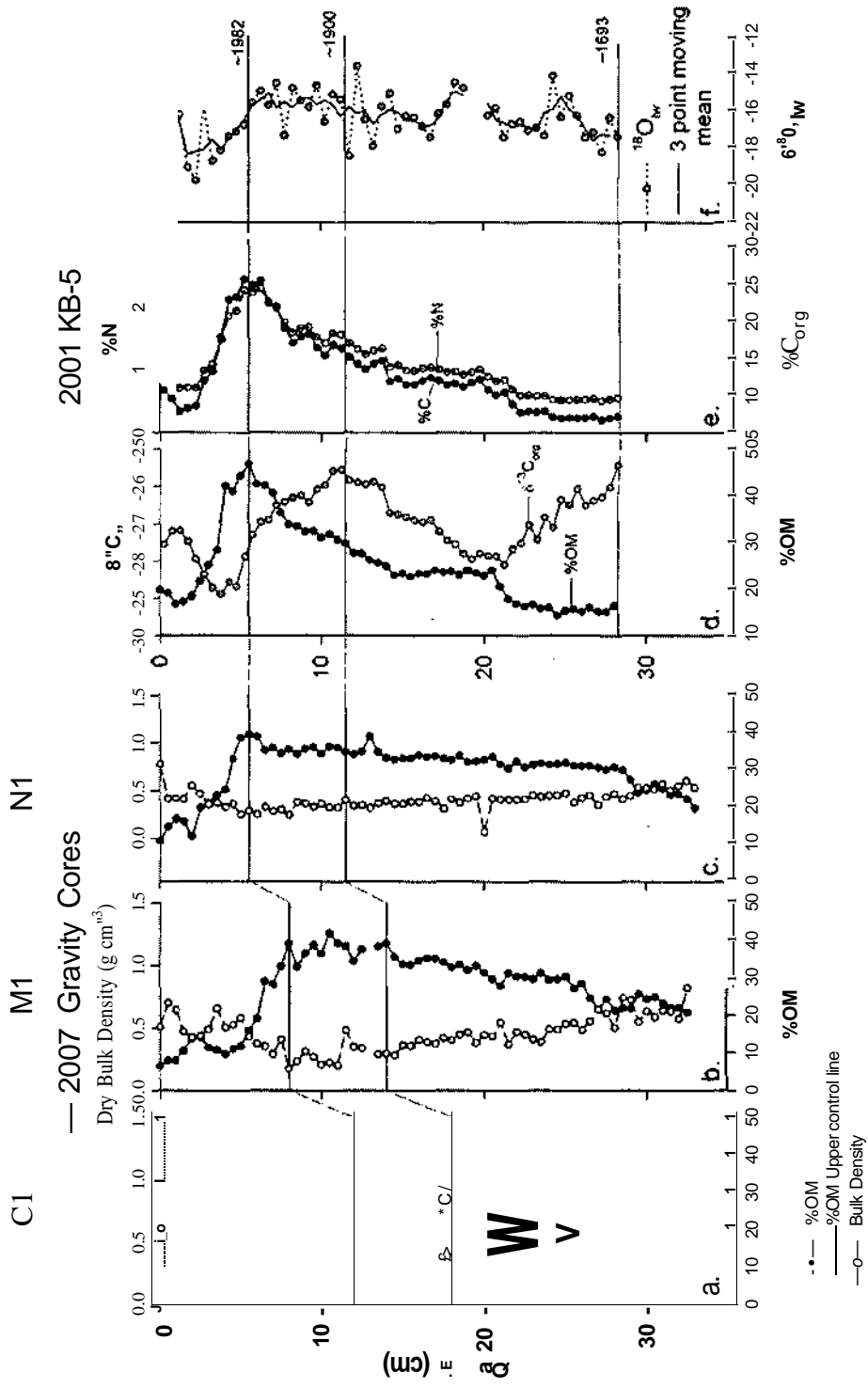


Figure 14: Organic matter and dry bulk density from sediment cores collected in the summer, 2007 from PAD 31 spanning a pond-depth gradient from the centre (C1) to the mid-basin (M1) and near-shore (N1) areas. Organic content, elemental C, N and cellulose inferred $\delta^{18}\text{O}_{\text{iw}}$ composition is also shown from a sediment core obtained in 2001. Horizontal lines indicate the base of core C1O, the end of the LIA and the 1982 Embarras Breakthrough.

Table 1: PAD 1 peat and sediment core depths, categories and hydro-intervals of selected sections used for incubation treatments.

PAD1 Core Name	<u>Incubated Depth (cm)</u>	Depth Category	Hydro Interval
Peat			
CP1	0	near-surface	Recent
	10	near-surface	Recent
	20	<u>mid-depth</u>	LIA
CP2	4	near-surface	Recent
	20	mid-depth	LIA
	40	<u>deep</u>	LIA
CP3	4	near-surface	Recent
	14	near-surface	LIA
	4	near-surface	Recent
CP4	12	near-surface	LIA
	26	mid-depth	LIA
	52	deep	MP
	70	<u>deep</u>	MP
	70	<u>deep</u>	MP
CP6	0	near-surface	Recent
	8	near-surface	Recent
CP7	4	near-surface	Recent
	10	near-surface	Recent
	28	mid-depth	LIA
Sediment			
CI	5	near-surface	Recent
	15	mid-depth	LIA
	25	deep	LIA
M1	5	near-surface	Recent
	15	mid-depth	LIA
	25	deep	LIA
N1	5	near-surface	Recent
	15	mid-depth	LIA
	25	deep	LIA

Table 2: Selected depth intervals, categories and hydro-intervals of PAD 31 peat and lake sediment selected for laboratory incubation treatments.

PAD 31			
Core	Depth (cm)	Depth Category (cm)	Hydro Interval
Peat			
CP1	2	near-surface	Post-1982
	12	near-surface	Closed
	20	mid-depth	LIA
	38	deep	LIA
CP3	0	near-surface	Post-1982
	18	mid-depth	Closed
	24	mid-depth	LIA
	48	deep	LIA
	60	deep	LIA
	68	deep	LIA
CP4	10	near-surface	Post-1982
	26	mid-depth	Closed
	36	deep	LIA
	54	deep	LIA
	62	deep	LIA
CP5	8	near-surface	Post-1982
	22	mid-depth	Closed
	38	deep	LIA
	52	deep	LIA
CP6	6	near-surface	Post-1982
	20	mid-depth	Closed
	22	mid-depth	Closed
	38	deep	LIA
	52	deep	LIA
	72	deep	LIA
CP7	4	near-surface	Post-1982
	16	mid-depth	Closed
	26	mid-depth	LIA
	38	deep	LIA
CP8	6	near-surface	Post-1982
	10	near-surface	Post-1982
	42	deep	Closed
	58	deep	Closed

Table 2 continued...

„	Depth (cm)	Depth Category (cm)	Hydro Interval
Sediment	3	near-surface	Post-1982
	5	near-surface	Post-1982
	15	mid-depth	Closed
	30	deep	LIA
	3	near-surface	Post-1982
	5	near-surface	Post-1982
	15	mid-depth	Closed
	30	deep	LIA
	3	near-surface	Post-1982
	5	near-surface	Closed
	15	mid-depth	Closed
	30	deep	LIA

Lake sediment and peat soil characteristics and substrate quality

Lake sediment and peat soil physical and chemical properties from PAD 1 show distinct differences and are listed in Table 3. Peat soils from PAD 1 (Table 3 a) have high organic content in near surface and mid-depth intervals. C/N ratios <15 occur in all depth intervals with the maximum in mid-depths at a value of 14.69. PAD 1 sediment substrates (Table 3 a) have lower organic content, indicated by lower %C_{org} ranging between 12.31 and 14.50 from deep to near-surface depth intervals. %C_{org} declines with depth in the sediments while C/N ratios increase from 9.67 to 10.22 in near-surface to deep intervals, respectively.

PAD 31 peat soils (Table 3 b) are generally less organic than PAD 1 and are variable with depth. Highest %C and %N are found at mid-depths, while the highest C/N ratios are in near-surface intervals. Sediment substrates (Table 3 b) obtained from PAD 31 also

shows similar variability of physical and chemical properties with depth. The highest %C and %N values are found in mid-depths concomitant with the lowest C/N value.

PAD 31 has generally higher C/N values compared to PAD 1, consistent with generally lower %N values.

Table 3: Mean elemental and isotopic carbon and nitrogen composition, and physical properties (mean %OM, B.D.) of peat and sediment depth intervals obtained from a. PAD 1 and b. PAD 31.

a. PAD 1

Depth	% C _{org}	% N	C/N	$\delta^{13}C_r$ (‰)	$\delta^{15}N$ (‰)	% OM	B.D	N
Peat								
Near-surface (0-15 cm)	19.23	1.41	13.45	-26.99	0.22	44.77	0.42	11
Mid (15-30 cm)	24.06	1.58	14.69	-27.37	0.41	31.76	0.51	4
Deep (30-bottom cm)	15.47	1.11	13.58	-27.46	0.23	36.79	0.42	3
Sediment								
Near-surface (0-15cm)	14.50	1.50	9.67	-24.72	0.26	27.59	0.30	3
Mid(15-30cm)	13.35	1.33	10.09	-24.25	0.32	25.39	0.37	3
Deep (30 cm-bottom)	12.31	1.20	10.22	-24.14	0.37	23.86	0.40	3

b. PAD 31

Depth	% C _{org}	% N	C/N	$\delta^{13}C_{v-org}$ (‰)	$\delta^{15}N$	% OM	B.D.	N
Peat								
Near-surface (0-15 cm)	15.41	0.93	16.54	-28.61	0.23	23.56	0.51	8
Mid (15-30 cm)	18.66	1.21	15.57	-28.42	-0.35	42.60	0.35	9
Deep (30 cm-bottom)	12.47	0.88	14.32	-28.15	-0.15	33.01	0.50	15
Sediment								
Near-surface (0-15cm)	6.53	0.57	12.08	-26.85	0.53	17.58	0.47	6
Mid(15-30cm)	17.65	1.61	10.95	-26.88	-0.33	35.19	0.33	3
Deep (30 cm-bottom)	10.52	0.90	11.74	-27.07	-0.42	24.31	0.55	3

4.3 Peat and lake sediment laboratory incubation results

Grouped, mean depth-integrated CO₂ fluxes

Grouped mean depth-integrated CO₂ production potentials from peat and lake sediment substrates are shown in Figure 15. Highest CO₂ fluxes occur from PAD 1 peat under cool, saturated conditions ($1.084 \pm 0.693 \text{ mg CC}^{\wedge}\text{-g}^{\wedge}\text{-day}^{\wedge 1}$). Maximum sediment CO₂ production occurs under the same conditions at a value of $0.625 \pm 0.569 \text{ mg CCVg}^{\wedge} \bullet \text{day}^{\wedge 1}$. PAD 1 CO₂ production during dry conditions is the least, and ranges from $0.000 \pm 0.003 \text{ mg CO}_2\text{-g}^{\wedge}\text{-day}^{\wedge 1}$ to $0.009 \pm 0.003 \text{ mg CO}_2\text{-g}^{\wedge}\text{-day}^{\wedge 1}$.

Mean depth-integrated CO₂ fluxes from PAD 31 peat range from under warm, dry conditions at $0.00 \pm 0.007 \text{ mg CO}_2\text{-g}^{\wedge}\text{-day}^{\wedge 1}$ to $0.929 \pm 0.207 \text{ mg CO}_2\text{-g}^{\wedge}\text{-day}^{\wedge 1}$ during warm, moist conditions. Highest CO₂ production occurs from PAD 31 peat substrates under warm, moist conditions ($0.929 \pm 0.207 \text{ mg CO}_2\text{-g}^{\wedge}\text{-day}^{\wedge 1}$). Maximum sediment CO₂ production occurs under saturated, moist conditions ($0.329 \pm 0.082 \text{ mg CCVg}^{\wedge} \text{-day}^{\wedge 1}$). The least CO₂ production occurs under dry moisture treatments.

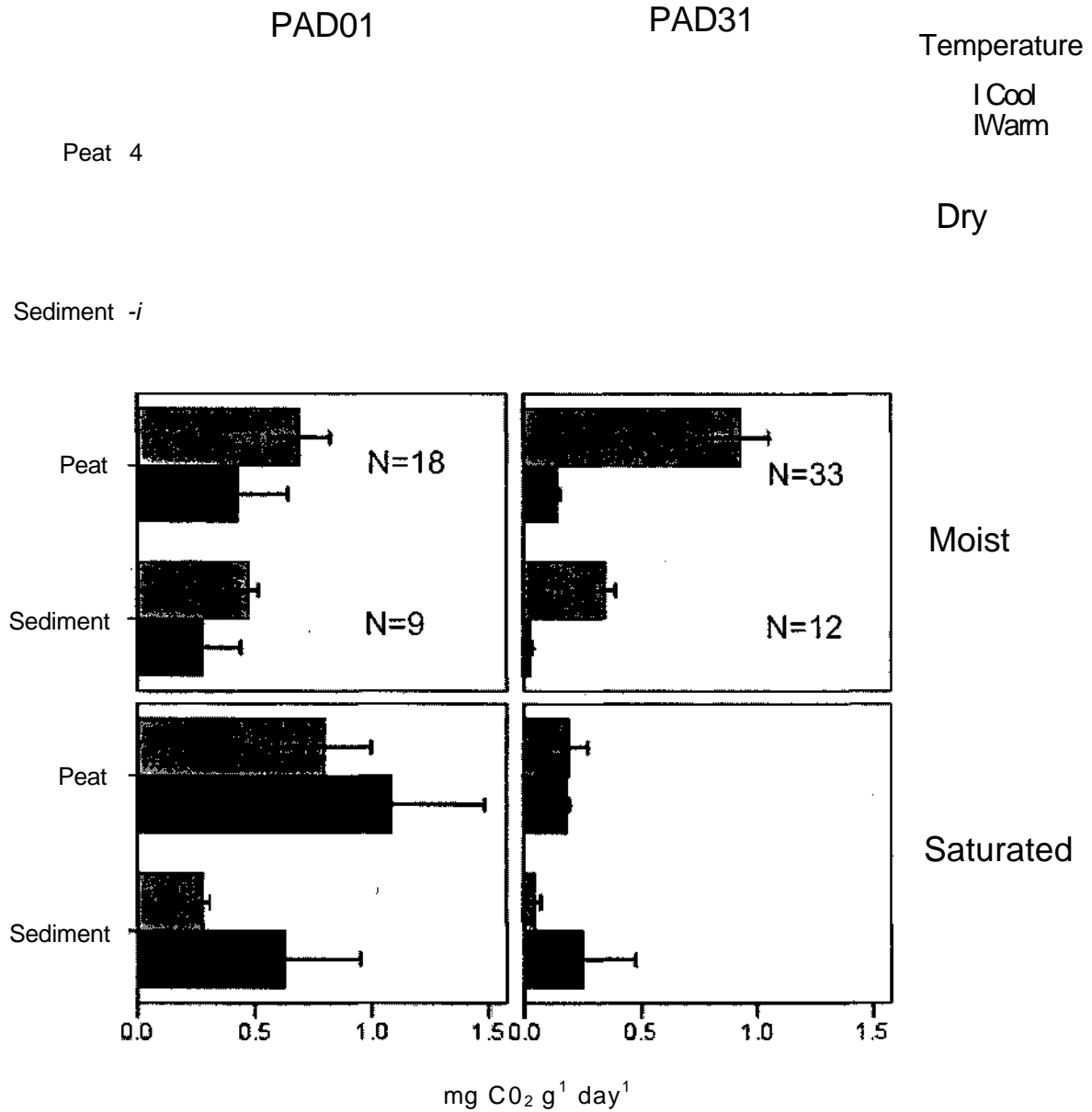


Figure 15: Grouped depth-integrated CO₂ production rates for PAD 1 and PAD 31 under all simulated moisture and temperature conditions. Gray bars indicate the warm temperature (20°C) while black bars indicate the cool temperature (4°C) treatments. Error bars represent one standard error (S.E.) of the grouped mean flux values.

CO₂ production at different stratigraphic depths

Sediment and peat laboratory incubation CO₂ production results according to depth intervals (see Table 1) are displayed in Figure 16 for all simulated temperature and moisture conditions for PAD 1 and PAD 31. Dry treatments produce the lowest potential CO₂ flux values, while the highest mean CO₂ production rates were observed under saturated and cool conditions. Moist treatments produced variable, although lower rates of CO₂ production than saturated conditions.

For PAD 1, peat CO₂ production is variable with depth, with maximum values of $2.175 \pm 0.968 \text{ mg CO}_2\text{-g}^{-1}\text{-day}^{-1}$ during cool, saturated conditions and in near-surface intervals. Minimum ($0.00 \pm 0.005 \text{ mg CO}_2\text{-g}^{-1}\text{-day}^{-1}$) CO₂ production from peat occurs in all depth intervals under dry treatments. Maximum CO₂ production from PAD 1 sediments occurs in near surface intervals under cool, saturated treatments at $1.410 \pm 0.202 \text{ mg CO}_2\text{-g}^{-1}\text{-day}^{-1}$. Negligible CO₂ production ($0.00 \pm 0.005 \text{ mg CO}_2\text{-g}^{-1}\text{-day}^{-1}$) occurs during dry incubation conditions.

Production of CO₂ from PAD 1 deep peat substrates (Figure 16) ranges from $0.101 \pm 0.042 \text{ mg CO}_2\text{-g}^{-1}\text{-day}^{-1}$ (cool, moist treatments) to $0.519 \pm 0.169 \text{ mg CO}_2\text{-g}^{-1}\text{-day}^{-1}$ (warm, moist treatments). Minimum CO₂ production (excluding dry treatments) from mid-depth intervals are $0.060 \pm 0.016 \text{ mg CO}_2\text{-g}^{-1}\text{-day}^{-1}$ (cool, moist) and maximum values are $0.253 \pm 0.022 \text{ mg CO}_2\text{-g}^{-1}\text{-day}^{-1}$ (cool, saturated) and. Near-surface intervals range from a minimum of $0.959 \pm 0.545 \text{ mg CO}_2\text{-g}^{-1}\text{-day}^{-1}$ (cool, moist) to maximum production of $2.175 \pm 0.986 \text{ mg CO}_2\text{-g}^{-1}\text{-day}^{-1}$ (cool, saturated). Sediment CO₂ production from deep intervals ranges from $0.005 \pm 0.031 \text{ mg CO}_2\text{-g}^{-1}\text{-day}^{-1}$ (cool, moist) to $0.183 \pm 0.061 \text{ mg CO}_2\text{-g}^{-1}\text{-day}^{-1}$ (warm, saturated). Mid-depth intervals range from $0.009 \pm 0.031 \text{ mg CO}_2\text{-g}^{-1}\text{-day}^{-1}$

'day⁻¹ (cool, moist) to 0.302±0.159 mg CC^{-g}-day⁻¹ (warm, saturated). The highest production occurs in near surface intervals from sediments, ranging from 0.013±0.217 mg CCVg^{-day}⁻¹ (cool, moist) to 1.410±0.202 mg CC^{-g}-day⁻¹ (warm, moist).

Incubation results for PAD 31 depth intervals (see Table 2) are also displayed in Figure 16 for all simulated temperature and moisture conditions. Dry treatments produce the lowest potential CO₂ flux values, while the highest mean CO₂ production rates were observed under moist and warm conditions. Saturated moisture conditions produced variable, although lower rates of CO₂ production than moist conditions.

PAD 31 deep peat substrate CO₂ production ranged from 0.000±0.013 mg CCVg^{-day}⁻¹ in cool, moist conditions to 0.835±0.066 mg CC^{-g}-day⁻¹ under warm, moist conditions. Mid-depth CO₂ production values range from 0.000±0.050 mg CC^{-g}-day⁻¹ in cool, moist conditions to 1.043±0.737 mg CCVg^{-day}⁻¹ during warm, moist conditions. Near-surface production values are the highest, and range from 0.000±0.015 mg CO₂-g^{-day}⁻¹ in cool, moist conditions to 1.179±0.117 mg CCVg^{-day}⁻¹ in warm, moist conditions. Sediment CO₂ production from deep sections range from 0.000±0.015 mg CCVg^{-day}⁻¹ in cool, saturated conditions to 0.046±0.046 mg CCVg^{-day}⁻¹ in warm, moist conditions. Mid-depth layer sediment CO₂ production ranged from 0.000±0.006 mg CCVg^{-day}⁻¹ in cool, moist conditions to 0.142±0.183 mg CCVg^{-day}⁻¹ in warm, moist conditions. Similarly, near surface sediments produced the highest CO₂ values ranging from 0.010±0.012 mg CO₂-g^{-day}⁻¹ in cool, moist conditions to 0.399±0.088 mg CCVg^{-day}⁻¹ during warm, moist simulations.

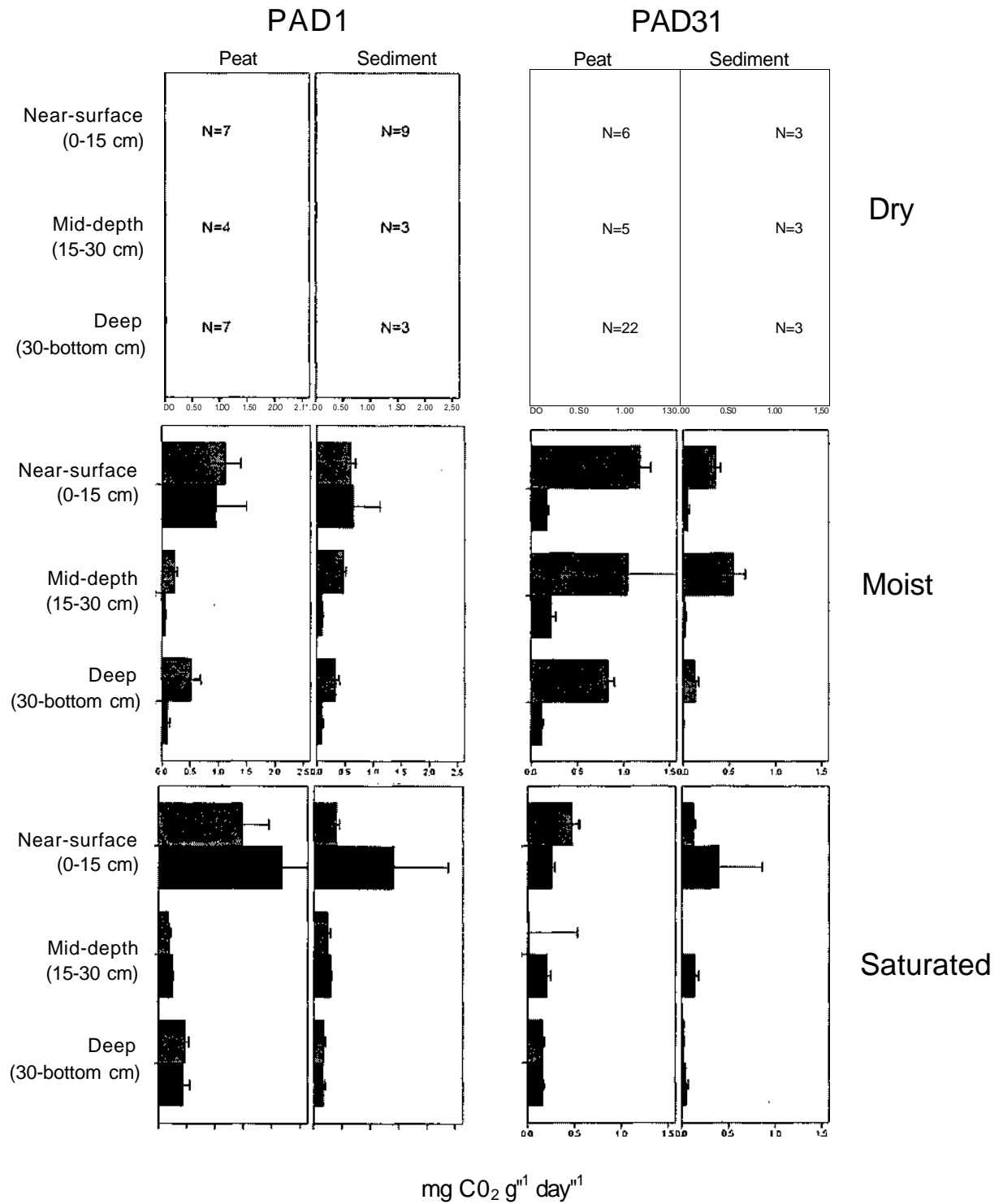


Figure 16: Mean CO₂ fluxes grouped by depth category (near-surface, mid and deep sections) for incubated samples during each moisture (dry, moist and saturated) and temperature (warm and cool) treatment. Incubated samples are separated according to substrate type (peat and sediment). Error bars indicate ± 1 standard error (SE).

PAD 1 CO₂ fluxes from major hydrological intervals spanning the last ~600 years

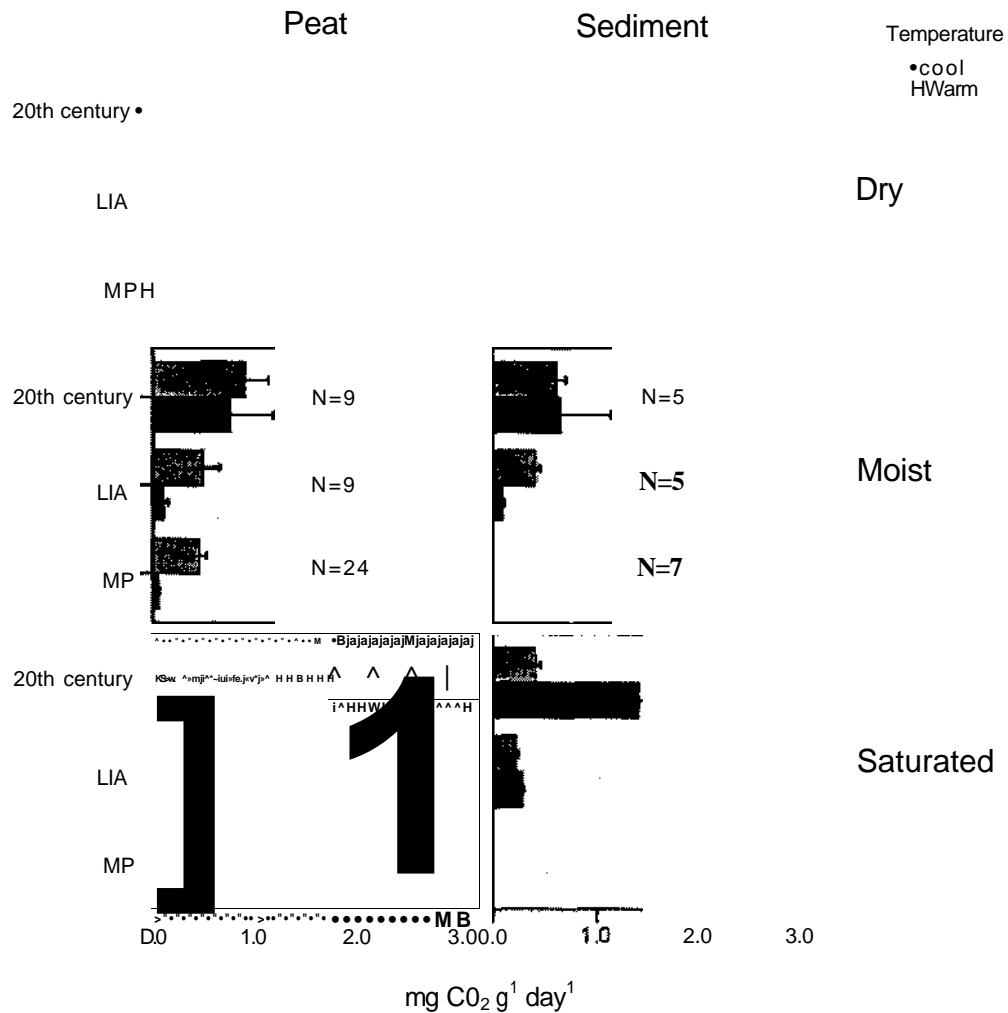


Figure 17: Potential CO₂ production from peat and lake sediment substrates at PAD 1, grouped into major hydrological intervals spanning the last ~600 years including the Medieval Period (MP), Little Ice Age (LIA) and the 20th century.

Mean CO₂ flux values from peat and sediment substrates from PAD 1 were grouped according to major paleohydrological intervals (20th century, LIA and MP) delineated in section 3.3 and are shown in Figure 17. Peat CO₂ production from the 20th century interval is greatest under cool, saturated conditions (1.171 ± 0.670 mg CO₂ g⁻¹ day⁻¹). Warm, saturated treatments for the 20th century interval produce more CO₂ than warm, moist treatments (0.754 ± 0.741 mg CO₂ g⁻¹ day⁻¹) conditions. Dry treatments produced

negligible amounts of CO₂ for all intervals. The highest CO₂ production from sediments is also greatest in the 20th century interval ($0.606 \pm 0.153 \text{ mg CC}^{-1}\text{-g}^{-1}\text{-day}^{-1}$) under cool, saturated conditions.

CO₂ production from peat and lake sediment from the LIA intervals is greatest under warm, moist treatments. Saturated treatments of the LIA substrates produce more CO₂ under cool than warm temperatures. Peat substrates produced the greatest amount of CO₂ during warm, saturated treatments. Comparable CO₂ production also occurs under warm, moist treatments for peat under No material from the MP interval was incubated from PAD 1 sediments.

The Embarras Breakthrough and PAD 31 CO₂ production

PAD 31 peat and lake sediment CO₂ production are grouped according to hydrological intervals identified in the stratigraphic record, including the LIA, closed-drainage (pre-1982) and post-1982 (following the Embarras Breakthrough event) and are shown in Figure 18. Lake sediment and peat substrate depth intervals identified as being deposited in the 20th century prior to the 1982 Embarras Breakthrough event occurred below the distinct peak in %OM and trough in dry bulk density (Figure 13 and Figure 14). Intervals identified as post-1982 occur in depths above the %OM and trough bulk density peak.

Figure 18 shows peat and lake sediment CO₂ production in all temperature and moisture treatments grouped according to three identified hydrological intervals. Maximum peat CO₂ production occurs during moist, warm treatments from peat and sediment substrates, with the exception of recently deposited (post-1982) sediments under cool, saturated conditions. Peat substrates deposited following the 1982 Embarras Breakthrough event contribute the greatest amount of CO₂ while 20th century intervals

prior to 1982 (closed) in sediments contribute more CO₂ than other hydrological intervals. Less CO₂ production from peat occurs under saturated treatments. Maximum, although variable sediment CO₂ production occurs under cool, saturated treatments.

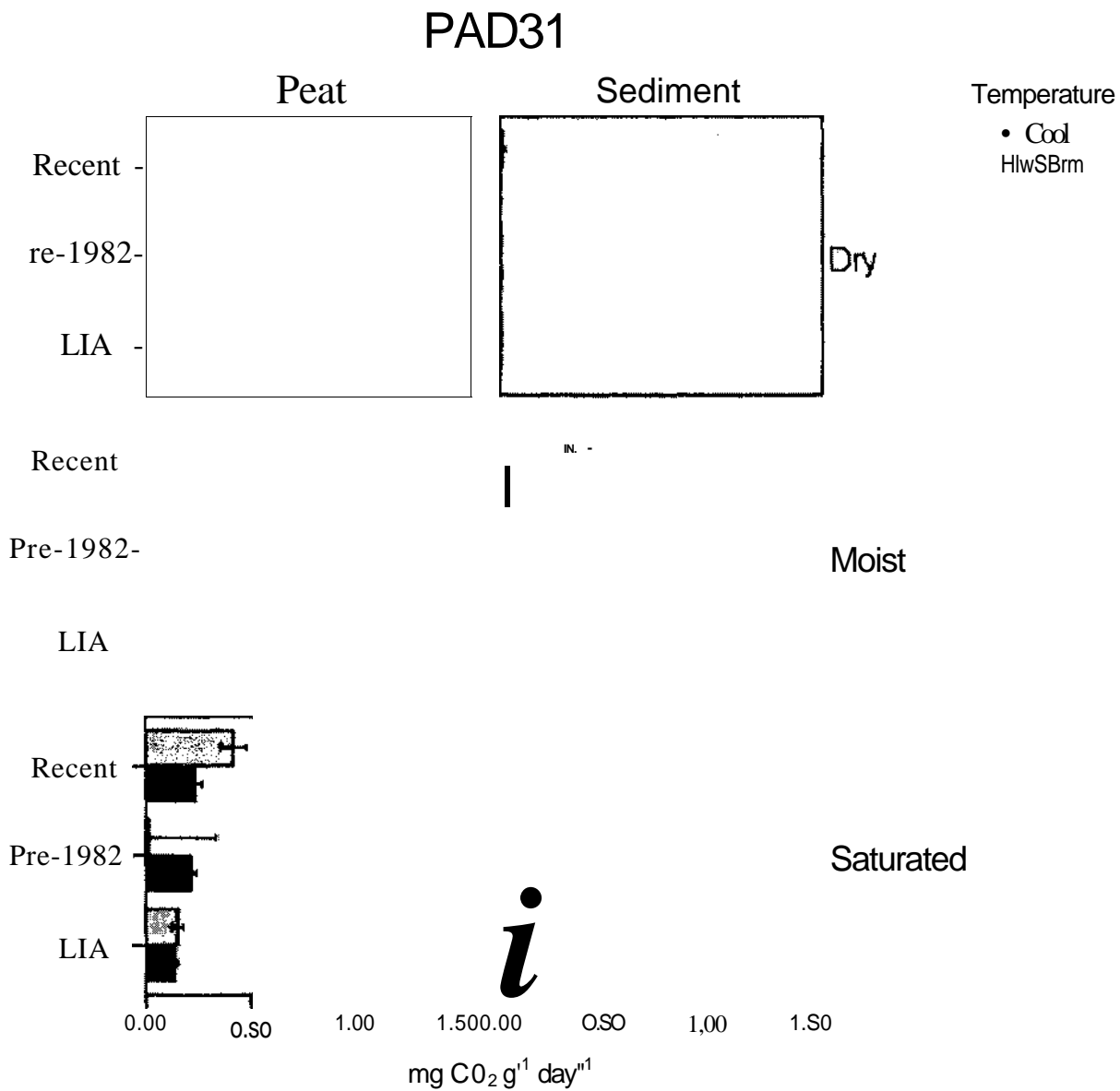


Figure 18: CO₂ production potentials (mg CO₂ g⁻¹ day⁻¹) from peat and sediment substrates deposited during hydrological intervals at PAD 31 including prior to and following increased river influence after the Embarras Breakthrough event in 1982 and during the LIA for each simulated moisture and temperature treatment. Error bars represent one standard error (S.E.) about the mean.

Respiration and oxidation quotients (Qio) from peat and sediment substrates

The factor by which the concentration of end-products of a reaction rate changes (increases) over a 10°C temperature change is expressed as the "Qio" value [Yavitt et al., 1997; Moore and Dalva, 1997a; McKenzie et al., 1998]. Peat CO₂ production rates increase by 2-3 times for every 10^DC [Moore and Dalva, 1997a; McKenzie et al., 1998]. This value is a good indication of how susceptible and temperature-sensitive the organic substrate (peat soil and lake sediment) is to oxidation. Mean, depth-integrated Qio values for peat and lake sediment incubations for PAD 1 and PAD 31 during each moisture treatment are displayed in Table 4. Highest Qio values are recorded during moist treatments in PAD 31 peat (Q₁₀ =3.94±0.43) and sediment (Qio =3.87±0.64). Moist treatments at PAD 1 also have the highest temperature sensitivity in peat (Qio =3.16±0.43) and sediment (Qio =3.15±1.05). All other moisture treatments have little CO₂ production temperature-dependence, with the exception of PAD 1 peat during dry treatments (Qio =1.22±0.28) and PAD 31 peat during saturated treatments (Qio =1.15±0.12).

Table 4: Depth-integrated, mean Qio values for PAD 1 and PAD 31 (a.) peat and (b.) lake sediment during each moisture treatment. Error estimates are one standard error (S.E.) about the mean.

a. Peat						
Site	Dry	± S.E	Moist	± S.E	Saturated	± S.E
PAD1	1.22	0.28	3.16	0.43	0.95	0.10
PAD 31	0.17	0.07	3.94	0.43	1.15	0.12
b. Sediment						
Site	Dry	±S.E	Moist	±S.E	Saturated	±S.E
PAD 1	0.85	0.17	3.15	1.05	0.75	0.12
PAD 31	0.56	0.28	3.87	0.64	0.89	0.32

Sediment substrates show an increase in the temperature sensitivity of CO₂ production under moist regimes, and a decline with depth during the saturated treatment (Table 5). The most temperature-dependent (highest Q₁₀ values) depth intervals for PAD 1 occur in peat substrates under moist treatments at mid-depths (Q₁₀ =3.98±0.17). PAD 31 maximum Q₁₀ values are found in sediments from mid-depths under moist treatments (Q₁₀ =5.09±0.40) (Table 5). CO₂ production is apparently not sensitive to temperature during dry moisture treatments, with the exception of PAD 1 peat at all depth intervals (Table 5 a) and near-surface sediments (Q₁₀ =1.06±0.39). Similarly, saturated moisture treatments exhibit no temperature sensitivity with the exception of PAD 31 near-surface peat (Q₁₀ =1.59±0.06) and sediments (Q₁₀ =1.32±0.10).

Table 5: Mean QJO values for peat and lake sediment substrates at each study site, according to depth categories. Error estimates are one standard error (S.E.) about the mean.

a. Peat

Site	Depth	Dry	± S.E	Moist	± S.E	Saturated	± S.E	N
PAD1	near-surface	1.24	0.25	2.73	0.23	0.87	0.05	11
	mid	1.29	0.20	3.98	0.17	0.81	0.07	4
	deep	1.06	0.15	3.65	0.17	1.41	0.04	3
PAD 31	near-surface	0.26	0.05	3.33	0.20	1.59	0.06	9
	mid	0.20	0.11	4.25	0.19	1.22	, 0.07	9
	deep	0.10	0.08	4.11	0.40	0.84	0.04	13

b. Sediment

Site	Depth	Dry	±S.E	Moist	±S.E	Saturated	±S.E	N
PAD1	near-surface	1.06	0.39	2.05	0.09	0.87	0.05	3
	mid	0.90	0.15	3.74	0.22	0.88	0.06	3
	deep	0.58	0.24	3.65	0.50	0.50	0.06	3
PAD 31	near-surface	0.60	0.11	3.38	0.25	1.32	0.10	6
	mid	0.61	0.14	5.09	0.45	0.24	0.15	
	deep	0.43	0.14	3.62	0.69	0.67	0.12	3

Q₁₀ values for PAD 1 peat (a) and lake sediments (b) according to the MP, LIA and 20th century climatic intervals are listed in Table 6. Highest Q₁₀ values (3.80±0.47) are from peat sediments deposited during the LIA interval during moist treatments. Sediment substrates also have the highest Q₁₀ values (3.69±1.51) under moist conditions from the LIA interval (Table 6 b). Q₁₀ values from dry moisture treatments are all less than 1.0, except for peat substrates from the MP interval (Q₁₀=1.10±0.30) and the LIA interval (Q₁₀=1.68±0.47). Q₁₀ values of 1.0 or less indicate that production of CO₂ is independent of incubation temperature. No sediment sections representative of the MP were incubated.

Table 6: Temperature sensitivity quotients (Q₁₀) for potential CO₂ production in PAD 1 from peat and sediment substrates deposited during hydrologically distinct intervals

a. Peat	Hydrologic Interval						
	Moisture	20 th century	±S.E.	LIA	±S.E.	MP	±S.E.
	Dry	0.89	0.38	1.68	0.47	1.10	0.30
	Moist	2.63	0.50	3.08	0.83	3.29	0.59
	Saturated	0.85	0.13	0.90	0.12	1.57	0.26

b. Sediment	Hydrologic Interval						
	Moisture	20 th century	±S.E.	LIA	±S.E.	MP	±S.E.
	Dry	0.06	0.33	0.74	0.18		
	Moist	2.05	0.56	3.69	1.51	-	-
	Saturated	0.87	0.18	0.69	0.15		

Table 7 lists Q₁₀ values for peat and lake sediment from PAD 31 during all moisture treatments grouped according to the three stratigraphically identified hydrological intervals. Peat substrates during moist conditions have the highest temperature sensitivity. Saturated treatment conditions show little change in temperature sensitivity.

Peat substrate from the LIA interval has the highest Q_{io} of 4.46 ± 0.47 during moist treatments. Sediment substrates under moist conditions show similar patterns. The closed-drainage interval (20th century pre-1982) has greater temperature sensitivity with $Q_{io} = 6.04 \pm 0.65$. Sediment from the LIA hydrologic interval ($Q_{io} = 4.32 \pm 0.57$) is more temperature-sensitive than the post-1982 interval substrates ($Q_{io} = 2.78 \pm 0.25$) under moist treatments.

Table 7: Potential respiration/oxidation Q_{io} values for PAD 31 peat (a.) and lake sediment (b.) substrates under all moisture regimes grouped according to major hydrological intervals identified in the sediment and peat stratigraphic record.

a. Peat		Hydrologic Interval				
Moisture	Post-1982	±S.E.	Closed (Pre-1982)	Q_{io}	LIA	±S.E.
Saturated	1.48	0.10	1.26	0.16	1.13	0.06
Moist	3.33	0.19	3.74	0.31	4.46	0.47

b. Sediment		Hydrologic Interval				
Moisture	Post-1982	±S.E.	Closed (Pre-1982)	Q_{io}	LIA	±S.E.
Saturated	1.06	0.18	2.61	1.01	0.85	0.20
Moist	2.78	0.25	6.04	0.65	4.32	0.57

4.4 Discussion

Combined (peat + sediment) total potential CO₂ production from the frequently flooded site (PAD 31) is greater than that from the closed-drainage site (PAD 1) under moist and warm temperature conditions (see Figure 15). PAD 31 sediment and peat substrates are also more sensitive to temperature changes compared to those from PAD 1 (Table 5)

The results also show that the sediment substrates produce less CO₂, on average, to the atmosphere than littoral peat substrates (Figure 15). Peat in littoral areas and paludal sediments contained in wetlands have been shown to be responsible for greater rates of decomposition and export of carbon as CO₂ compared to profundal sediments [Benoy et al., 2007]. These saturated areas are known to contain roughly 75% of the carbon in the boreal biome, despite containing organic matter that is less permanent than that found in profundal sediments [Benoy et al, 2007; Molot and Dillon, 1996]. The peat soils from littoral areas surrounding the ponds therefore have the capacity to be a large and more transient source of CO₂. This is particularly true during periods when moisture and temperature conditions are optimal for decomposition of organic matter, indicated by the higher CO₂ production potential during warm, moist conditions. Substrate conditions (aeration and moisture content) are improved when soils are disturbed, leading to greater rates of respiration [Schlesinger and Andrews, 2000]. Although some results have demonstrated that pond sediments in the Western Boreal Plain may be a large source of carbon during periods of prolonged drought [Petrone et al., 2005], simulated dry and warm conditions did not facilitate greater losses of CO₂ from peat or sediment substrates in this study.

Stratigraphic differences in CO₂ production from both PAD 1 and PAD 31 highlight the complexity of predicting CO₂ fluxes in changing climates. Hydrological connectivity and antecedent conditions (i.e., the frequency and duration of drought/flood periods) appear to play a role in determining the size and lability of the carbon pool contained within these pond - peatland systems. More stable water table positions and infrequent flooding by river water at PAD 1 is consistent with a larger and less labile carbon stock.

A less labile organic carbon fraction at PAD 1 may be partially explained by an accumulation of components (such as lignins, phenolic and humic substances) that restrict bacterial activity responsible for producing CO₂ [Williams and Crawford, 1984; Hogg et al., 1992]. Higher potential CO₂ production from surficial (near surface, 0-15 cm depths) peat and sediments also indicates that more recently deposited organic material is initially more labile and easily decomposed in the absence of these microbially unavailable compounds [Hogg et al., 1992]. The absence of water level fluctuations and hydrological inputs from riverine sources appear to be related to lower potential losses of CO₂ from organic matter.

Greater potential CO₂ production from the frequently flooded site (PAD 31) indicates that more frequent hydrological inputs and variability is related to elevated CO₂ losses. Frequent instances of flooding facilitates increased nutrient availability, greater microbial waste product removal, higher DOC concentrations and other changes in chemical properties that enhance the potential for CO₂ production [McKenzie et al., 1998]. The potential CO₂ production responses of PAD 1 and PAD 31 peat soils and sediments to moisture and temperature changes appear to be related to antecedent and contemporary hydrological conditions.

Surficial (0-10 cm) peat and sediments from both sites produce more CO₂ during both warm and cool temperatures in all moisture treatments (Figure 16). During warm temperatures, moist and saturated treatments have similar potential CO₂ production rates, with CO₂ production declining from near-surface to deep. It is expected that younger, surficial peat and sediments will contain more labile carbon sources from newly deposited organic matter that is easily mineralized [Bridgham et al., 1998]. Larger

production rates in the upper part of peat and lake sediment profiles are common [Moore and Dalva, 1997b]. A reduction in the rate of CO₂ production at depth may also be explained by an observed paucity of soil fauna (microbes) like bacterial grazers which lead to slow decomposition rates and consequently accumulation of bacterially-derived organic compounds [Lee, 1992]. These results highlight the capability of near-surface substrates to be more sensitive to moisture and temperature fluctuations, and potential to contribute greater amounts of CO₂ to the atmosphere independently of hydrological history.

Changes in the moisture status of the peat and lake sediment substrates at each site influence their capacity to produce CO₂. Dry moisture treatments produced negligible CO₂, likely due to insufficient moisture content that causes respiration and oxidation of organic matter to be suppressed. The dry conditions do not have sufficient volumetric moisture content to support microbial activity that would produce measurable amounts of CO₂ as an end product of metabolism. The greatest potential CO₂ production for all substrates at each site (with the exception of peat from PAD 1) is observed under moist conditions, indicating optimum moisture conditions for microbial activity. Simulated saturated conditions appear to suppress the production of CO₂, likely due to more anaerobic conditions that cause facultative anaerobes to shift to generating energy via anaerobic pathways [Lee, 1992]. Consequently, decomposition proceeds much more slowly and reduces the rate of CO₂ efflux.

Stratigraphic differences in the potential contribution of CO₂ from organic matter are evident from both sites. These differences are related to the type of organic matter (substrate quality), the hydrological conditions that it was deposited under and changes

that have occurred since. The frequency and duration of hydrological variability at these sites is one of the most influential post-depositional hydrological changes. Potential losses from stratigraphic intervals of peat and lake sediment identified as being from intervals characteristic of higher water levels and relatively 'wet' conditions, like the LIA at PAD 1 show greater sensitivity to simulated temperature and moisture changes. Medieval and 20th century interval organic matter stocks show less temperature sensitivity (lower Q_{10} values). These intervals have been identified in the PAD as being periods of lower water levels, locally drier and warmer than the LIA.

Contrasting results are observed at PAD 31 where stratigraphic intervals characteristic of frequent flooding (post-1982) and infrequent flooding (20th century pre-1982) show the opposite relationship. Organic matter deposited during the less frequently flooded period prior to the Embarras Breakthrough is more sensitive to temperature changes demonstrated by higher Q_{10} values than subsequent intervals. This may partially be explained by the higher bulk organic content of the pre-1982 20th century interval. Enhanced overland flooding as a result of increased susceptibility to flooding following upstream geomorphological changes results in increased deposition of inorganic sand, silt and clay material that is carried by river water. The organic matter deposited on the peat soil and sediment surface is diluted by inputs of inorganic material from overland flood events. An additional consideration is the physical protection that organic material experiences following an increase in the sedimentation of silt, sand and clay material. The 20th century interval prior to the 1982 Embarras Breakthrough has physical protection by overlain silt and clay, and likely maintained anaerobic conditions slowing the decomposition of that stratigraphic interval. If the currently saturated conditions and

physical protection were to be altered at this site, such as a reduction in flooding, hydroecological changes would be accompanied by an enhanced respiration and oxidation of the organic carbon pool currently held in peat and lake sediment deposits.

Chapter 5. Conclusions and Recommendations

5.1 Findings summary

The sustainability of carbon stores in northern freshwater wetlands like the PAD is influenced by a number of environmental stressors. In the PAD over different time scales, these stressors have changed due to variable climate patterns or localized geomorphic processes. The paleohydrological record of both PAD 1 and PAD 31 highlight these changes. The paleohydrological records also offer important information that help to better characterize the potential efflux of CO₂ as a greenhouse gas from the numerous pond-peatland complexes in the PAD as it relates to hydrology. An understanding of antecedent conditions and the hydrological history of the sediment and peat soil organic substrates help to explain the spatial and temporal variability of CO₂ exchange in the PAD. The carbon flux response of northern boreal wetlands to climate and hydrological changes thus relies partially on previous environmental conditions.

Sediment cores collected at PAD 1 provide a hydrological history of the basin spanning the last ~600 years, while sediment cores collected from PAD 31 span the last ~400 years and correlate closely with previously obtained sediment cores. PAD 1 has experienced periodic connectivity with Lake Athabasca during the LIA, indicated by variations in the $\delta^{13}\text{C}_{\text{org}}$ profile. Elevated $\delta^{13}\text{C}_{\text{org}}$ and generally lower $\delta^{15}\text{N}_{\text{org}}$ values suggest that this site was an embayment of Lake Athabasca. A number of processes that influence the deposition and preservation of lake sediment organic matter are illustrated by the $\delta^{13}\text{C}_{\text{org}}$ profiles from PAD 1 and PAD 31. Enhanced recycling and reutilization of organic matter in closed-drainage conditions contributes to lowering the lake water $\delta^{13}\text{C}_{\text{DIC}}$ reservoir and consequently lowering $\delta^{13}\text{C}_{\text{org}}$ values in sediment organic matter.

The variability in $\delta^{13}\text{C}_{\text{org}}$ profiles earmarks the influence that elevated water levels in Lake Athabasca during the LIA had on PAD 1 and PAD 31. Highest $\delta^{13}\text{C}_{\text{org}}$ values during the LIA interval reflect enhanced interaction of both PAD 1 and PAD 31 with Lake Athabasca. These results are consistent with similar findings from other basins in the PAD that support elevated water levels in Lake Athabasca during the LIA [Wolfe et al., 2008a; Sinnatamby et al., 2010; Johnston et al., 2010]. Notably, the highest $\delta^{13}\text{C}_{\text{org}}$ and lowest $\delta^{18}\text{O}_{\text{w}}$ values at -1700 mark the greatest influence of Lake Athabasca on PAD 1 and PAD 31.

Sediment records collected from PAD 31 provide additional evidence for hydrological change due to increased flood frequency following a natural upstream bifurcation of the Embarras River. Enhanced susceptibility to overland flooding as a result of increased discharge along Mamawi Creek following the Embarras Breakthrough in 1982 is clearly present in the sediment physical (%OM and BD) and geochemical ($\delta^{13}\text{C}_{\text{org}}$ and $\delta^{18}\text{O}_{\text{w}}$) records. Diluted %OM and high bulk BD in all sediment and peat cores provide a stratigraphic marker that indicates enhanced frequency of river flooding. Increases in $\delta^{13}\text{C}_{\text{org}}$ values following 1982 indicate a similar shift in the supply of DIC consistent with that of open-drainage type water bodies, like rivers. Declines in $\delta^{18}\text{O}_{\text{w}}$ values also indicate a significant shift in the frequency of river input due to higher frequency of overland flooding events at PAD 31. The sediment records obtained from PAD 1 and PAD 31 illustrates hydrological change in response to climate independently identified in the PAD and to geomorphic processes that occur in active fluviodeltaic environments.

Potential CO₂ contributions from lake sediment and peat in northern wetlands are related to contemporary and antecedent hydrological conditions. Less mean potential CO₂ efflux from the open-drainage site (PAD 31) was observed through the laboratory incubations. The frequently flooded pond (PAD 31) substrates had lower CO₂ flux potential but were also more highly sensitive to temperature. Peat substrates are generally capable of contributing greater amounts of CO₂ than lake sediments, due largely to the size and lability of the organic carbon source. Stratigraphic intervals identified in the sediment records also reveal interesting trends apparent in the potential fluxes of CO₂ from lake sediments and peat. Substrates from intervals at PAD 31 characterized by infrequent river water inputs (20th century pre-1982) have effluxes that are reduced when compared to intervals with frequent flooding (LIA and post-1982). Efflux of CO₂ from PAD 1 intervals with characteristically wet conditions have higher potential CO₂ production and greater sensitivity to temperature changes (higher Q₁₀ values) than the periods when relatively dry, disconnected conditions persisted.

The first research question guiding this study was to determine the relative roles that antecedent and contemporary hydroecological conditions have on the amount and lability of stored organic carbon to oxidation and respiration potential. The sediment hydrological reconstruction results and laboratory incubations simulating hydrological and climatic (temperature) changes indicate there is important information that the hydrological record can provide about the future contribution of CO₂ from wetland organic deposits to the atmosphere. Antecedent conditions dominated by fluctuating water levels (intervals of drying and wetting) typically reduce the susceptibility of stored organic matter to oxidation and remineralization despite relatively high organic matter

content. Stagnant conditions with water levels that fluctuate infrequently promote prolonged anoxic conditions and consequently suppressed decay rates of organic matter. The remaining organic content is susceptible to hydrologic and temperature changes, particularly warming and drying, and has the potential to be a major CO₂ source.

The second research question was to evaluate how the potential CO₂ emissions respond to anticipated directional change in hydrological conditions in the PAD. Recent evidence for shifting hydrological regimes in the PAD indicates that directional change will be towards reduced summer discharge and a delayed (and suppressed) spring freshet [Wolfe et al., 2008a]. The likelihood of a pronounced drying trend combined with elevated seasonal temperatures as a consequence of climate change can have a significant impact on the direction and magnitude of carbon fluxes in the PAD. Basins that rely on periodic connectivity to the river network (via overland flooding) may experience a reduction in water inputs and consequently reductions in water levels. This can expose organic matter in lake sediments and littoral peat deposits that originally remained anoxic under saturated conditions. Oxygenated conditions can facilitate the remineralization and oxidation of organic matter to CO₂.

High-latitude wetlands function as reservoirs for atmospheric carbon dioxide, accumulating organic carbon since the beginning of the Holocene. The PAD is a dynamic wetland comprised of vast peatland and small, perched basins, some of which have existed over many centuries. This ecosystem has vast amounts of organic deposits which have been shown to be dependent on the hydrological status of the basin. Variable hydroecological conditions also influence the amount, lability and sustainability of the organic carbon stocks contained in peat and lake sediments. Thus, understanding carbon

accumulation patterns and rates, as well as oxidation potential, within the context of long-term hydroecological change is essential to predicting the long-term sustainability of this vital carbon store.

5.2 Recommendations for future research

Several considerations need to be taken into account for any study investigating the relationship between greenhouse gas feedback processes and paleohydrological conditions. First and foremost, this study was limited by the incomplete understanding of the paleohydrology of both sites before sediment and peat intervals were selected for laboratory incubation. A complete understanding of the paleohydrological conditions of the pond-peatland system and associated stratigraphic intervals prior to laboratory incubations is critical. This would allow a more complete association of substrate origin and paleohydrology with potential CO₂ production.

Another consideration would be to incubate substrate intervals at a high resolution (0.5 cm or less), equal-depth intervals, rather than 'representative' intervals with 'unique' physical and chemical properties. Such an approach would have the advantage of performing laboratory incubations concurrently with the development of the paleohydrological record. The use of a gas chromatograph to sample headspace gas production during the laboratory incubations would allow for the analysis of more than one gas (e.g., CH₄ and N₂O in addition to CO₂). Laboratory incubations typically also employ the use of both aerobic and anaerobic simulations to isolate respiration and free oxidation of organic matter.

This study brought to light the differences in potential CO₂ production from different substrate types (peat and lake sediment) and from different past and present hydrological

conditions. To better answer questions regarding the relationship between hydrological connectivity and potential CO₂ production, focus would be best placed on a single substrate type (peat or lake sediments) over a greater hydrological spectrum (i.e., inclusive of hydrologically distinct basins). This approach would be better suited to extrapolating the contribution of the substrate types to the cycling of carbon on a landscape-scale, and the association with catchment hydrology.

Reference List

- Appleby, P. G. (2001), Chronostratigraphic techniques in recent sediments, in *Tracking Environmental Change Using Lake Sediments, Volume J: Basin Analysis, Coring, and Chronological Techniques* edited by W. M. Last and J. P. Smol, pp. 171-204, Kluwer Academic Publishers, Dordrecht.
- Asada, T., B. G. Warner, and S. L. Schiff (2005), Effects of shallow flooding on vegetation and carbon pools in boreal peatlands, *Applied Vegetation Science*, 8, 199-208.
- Benoy, G., K. Cash, E. McCauley, and F. Wrona (2007), Carbon dynamics in lakes of the boreal forest under changing climate, *Environmental Review*, 15, 175-189.
- Bhatti, J. S., M. J. Apps, and C. Tarnocai (2002), Estimates of soil organic carbon stocks in central Canada using three different approaches, *Canadian Journal of Forestry Research*, 32, 805-812.
- Bhatti, J. S., G. C. van Kooten, M. J. Apps, L. D. Laird, I. D. Campbell, C. Campbell, M. R. Turetsky, Z. Yu, and E. Banfield (2003), Chapter 20: Carbon balance and climate change in boreal forests, in *Towards sustainable management of the boreal forest*, edited by P. J. Burton, C. Messier, D. W. Smith and W. L. Adamowicz, pp. 799-855, NRC Press, Ottawa.
- Blodau, C, and T. R. Moore (2003), Experimental response of peatland carbon dynamics to a water table fluctuation, *Journal of Aquatic Science*, 65, 47-62.
- Bridgman, S. D., J. Pastor, B. Dewey, J. F. Weltzin, and K. Updegraff (2008), Rapid carbon response of peatlands to climate change, *Ecology*, 89(11), 3041-3048.
- Bridgman, S. D., J. P. Megnonigal, J. K. Keller, N. B. Bliss, and C. Trettin (2006), The carbon balance of North American wetlands, *Wetlands*, 26, 889-916.
- Bridgman, S. D., K. Updegraff, and J. Pastor (1998), Carbon, nitrogen, and phosphorus mineralization in northern wetlands, *Ecology*, 79(5), 1545-1561.
- Bubier, J. L. (1995), The relationship of vegetation to methane emission and hydrochemical gradients in northern peatlands, *Journal of Ecology*, 83, 403-420.
- Bubier, J. L., T. R. Moore, and N. T. Roulet (1993), Methane emissions from wetlands in the midboreal region of northern Ontario, Canada, *Ecology*, 74, 2240-2254.
- Buhay, W. M., S. Simpson, H. Thorleifson, M. Lewis, J. King, A. Telka, P. Wilkinson, J. Babb, S. Timsic, and D. Bailey (2009), A 1000-year record of dry conditions in the eastern Canadian prairies reconstructed from oxygen and carbon isotope

measurements on Lake Winnipeg sediment organics, *Journal of Quaternary Science*, 24(5), 426-436, doi: 10.1002/jqs.1293.

Campbell, I. D., C. Campbell, D. H. Vitt, D. Kelker, L. D. Laird, D. Trew, B. Kotak, D. LeClair, and S. Bayley (2000), A first estimate of organic carbon storage in Holocene lake sediments in Alberta, Canada, *Journal of Paleolimnology*, 24, 395-400.

Chapman, S. J., and M. Thurlow (1998), Peat respiration at low temperatures, *Soil Biology and Biochemistry*, 50(8/9), 1013 -1021.

Clymo, R. S., J. Turunen, and K. Tolonen (1998), Carbon Accumulation in Peatland, *Oikos*, 81(2), 368-388.

Cole, J. J., et al (2007), Plumbing the Global Carbon Cycle: Integrating Inland Waters into the Terrestrial Carbon Budget, *Ecosystems*, 10, 171-184, doi: 10.1007/s 10021-006-9013-8.

Dean, W. E. (1974), Determination of carbonate and organic matter in calcareous sediments and sedimentary rocks by loss on ignition: comparison with other methods. *Journal of Sedimentary Petrology*, 44, 242-248.

Devito, K. J., I. F. Creed, and C. J. D. Fraser (2005), Controls on runoff from a partially harvested aspen-forested headwater catchment, Boreal Plain, Canada, *Hydrological Processes*, 19,3-25.

Ecoregions Working Group (1989), *Ecoclimatic regions of Canada, first approximation. Ecological Land Classification Series., No. 23 ed.*, Sustainable Development Branch, Conservation and Protection, Environment Canada., Ottawa, Ontario.

Edwards, T. W. D., S. J. Birks, B. H. Luckman, and G. M. MacDonald (2008), Climatic and hydrologic variability during the past millennium in the eastern Rocky Mountains and northern Great Plains of western Canada, *Quaternary Research*, 70, 188-197.

Edwards, T. W. D., and J. H. McAndrews (1989), Paleohydrology of a Canadian Shield lake inferred from 18-0 in sediment cellulose. *Canadian Journal of Earth Sciences*, 26, 1850-1859.

Foote, L., and N. Krogman (2006), Wetlands in Canada's western boreal forest: Agents of Change, *The Forestry Chronicle*, 82(6), 825-833.

Frolking, S., N. Roulet, and J. Fuglestedt (2006), How northern peatlands influence the Earth's radiative budget: Sustained methane emission versus sustained carbon sequestration, *Journal of Geophysical Research*, 111.

Glew, J. R. (1988), A portable extruding device for close interval sectioning of unconsolidated core samples, *Journal of Paleolimnology*, 1, 235-239.

Glew, J. R. (1989), A new trigger mechanism for sediment samplers. *Journal of Paleolimnology*, 2, 241-244.

Gorham, E. (1991), Northern Peatlands: Role in the Carbon Cycle and Probable Responses to Climatic Warming, *Ecological Applications*, 1, 182-195.

Hall, R., B. Wolfe, and T. W. D. Edwards, Karst-Riddoch, T.L., Vardy, S., McGowan, S., Sjunneskog, C., Paterson, A., English, M.C., Sylvestre, F., Leavitt, P.R., Warner, B.G., Boots, B., Palmini, R., Clogg-Wright, K., Soka, M., Falcone, M., van Driel, P., and Asada, T. (2004), *A Multi-Century Flood, Climatic, and Ecological History of the Peace-Athabasca Delta, Northern Alberta, Canada*, Final Report to BC HYDRO, 163 pp.

Heiri, O., A. F. Lotter, and G. Lemcke (2001), Loss on ignition as a method for estimating organic and carbonate content in sediments: reproducibility and comparability of results, *Journal of Paleolimnology*, 25(1), 101-110.

Hodell, D. A., and C. L. Schelske (1998), Production, Sedimentation, and Isotopic Composition of Organic Matter in Lake Ontario, *Limnology and Oceanography*, 43(2), 200-214.

Hogg, E. H., V. J. Lieffers, and R. W. Wein (1992), Potential Carbon Losses from Peat Profiles: Effects of Temperature, Drought Cycles, and Fire, *Ecological Applications*, 2, 298-306.

IPCC (2007), *Climate Change 2007: The physical science basis. Contribution from Working Group 1 to the fourth assessment report of the Inter Governmental Panel on Climate Change*, in *IPCC Fourth Assessment Report* edited by S. Solomon, D. Qin, M. Manning, M. Marquis, K. Averyt, M. Tignor and H. L. Miller, Cambridge University Press, Cambridge, U.K.

Ise, T., and P. R. Moorcroft (2006), The global-scale temperature and moisture dependencies of soil organic carbon decomposition: an analysis using a mechanistic decomposition model, *Biogeochemistry*, 80, 217-231.

Johnston, J., D. Koster, B. B. Wolfe, R. I. Hall, T. W. D. Edwards, A. Endres, M. Martin, J. Wiklund, and C. Light (2010), Reconstruction of Lake Athabasca (Canada) water level during the Little Ice Age from paleolimnological and geophysical analyses of a transgressive barrier-beach complex, *The Holocene*.

Kettunen, A., V. Kaitala, A. Lehtinen, A. Lohila, J. Aim, J. Silvola, and P. J. Martikainen (1999), Methane production and oxidation potentials in relation to water table fluctuations in two boreal mires, *Soil biology and Biochemistry*, 31, 1741-1749.

Kirschbaum, M. (2006), The temperature dependence of organic-matter decomposition—still a topic of debate, *Soil Biology and Biochemistry*, 38(9), 2510-2518.

Kortelainen, P., H. Pajunen, M. Rantakari, and M. Saarnisto (2004), A large carbon pool and small sink in boreal Holocene lake sediments, *Global Change Biology*, 10, 1648-1653.

Lee, C. (1992), Controls on organic carbon preservation: the use of stratified water bodies to compare intrinsic rates of decomposition in oxic and anoxic systems. *Geochimica Cosmochimica Acta*, 56, 3323-3335.

Leng, M., A. Lamb, T. Heaton, J. Marshall, B. Wolfe, M. Jones, J. Holmes, and C. Arrowsmith (2005), Isotopes in Lake Sediments, in *Isotopes in Paleoenvironmental Research* edited by M. Leng, pp. 147-184, Springer, The Netherlands.

Lyons, S. (M.Sc. in progress), The influence of flooding on the aquatic food-web in the Peace-Athabasca Delta, Department of Biology, University of Waterloo.

McKenzie, C, S. Schiff, R. Aravena, C. Kelly, and V. St. Louis (1998), Effect of temperature on production of CH₄ and CO₂ from peat in a natural and flooded boreal forest wetland, *Climatic Change*, 40, 247-266.

Meyers, P. (1997), Organic geochemical proxies of paleoceanographic, paleolimnologic, and paleoclimatic processes, *Organic Geochemistry*, 114, 289-302.

Meyers, P., and J. Teranes (2001), Sediment Organic Matter, in *Tracking Environmental Change Using Lake Sediments: Volume 2: Physical and Geochemical Methods* edited by Last, W. and Smol, J, pp. 239-269, Kluwer Academic, Dordrecht.

Meyers, P. A., and E. Lallier-Verges (1999), Lacustrine sedimentary organic matter records of late Quaternary paleoclimates, *Journal of Paleolimnology*, 21, 345-372.

Molot, L. A. and P. J. Dillon (1996), Storage of terrestrial carbon in boreal lake sediments and evasion to the atmosphere, *Global Biogeochem. Cycles*, 10(3), 483-492.

Moore, T. R., J. L. Bubier, S. E. Frohling, P. M. Lafleur, and N. T. Roulet (2002), Plant biomass and production and CO₂ exchange in an ombrotrophic bog, *Journal of Ecology*, (90), 25-36.

Moore, T. R., and M. Dalva (1997a), Methane and carbon dioxide exchange potentials of peat soils in aerobic and anaerobic laboratory incubations, *Soil Biology Biochemistry*, 29, 1157-1164.

Moore, T. R., and M. Dalva (1997b), Methane and Carbon Dioxide Exchange Potentials of Peat Soils in Aerobic and Anaerobic Laboratory Incubations, *Soil Biology and Biochemistry*, 29(8), 1157-1164.

Moore, T. R., and R. Knowles (1989), The influence of water table levels on methane and carbon dioxide emissions from peatland soils, *Canadian Journal of Soil Science*, 69, 33-38.

National Research Council Canada (1998), *The Canadian System of Soil Classification*, Third ed., NRC Research Press, Ottawa.

Peace-Athabasca Delta Technical Studies (PADTS) (1996), *Final Report*, 106 pp., PADTS Steering Committee, Fort Chipewyan, Alberta.

Peace-Athabasca Delta Project Group (PADPG) (1973), *Peace-Athabasca Delta Project, Technical Report and Appendices.*, Volume 1: Hydrological Investigations, Volume 2: Ecological Investigations, ed.

Peters, D. L., T. D. Prowse, P. Marsh, P. M. Lafleur, and J. M. Buttle (2006a), Persistence of water within perched basins of the Peace-Athabasca Delta, Northern Canada, *Wetlands Ecology and Management*, 14, 221-243.

Peters, D. L., T. D. Prowse, A. Pietroniro, and R. Leconte (2006b), Flood Hydrology of the Peace-Athabasca Delta, northern Canada, *Hydrological Processes*, 20, 4073-4096.

Petrone, R. M., K. J. Devito, S. Kaufman, M. L. Macrae, and J. M. Waddington (2005), Potential carbon losses from boreal pond and riparian areas: influence of temperature and drought, *Dynamics and Biogeochemistry of River Corridors and Wetlands (Proceedings of symposium S4 held during the Seventh IAHS Scientific Assembly at Foz do Iguacu, Brazil)*, 294, 10-18.

Prowse, T. D., and F. M. Conly (2002), A review of hydroecological results of the Northern River Basins Study, Canada. Part 2. Peace - Athabasca Delta, *River Research and Applications*, 18, 447-460.

Prowse, T. D., and F. M. Conly (2000), Multiple-hydrologic stressors of a northern delta ecosystem, *Journal of Aquatic Ecosystem Stress and Recovery*, 8(\), 17-26.

Raich, J. W., and W. H. Schlesinger (1992), The global carbon dioxide flux in soil respiration and its relationship to vegetation and climate, *Tellus*, 44B, 81-99.

Rood, S. B., G. M. Samuelson, J. K. Weber, and K. A. Wywrot (2005), Twentieth-century decline in streamflows from the hydrographic apex of North America, *Journal of Hydrology*, 306(1-4), 215-233.

Roulet, N. T. (2000), Peatlands, Carbon Storage, Greenhouse Gases, and the Kyoto Protocol: Prospects and significance for Canada, *Wetlands*, 20, 605-615.

Schelske, C. L., and D. A. Hodell (1995), Using carbon isotopes of bulk sedimentary organic matter to reconstruct the history of nutrient loading and eutrophication in Lake Erie, *Limnology and Oceanography*, 40(5), 918-929.

Schindler, D. W., and W. F. Donahue (2006), An impending water crisis in Canada's western prairie provinces, *Proceedings of the National Academy of Science, U.S.A.*, 103, 7210-7216.

Schindler, D. W. (2001), The cumulative effects of climate warming and other human stresses on Canadian freshwaters in the new millennium, *Canadian Journal of Fisheries and Aquatic Sciences*, 55(1), 18-29.

Schlesinger, W., and J. Andrews (2000), Soil respiration and the global carbon cycle, *Biogeochemistry*, 48, 7-20.

Silvola, J., J. Aim, U. Ahlholm, H. Nykanen, and P. J. Martikainen (1996), CO₂ Fluxes from Peat in Boreal Mires under Varying Temperature and Moisture Conditions, *J.EcoL*, 84(2), 219-228.

Sinnatamby, R. N., et al (2010), Historical and paleolimnological evidence for expansion of Lake Athabasca (Canada) during the Little Ice Age, *Journal of Paleolimnology*, in press.

Talbot, M. R. (2001), Nitrogen isotopes in paleolimnology, in *Tracking Environmental Change Using Lake Sediments. Volume 2: Physical and Geochemical Methods*, edited by W. M. Last and J. P. Smol, pp. 401-439, Kluwer Academic Publishers, Dordrecht, The Netherlands,.

Tarnocai, C. (2006), The effect of climate change on carbon in Canadian peatlands, *Global and Planetary Change*, 53, 222-232.

Timoney, K., G. Peterson, P. Fargey, M. Peterson, S. McCanny, and R. Wein (1997), Spring ice-jam flooding of the Peace-Athabasca Delta: evidence of a climatic oscillation, *Climatic Change*, 35, 463-483.

Timoney, K. P. (2002), A dying delta? A case study of a wetland paradigm. *Wetlands*, 22, 282-300.

Trumbore, S. E., O. A. Chadwick, and R. Amundson (1996), Rapid exchange between soil carbon and atmospheric carbon dioxide driven by temperature change, *Science*, 272, 393-396.

Updegraff, K., S. D. Bridgham, J. Pastor, and P. Weishampel (1998), Hysteresis in the temperature response of carbon dioxide and methane production in peat soils. *Biogeochemistry*, 43, 253-272.

van Seters, T. E., and J. S. Price (2001), The impact of peat harvesting and natural regeneration on the water balance of an abandoned cutover bog, Quebec. *Hydrological Processes*, 15, 233-248.

Vasander, H., and A. Kettunen (2006), Carbon in Boreal Peatlands, in *Ecological Studies, Volume 188* edited by R. K. Wieder and D. H. Vitt, pp. 165-194, Springer-Verlag, Berlin, Heidelberg.

Vitt, D. H., L. A. Halsey, I. E. Bauer, and C. Campbell (2000), Spatial and temporal trends in carbon storage of peatlands of continental western Canada through the Holocene, *Canadian Journal of Earth Science*, 37, 683-693.

Waddington, J. M., P. A. Rotenberg, and F. J. Warren (2001), Peat CO₂ production in a natural and cutover peatland: Implications for restoration, *Biogeochemistry*, 54, 115-130.

Williams, R. T., and R. L. Crawford (1984), Methane production in Minnesota peatlands, *Applied and Environmental Microbiology*, 47, 1266-1271.

Winkler, J. P., R. S. Cherry, and W. H. Schlesinger (1996), The Q₁₀ relationship of microbial respiration in a temperate forest soil. *Soil Biology and Biochemistry*, 28, 1067-1072.

Wolfe, B. B., T. W. D. Edwards, and R. Aravena (1999), Changes in carbon and nutrient cycling during tree-line retreat recorded in the isotopic content of lacustrine organic matter, western Taimyr Peninsula, Russia, *The Holocene*, 9, 215-222.

Wolfe, B., T. W. D. Edwards, and H. C. Duthie (2000), A 6000-year record of interaction between Hamilton Harbour and Lake Ontario: quantitative assessment of recent hydrologic disturbance using ¹³C in lake sediment cellulose. *Aquatic Ecosystem Health and Management*, 3, 47-54.

Wolfe, B. B., T. W. D. Edwards, R. J. Elgood, and K. R. M. Beuning (2001), Carbon and oxygen isotope analysis of lake sediment cellulose: methods and applications, in *Tracking Environmental Change Using Lake Sediments. Volume 2: Physical and Chemical Techniques, Developments in Paleoenvironmental research*. edited by Last, W.M. and Smol, J.P., pp. 373-400, Kluwer Academic Publishers, Dordrecht.

Wolfe, B. B., T. L. Karst-Riddoch, S. R. Vardy, M. D. Falcone, R. I. Hall, and T. W. D. Edwards (2005), Impacts of climate and river flooding on the hydro-ecology of a

floodplain basin, Peace-Athabasca Delta, Canada since A.D, 1700. *Quaternary Research*, 64, 147-162.

Wolfe, B. B., R. I. Hall, W. M. Last, T. W. D. Edwards, M. C. English, T. L. Karst-Riddoch, A. Patterson, and R. Palmi (2006), Reconstruction of multi-century flood histories from oxbow lake sediments, Peace-Athabasca Delta, Canada. *Hydrological Processes*, 20, 4131-4153.

Wolfe, B. B., M. D. Falcone, K. Clogg-Wright, C. Mongeon, Y. Yi, B. Brock, N. St. Amour, W. Mark, and T. W. D. Edwards (2007), Progress in isotope paleohydrology using lake sediment cellulose, *Journal of Paleolimnology*, 37, 221-231.

Wolfe, B. B., T. L. Karst-Riddoch, R. I. Hall, T. W. D. Edwards, M. C. English, R. Palmi, S. McGowan, P. R. Leavitt, and S. Vardy (2007), Classification of hydrological regimes of northern floodplain basins (Peace-Athabasca Delta, Canada) from analysis of stable isotopes (^{18}O , ^3H) and water chemistry, *Hydrological Processes*, 21, 151-168.

Wolfe, B. B., R. I. Hall, T. W. D. Edwards, S. R. Jarvis, R. N. Sinnatamby, Y. Yi, and J. Johnston (2008a), Climate-driven shifts in quantity and seasonality of river discharge over the past 1000 years from the hydrographic apex of North America, *Geophysical Research Letters*, 35, L24402, doi: 10.1029/2008GL036125.

Wolfe, B. B., R. I. Hall, T. W. D. Edwards, S. R. Vardy, M. D. Falcone, C. Sjunneskog, F. Sylvestre, S. McGowan, P. R. Leavitt, and P. Van Driel (2008b), Hydroecological responses of the Athabasca Delta, Canada, to changes in river flow and climate during the 20th century, *Ecohydrology*, 1, 131-148.

Yavitt, J. B., C. J. Williams, and R. K. Wieder (1997), Production of methane and carbon dioxide in peatland ecosystems across North America: effects of temperature, aeration, and organic chemistry of peat, *Geomicrobiology Journal*, 14, 299-316.

Appendix A: ^{210}Pb , ^{137}Cs and ^{214}Bi Activity in PAD 1 CIO

Coring Date: 25-Aug-07

Total Activity - Corrected to coring date					
Depth Interval		Mid-depth (cm)	^{210}Pb (dpm/g)	^{214}Bi (dpm/g)	^{137}Cs (dpm/g)
(cm)					
0	1	0.5	6.361	1.100	0.369
1.5	2	1.75	4.442	1.569	0.711
2.5	3	2.75	3.413	1.163	0.565
3.5	4	3.75	4.426	1.179	0.668
4.5	5	4.75	3.066	1.073	0.659
5.5	6	5.75	2.803	1.967	0.536
6.5	7	6.75	2.380	1.114	0.745
7.5	8	7.75	2.169	1.375	0.739
8.5	9	8.75	2.999	1.157	0.718
9.5	10	9.75	2.756	1.569	0.599
10.5	11	10.75	2.183	1.295	0.791
11.5	12	11.75	2.718	1.549	0.577
12.5	13	12.75	2.862	1.105	0.560
13.5	14	13.75	2.830	1.579	0.647
14.5	15	14.75	2.791	0.880	0.542
15.5	16	15.75	2.667	1.578	0.649
16.5	17	16.75	2.580	1.802	0.678
17.5	18	17.75	2.912	1.706	0.684
18.5	19	18.75	2.179	1.034	0.739
19.5	20	19.75	3.578	1.489	0.782
20.5	21	20.75	2.069	1.159	0.719
21.5	22	21.75	2.179	1.508	0.730
22.5	23	22.75	1.921	1.253	0.589
23.5	24	23.75	3.769	1.462	0.665
24.5	25	24.75	2.837	0.995	0.652
25.5	26	25.75	2.213	1.479	0.593
26.5	27	26.75	1.983	1.062	0.469
27.5	28	27.75	1.601	1.503	0.497
28.5	29	28.75	1.878	1.180	0.314
29.5	30	29.75	2.095	1.661	0.317
30.5	31	30.75	2.523	1.343	0.374
31.5	32	31.75	2.181	1.745	0.495
32.5	33	32.75	2.074	1.231	0.475
33	33.5	33.25	2.280	1.602	0.469
33.5	34	33.75	2.617	1.470	0.443
34.5	35	34.75	1.857	1.031	0.370
35.5	36	35.75	2.068	1.505	0.107
36.5	37	36.75	2.679	2.206	0.069
37.5	38	37.75	1.760	1.508	0.035
38.5	39	38.75	2.377	1.458	-0.052
39.5	40	39.75	2.072	1.581	0.036
40.5	41	40.75	1.721	1.293	0.039

Depth Interval (cm)		Mid-depth (cm)	²¹⁰ Pb(dpm/g)	²¹⁴ Bi (dpm/g)	¹³⁷ Cs (dpm/g)
41.5	42	41.75	2.153	1.538	0.006
42.5	43	42.75	2.477	1.528	-0.027
43.5	44	43.75	2.027	1.637	-0.063
44.5	45	44.75	2.314	1.278	-0.024
45.5	46	45.75	2.348	1.403	-0.063
46.5	47	46.75	2.401	1.574	-0.036
47.5	48	47.75	2.272	1.862	0.011

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Appendix C: Cellulose Oxygen Isotope Analysis

PAD 1 CIO

Sample mid-depth (cm)	Year (AD)	O (%)	Rpt	Avg	S ¹⁸ O (‰)	Rpt	Avg	S ¹⁸ O _{lw} (‰)
0.25	2007.7	13.21		13.21	9.38		9.38	-18.12
0.75	2002.9	9.95		9.95	10.69		10.69	-16.84
1.25	2001.2	9.03		9.03	10.38		10.38	-17.14
1.75	1999.0	3.34		3.34	8.52		8.52	-18.95
2.75	1997.7	3.33		3.33	5.15		5.15	-22.23
3.25	1995.7	3.24		3.24	7.55		7.55	-19.89
3.75	1993.2	3.09		3.09	6.43		6.43	-20.99
4.25	1989.3	4.50		4.50	6.57		6.57	-20.85
4.75	1985.8	4.51	3.71	4.11	6.94	6.62	6.78	-20.65
5.25	1983.5	6.21		6.21	8.80		8.80	-18.67
5.75	1981.6	11.29		11.29	10.37		10.37	-17.15
6.25	1979.7	9.21		9.21	9.60		9.60	-17.90
6.75	1978.6	7.02		7.02	9.86		9.86	-17.64
7.25	1978.3	5.01		5.01	9.30		9.30	-18.19
7.75	1978.3	7.13		7.13	8.18		8.18	-19.28
8.25	1978.6	3.62		3.62	6.18		6.18	-21.23
8.75	1977.4	6.86		6.86	7.85		7.85	-19.61
9.25	1974.5	4.43		4.43	7.31		7.31	-20.13
9.75	1972.0	4.59	6.39	5.49	7.09	6.17	6.63	-20.79
10.25	1969.4	4.74		4.74	7.16		7.16	-20.28
10.75	1968.4	5.12		5.12	7.04		7.04	-20.39
11.25	1968.9	6.39		6.39	7.92		7.92	-19.54
11.75	1967.8	5.25		5.25	7.28		7.28	-20.15
12.25	1965.4	3.46		3.46	7.31		7.31	-20.13
12.75	1962.5	4.66		4.66	6.56		6.56	-20.85
13.25	1959.1	5.12		5.12	7.80		7.80	-19.65
13.75	1954.7	5.10		5.10	7.21		7.21	-20.22
14.25	1950.4	5.58		5.58	7.75		7.75	-19.70
14.75	1945.6	4.44	4.60	4.52	7.10	6.99	7.05	-20.38
15.25	1939.2	2.97		2.97	6.34		6.34	-21.07
15.75	1933.0	5.33		5.33	8.01		8.01	-19.44
16.25	1926.1	3.61		3.61	7.69		7.69	-19.76
16.75	1918.0	5.47		5.47	9.30		9.30	-18.19
17.25	1909.9	3.28		3.28	8.66		8.66	-18.81
17.75	1888.6	4.44		4.44	7.29		7.29	-20.14
18.25	1895.1	3.43		3.43	7.17		7.17	-20.27
18.75	1888.3	6.17		6.17	8.53		8.53	-18.94
19.25	1881.8	2.86		2.86	9.08		9.08	-18.41
19.75	•1875.1	3.82	3.71	3.76	6.63	6.84	6.74	-20.68
20.25	1867.9	2.69		2.69	7.86		7.86	-19.59
20.75	1861.3	3.06		3.06	6.69		6.69	-20.73
21.25	1854.9	3.51		3.51	9.43		9.43	-18.06
21.75	1848.0	2.29		2.29	5.55		5.55	-21.84
22.25	1841.2	3.42		3.42	11.34		11.34	-16.21
22.75	1834.2	3.38		3.38	6.51		6.51	-20.91

Sample mid-depth (cm)	Year (AD)	O (%)	Rpt	Avg	S ¹⁸ Q (‰)	Rpt	Avg	S ¹⁸ Q _w (‰)
23.25	1826.4	4.38		4.38	6.98		6.98	-20.45
23.75	1817.9	4.96		4.96	10.08		10.08	-17.43
24.25	1810.9	3.90		3.90	6.20		6.20	-21.21
24.75	1804.4	4.69	3.80	4.25	7.86	7.83	7.85	-19.61
25.25	1797.0	3.57		3.57	7.21		7.21	-20.22
25.75	1790.2	3.65		3.65	6.02		6.02	-21.38
26.25	1782.7	3.17		3.17	5.44		5.44	-21.95
26.75	1775.7	4.51		4.51	10.11		10.11	-17.40
27.25	1768.4	2.88		2.88	6.35		6.35	-21.06
27.75	1760.6	3.58		3.58	7.10		7.10	-20.33
28.25	1752.3	3.36		3.36	8.89		8.89	-18.59
28.75	1744.4	3.17		3.17	4.70		4.70	-22.66
29.25	1735.9	1.49		1.49	2.00		2.00	-25.29
29.75	1727.8	3.09	3.89	3.49	5.71	10.78	8.24	-19.22
30.25	1719.4	2.37		2.37	4.03		4.03	-23.31
30.75	1712.4	3.29		3.29	6.32		6.32	-21.09
31.25	1705.6	2.74		2.74	5.05		5.05	-22.33
31.75	1698.7	2.45		2.45	5.58		5.58	-21.81
32.25	1691.4	2.23		2.23	5.49		5.49	-21.90
32.75	1683.5	2.94		2.94	4.94		4.94	-22.44
33.25	1676.2	3.81		3.81	9.67		9.67	-17.83
33.75	1668.4	3.54		3.54	6.06		6.06	-21.35
34.25	1659.9	2.64		2.64	8.79		8.79	-18.69
34.75	1652.4	3.83	3.15	3.49	5.71	4.86	5.28	-22.10
35.25	1642.7	3.81		3.81	7.64		7.64	-19.80
35.75	1634.3	3.12		3.12	5.24		5.24	-22.14
36.25	1626.9	3.94		3.94	6.84		6.84	-20.58
36.75	1617.9	2.35		2.35	5.35		5.35	-22.03
37.25	1610.0	4.17		4.17	6.93		6.93	-20.49
37.75	1601.1	4.99		4.99	7.73		7.73	-19.72
38.25	1593.7	5.14		5.14	8.33		8.33	-19.13
38.75	1585.2	4.82		4.82	7.97		7.97	-19.49
39.25	1577.1	4.46		4.46	6.99		6.99	-20.44
39.75	1569.8	4.27	5.30	4.78	6.19	6.83	6.51	-20.90
40.25	1562.1	2.90		2.90	7.74		7.74	-19.71
40.75	1553.9	4.69		4.69	11.62		11.62	-15.93
41.25	1547.1	3.28		3.28	8.31		8.31	-19.15
41.75	1538.5	2.84		2.84	6.68		6.68	-20.74
42.25	1530.0	8.57		8.57	9.84		9.84	-17.67
42.75	1521.5	2.42		2.42	5.46		5.46	-21.93
43.25	1512.4	2.41		2.41	6.58		6.58	-20.83
43.75	1502.5	5.29		5.29	10.65		10.65	-16.88
44.25	1492.7	3.24		3.24	11.90		11.90	-15.66
44.75	1482.2	3.12	1.59	2.36	6.83	7.69	7.26	-20.17
45.25	1472.8	3.33		3.33	8.85		8.85	-18.62
45.75	1463.1	2.10		2.10	6.42		6.42	-20.99
46.25	1453.7	3.17		3.17	6.59		6.59	-20.82
46.75	1442.7	3.28		3.28	11.44		11.44	-16.11

Sample mid-depth (cm)	Year (AD)	$\delta^{18}O$ (‰)	Rpt	Avg	$\delta^{18}O$ (‰)	Rpt	Avg	$\delta^{18}O_w$ (‰)
47.25	1432.9	4.39		4.39	10.78		10.78	-16.75
47.75	1423.9	4.59		4.59	9.91		9.91	-17.60

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