Lakes of the Peace-Athabasca Delta:

Controls on nutrients, chemistry, phytoplankton, epiphyton and deposition of polycyclic aromatic compounds (PACs)

by

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Author's Declaration

I hereby declare that I am the sole author of this thesis. This is a true copy of the thesis, including any required final revisions, as accepted by my examiners.

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Abstract

Floodplain lakes are strongly regulated by river connectivity because floodwaters exert strong influence on the water balance, the physical, chemical and biological limnological conditions, and the influx of contaminants. The Peace-Athabasca Delta (PAD) in northern Alberta (Canada) is a hydrologically complex landscape and is an important node in the upper Mackenzie River Drainage Basin. The ecological integrity of the PAD is potentially threatened by multiple environmental stressors, yet our understanding of the hydroecology of this large floodplain remains underdeveloped. Indeed, ever since the planning and construction of the WAC Bennett Dam (1960s), concerns have grown over the effects of upstream human activities on the lakes of the PAD. More recently, concerns over the health of the PAD have intensified and come to the fore of national and international dialogue due to water abstraction and mining and processing activities by the rapidly expanding oil sands industry centred in Fort McMurray Alberta. Currently, widespread perception is that upstream human activities have reduced water levels and frequency of flooding at the PAD, which have lowered nutrient availability and productivity of perched basin lakes, and have increased supply of pollutants from oil sands. However, these perceptions remain based on insufficient knowledge of pre-impact conditions and natural variability. Current and past relations between hydrology and limnology of PAD lakes are mostly undocumented, particularly during the important spring freshet period when the effects of river flood waters are strongest. Similarly, knowledge of the deposition of oil-sands-related contaminants in the PAD remains insufficient to determine whether anthropogenic activities have increased the deposition of important oil-sands-related contaminants such as polycyclic aromatic compounds (PACs) relative to natural processes. Such knowledge gaps must be filled to achieve effective monitoring, policy and governance concerning impacts of industrial

development and the protection of human and environmental health within the PAD and Mackenzie drainage basin. This thesis examines the effects of river flooding (and the lack of) on water clarity, nutrients, chemistry, phytoplankton abundance, epiphyton community composition and the deposition of polycyclic aromatic compounds (PACs) in lakes of the Peace-Athabasca Delta.

To determine the role of flooding on contemporary epiphytic diatom communities (an abundant and diverse guild of primary producers in PAD lakes), a field experiment was conducted examining the community composition and abundance of epiphytic diatoms in four PAD lakes. Two of these four lakes had received floodwaters that spring and two had not. Epiphytic diatom communities in each lake were sampled during the peak macrophyte biomass period (summer) from two macrophyte taxa (*Potamogeton zosteriformis*, *P. perfoliatus var. richardsonii*) and from polypropylene artificial substrates previously deployed that spring. A two-way analysis of similarity (ANOSIM) test identified that epiphytic diatom community composition differed between lakes that flooded and those that did not flood. From the use of similarity percentage (SIMPER) analysis, diatom taxa were identified that discriminate between flooded and non-flooded lakes. The relative abundance of 'strong flood indicator taxa' was used to construct an event-scale flood record spanning the past ~180 years using analyses of sedimentary diatom assemblages from a closed-drainage lake (PAD 5). Results were verified by close agreement with an independent paleo-flood record from a nearby flood-prone oxbow lake (PAD 54) and historical records. Comparison of epiphytic diatoms in flooded and non-flooded lakes in this study provides a promising approach to detect changes in flood frequency, and may have applications for reconstructing other pulse-type disturbances such as hurricanes and pollutant spills. Additionally, this study demonstrates that artificial substrates can provide an effective bio-monitoring tool for lakes of the PAD and elsewhere.

To improve our understanding of the hydrolimnological responses of lake in the PAD to flooding, repeated measurements over three years (2003-05) were made on a series of lakes along a hydrological gradient. This allowed the role of river flooding to be characterized on limnological conditions of lakes and to identify the patterns and timescales of limnological change after flooding. River floodwaters elevate lake water concentrations of suspended sediment, total phosphorus (TP), SO_4 and dissolved Si (DSi), and reduce concentrations of total Kjeldahl nitrogen (TKN), DOC and most ions. River flooding increases limnological homogeneity among lakes, because post-flood conditions are strongly affected by the river water properties. After floodwaters recede, limnological conditions become more heterogeneous among lakes in response to diversity of local basin influences (geology, slope, vegetation, depth, fetch, and biological communities and processes), and limnological changes occur at two distinct timescales. In the weeks to months after flooding, water clarity increases as suspended sediments and TP settle out of the water column. In the absence of flooding for many years to decades, evaporative concentration leads to an increase in most nutrients (TKN, inorganic N, and dissolved P), DOC and ions. Contrary to a prevailing paradigm, these results suggest that regular flooding is not required to maintain high nutrient concentrations. In light of anticipated declines in river discharge, limnological conditions in the southern Athabasca sector will become increasingly less dominated by the short-term effects of flooding, and resemble nutrient- and solute-rich lakes in the northern Peace sector that are infrequently flooded.

To determine the roles of the Athabasca River and atmospheric transport as vectors for the deposition of PACs in the PAD, sediment cores spanning the last ~200 years were collected

from three lakes within the delta. A closed-drainage basin elevated well above the floodplain (PAD 18) was selected to determine temporal patterns of change in PAC concentration due to atmospheric deposition and within-basin production of PACs. Known patterns of paleohydrological changes at the other two lakes (PAD 23 and 31) were used to assess the role of the Athabasca River in delivering PACs to the Athabasca Delta during the ~200 year. Well-dated sediment core samples were analysed for 52 alkylated and non-alkylated PACs (method EPA 3540/8270-GC/MS). Sediments deposited in the non-flood prone lake (PAD 18) contained lower concentrations of total PACs compared to sediments deposited during flood-prone periods in the other study lakes, and were dominated by PACs of a pyrogenic rather than bitumen origin. Multivariate analysis of similarity tests identified that the composition of PACs differs between sediments deposited during not flood-prone and flood-prone periods. Subsequent Similarities Percentage (SIMPER) analysis was used and identified seven PACs that are preferentially deposited during flood-prone periods. These seven PACs are bitumen-associated, river-transported and account for 51% of the total PACs found in oil-sands sediment. At PAD 31, which has been flood-prone both before and since onset of Athabasca oil sands development, identified no measureable differences in both the proportion and concentration of the river-transported indicator PACs in sediments deposited pre-1940s versus post-1982. Our findings suggest that natural erosion of exposed bitumen along the banks of the Athabasca River and its tributaries is the main process delivering PACs to the Athabasca Delta, and that the spring freshet is a key period for contaminant mobilization and transport. Such key baseline environmental information is essential for informed management of natural resources and human-health concerns by provincial and federal regulatory agencies and industry, and for designing effective long-term monitoring and surveillance programs for the lower Athabasca

River watershed in the face of future oil sands development. Further monitoring activities and additional paleolimnological studies of the depositional history of PACs and other oil-sands- and non-oil-sands-related contaminants is strongly recommended.

Overall, results of this research identify that river flooding exerts strong control on physical, chemical and biological conditions of lakes within the PAD. However, contrary to prevailing paradigms, the PAD is not a landscape that has been adversely and permanently affected by regulation of the Peace River and industrial development of the oil sands along the Athabasca River. Instead, data from contemporary and paleolimnological studies identify that natural processes continue to dominate the delivery of water and contaminants to the delta. Regular and frequent flooding is not essential to maintain the supply of nutrients and productivity of delta lakes, which has been a widespread paradigm that developed in the absence of objective scientific data. Instead, nutrient concentrations rise over years to decades after flooding and lake productivity increases. During the thesis research, novel approaches were developed and demonstrated to be effective. Namely, new artificial substrate samplers were designed for aquatic biomonitoring that accrue periphyton and can identify the occurrence of flood events. Also, paleolimnological methods were employed to characterize the composition and concentration of PACs supplied by natural processes prior to oil sands industrial activity, which serves as an important benchmark for assessing industrial impacts. These are effective methods that can be employed to improve monitoring programs and scientific understanding of the factors affecting this world-renowned landscape, as well as floodplains elsewhere.

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Dedication

I dedicate this thesis to my loving and supportive Wife Mandy.

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Chapter 1
General Introduction

1.1 Anthropogenic influences: from landscapes to global impacts

Humanity's influence on the Earth's natural processes is recognized to be so extensive and wide reaching that it is now widely accepted that we are in a new geological epoch labeled as the Anthropocene (Zalasiewicz *et al*., 2010, 2011; Vince, 2011). The modification of natural landscapes and sedimentary processes is a large and recognizable part of humanity's influence on the planet (Hooke, 2000; Syvitski *et al*., 2005; Wilkinson, 2005; Grimm *et al*., 2008) and a key basis for the designation of the Anthropocene Epoch (Zalasiewic *et al*., 2010; 2011; Price *et al*., 2011; Vince, 2011). Freshwater landscapes and their contributing basins have long been affected by anthropogenic influences. They are often the focal points of municipal, agricultural and industrial development due to access to fresh water and food, as well as aiding the transportation of people and goods (Jungwirth *et al*., 2002; Gummer *et al*., 2000, 2006; Grimm *et al*., 2008).

In northern freshwater landscapes in Canada, human activities arrived later than in many other places on Earth (late 1700s to early 1900s) and they remain generally less intense than in more temperate systems. Nevertheless, northern freshwater landscapes are increasingly under pressure due to growing forestry, mining, industrial, municipal and agricultural development (Wrona *et al*., 2000; Gummer *et al*., 2000, 2006). Furthermore, these systems are considered especially vulnerable to effects of global climate change (Prowse *et al*., 2006b; Schindler and Smol, 2006). Increasing temperatures are expected to have a strong effect on the ecohydrology of high-latitude systems via changes in the timing and quantity of snow and ice melt contributions to streamflow (Marsh and Hey, 1989; English *et al*., 1997; Prowse and Conly, 1998; Schindler and Smol, 2006; Prowse *et al*., 2006a,b; Wolfe *et al*., 2007a).

The largest river in Canada, the Mackenzie, is also North America's largest source of freshwater flow to the Arctic Ocean (Rouse *et al*., 2003; Woo and Thorne, 2003). An important node in the Mackenzie River Drainage Basin is the Peace-Athabasca Delta (PAD). Approximately one third of the Mackenzie River's mean annual discharge of 325 km^3/y (Gummer *et al*., 2006; Schindler and Smol 2006) originates upstream of the PAD, as does the majority of the human development (Gummer *et al*., 2006).

1.2 The Peace-Athabasca Delta

The Peace-Athabasca Delta (PAD) is situated in northern Alberta, Canada, at the confluence of the Peace, Athabasca, Richardson and Birch rivers (Figure 1.1). It is one of three major fluviodeltaic landscapes within the Mackenzie River Drainage Basin: the Mackenzie Delta (MD, ~68^{o} 30'N), the Slave Delta (SD, ~61^{o} 20'N) and the Peace-Athabasca Delta (PAD, ~58^{o} 40'N). A dominant feature of all three of these deltas is an abundance of shallow, productive, macrophyte-dominated lakes and ponds. These lakes experience varying degrees of hydrologic connectivity and regularity of river flooding (Marsh and Hey, 1989; Wolfe *et al.*, 2007b, Sokal *et al.*, 2008; Squires *et al.*, 2009). Extensive flooding of the three deltas predominantly occurs during the spring freshet due to ice-jams that form at meander bends or shallow-river reaches. The ice-jams lead to large-scale overland flooding that recharges and flushes the perched basin lakes beyond what a similar level of river discharge is capable of during the ice-free season

(Prowse, 1986; Prowse and Conly 2000; Prowse *et al*., 2002; Beltaos *et al*., 2006; Emmerton *et al*., 2007).

The PAD is the world's largest freshwater boreal delta and covers an area of ~6,000 km^2 (Peters *et al*., 2006a). The landscape is recognized as a UNESCO World Heritage Site and a Ramsar Wetland of International Importance for its ecological and cultural significance. The PAD provides important habitat for migratory birds and serves as a key node for four North American flyways used by waterfowl (MRBC, 1981; Prowse and Conly, 2000). Historically the PAD and Fort Chipewyan (which is the oldest town in Alberta, established in 1788) were major focal points of the fur trade (Timoney 2009). Today, the PAD continues to provide important habitat for furbearing mammals (muskrat, beaver, mink), as well as major game animals (moose, bison) and large predators (black bears, wolves, wolverines). The PAD continues to be highly important for hunting and fishing by First Nations (Mikisew Cree, Athabasca Chipewyan), and Métis. Being a nexus of two major rivers and adjoining Lake Athabasca, the 8th largest lake in Canada, the PAD provides important fish habitat (Bradford and Hanson 1990). Specifically, lakes Claire and Mamawi are important spawning areas for goldeye (*Hiodon alosoides*) (Donald and Aitken, 2005). The Athabasca sector of the delta (Maybelle River via Lake Richardson) is a major spawning area for walleye (*Sander vitreus*) (Bidgood 1971).

The PAD is situated in a lowland bordered by Lake Athabasca to the east, the Canadian Shield to the northeast, the Birch Mountains to the southwest, the Caribou Mountains to the west and the Athabasca sand dunes to the south. Granitic bedrock of the Canadian Shield forms small inliers that rise above the delta plain, and are located near and north of the 'fork' where channels of the Quatre Fourches River intersect. These bedrock inliers increase in size and abundance to the northeast, where they rise over 50 m above the delta plain in some places. Along the Peace

River west of the Quatre Fourches River intersection and to the north of the PAD, outcrops of Devonian limestone are present along with Devonian gypsum farther west. Both of these sedimentary rock units extend southwards, dipping underneath the delta where they are deeply overlain with alluvial sediment. Mesoproterozoic (Helikian) sandstone underlies the south and southeast section of the PAD and extends for much of the southern shore of Lake Athabasca (Hamilton *et al*., 1998).

The PAD includes the northern Peace Delta (1685 km^2), the southern Athabasca Delta (1970 km^2), the western Birch River Delta (170 km^2) and a central sector dominated by four large, shallow lakes (Claire, Baril, Mamawi and Richardson, see Figure 1.1). These lakes are the largest remnants of a shallow former embayment of Lake Athabasca that once existed across what is now the PAD (Johnston *et al*., 2010). Progressive infilling by levees and river sediment, which began forming the delta complex in the early Holocene ~8.3k years ago, have led to the dissection and terrestrialization of much of this former embayment of Lake Athabasca (Smith, 1994). Lake Athabasca is a remnant of glacial Lake McConnell, which occupied the basins of what are now lakes Athabasca, Great Slave and Great Bear during 11.8 to 8.3 k years BP. Glacial Lake McConnell held water levels at times >100 m above the current level of Lake Athabasca (~209 m above sea level) (Smith, 1994).

Except for the elevated river levees, the Athabasca Delta has very low topographic relief, and is an active delta that floods frequently. In contrast, the Peace Delta is a relict delta that has greater topographic relief than the Athabasca Delta. Consequently, lakes in the northern Peace sector generally receive river floodwaters only during ice-jams that occasionally form on the Peace River (Prowse and Conly, 2000). In contrast, lakes of the Athabasca sector may also flood during the open-water season.

The low relief and countless meander scars within the delta have given rise to hundreds of shallow waterbodies. Most of them are small and are defined as shallow-water wetlands (Warner and Rubec, 1997). For simplicity, hereafter all waterbodies are referred to as lakes. The lakes span a broad range of hydrological conditions largely related to differences in the role of river flooding and evaporation on lake water balance. They have been functionally categorized as open-, restricted- or closed-drainage basins (Pietroniro *et al*., 1999; Wolfe *et al*., 2007b). Open-drainage lakes are perennially connected to the river network. Restricted-drainage lakes periodically receive river waters during floods. Closed-drainage lakes do not receive any river input except during major ice-jam flood events.

1.3 Natural and human drivers of change in the Peace-Athabasca Delta

This thesis focuses on improving our understanding of how the PAD responds, and has responded to both natural and human drivers of change. This knowledge is needed to help address current and future concerns about human impacts in the PAD and is also relevant for effective stewardship of other downstream and upstream landscapes. In particular, there is a lack of knowledge concerning the limnology of PAD lakes and how hydrological processes affect delta lake physical, chemical and biological conditions, as well as the transport and deposition of pollutants. This knowledge of system behaviour is needed to assess how PAD lakes respond to changes in flood frequency and water levels. And, it provides essential information to characterize baseline, or pre-development, conditions required to assess system alteration due to human and climatic factors.

Of the three major deltas of the Mackenzie drainage system, concerns are greatest at the Peace-Athabasca Delta about human impacts and hydroecological “health”. This is likely due to the greater proximity to human population centres and earlier onset of industrial activities upstream of the PAD compared to the SD and MD (see Gummer *et al*., 2000; Wrona *et al*., 2000). While many different types of human disturbance exist within the catchment of the Peace and Athabasca rivers (i.e., pulp and paper mill effluent, nutrient enrichment due to agriculture and sewage treatment plants), two highly controversial energy development projects upstream of the PAD have most often been implicated for negative impacts. The WAC Bennett Dam on the Peace River in British Columbia regulates river discharge while generating electricity. This has altered the downstream seasonal pattern of discharge and river stage hydrograph, which is reduced in summer and increased in winter compared to natural flow conditions (Prowse and Conly, 1998). The Athabasca Oil Sands mining and production facilities on the Athabasca River generate several environmental concerns: large-scale land disturbance, high rates of water consumption, generation of large tailings ponds (which may leak) as well as release of airborne and waterborne contaminants (Timoney and Lee, 2009; Schindler 2010; Gosselin *et al*., 2010; Environment Canada 2011a). These industrial developments began in the late 1960s, a period when climatic changes had altered the quantity and timing of river discharge and flood frequency. Yet, the importance of climate on the hydroecology of the PAD and the Mackenzie Drainage system has been underappreciated (Prowse and Conly, 2000; Timoney 2002; Prowse *et al*., 2006a,b). Of the multiple hydroecological stressors that may affect the PAD, climate change is likely to be the most significant long-term concern (Wolfe *et al*., 2008a, 2011). Furthermore, climatic effects will overlay other drivers of hydroecological change, and need to be accounted for before we can begin to attribute ecosystem degradation to effects of industrial development.

While there has been growing recognition of the importance of climate as a driver of hydrology in northern aquatic systems (Prowse and Conly, 2000; Prowse *et al*., 2006a,b), the implications for the ecology of floodplain landscapes is not well understood. To a large extent, this is due to a lack of observational studies of sufficient spatial and temporal scales that assess linkages between hydrology and limnological status. Furthermore, insufficient duration of long-term monitoring data creates challenges to identify accurately trends in water levels, flood frequency, water quality and the transport and deposition of contaminants in northern floodplain landscapes, as well as their causes. Contemporary field studies are needed to discern the effects of hydrologic gradients on the limnology of PAD lakes, while paleolimnological studies are needed to characterize natural variability and system responses to differing climatic conditions and human activities.

The following sections provide background information to outline the nature of major controversies and suspected ecohydrologic stressors acting in the PAD: 1) the WAC Bennett Dam, 2) climate change, 3) effects of river flooding on nutrient availability and productivity in PAD lakes, and 4) effects of Athabasca Oil Sands development on the deposition of polycyclic aromatic compounds (PACs) in the PAD. The following sections examine relevant literature on the above issues and identify research questions and topics that are addressed in this thesis.

1.3.1 The WAC Bennett Dam, Lake Athabasca water levels and ice-jam flooding in the PAD

Controversy has swirled around the PAD ever since the planning and construction of the WAC Bennett Dam in British Columbia more than 40 years ago. Declining water levels within the open-drainage system (particularly that of summer water levels) of the PAD and perceived reductions in the recharge of the perched (i.e., restricted- and closed-drainage) lakes by river floodwaters lie at the centre of the controversies. River flooding was assumed to be required to maintain water levels, nutrient supplies and aquatic productivity of the perched basins in this semi-arid region (Fuller and LaRoi, 1971; Dirschl, 1972).

The paradigm of the PAD as a "dying delta" was brought to the public eye in 1972 following the documentary "Death of a Delta" (Radford, 1972), and in conjunction with some studies and reports conducted during 1970-72 (PPADS, 1971; PADPG, 1973; Gill, 1973) The filling of the Bennett Dam's Williston Reservoir began in December of 1967 and was completed in 1971. During the 1968-1971 filling period, the summer maximum water levels in Lake Athabasca (and presumably the open-drainage network of the PAD) dropped ~1.5 m and ~1 m compared to the 1960-67 and long-term (1934-1967) averages of summer maximum water levels, respectively (Kellerhals, 1971).

The drop in water level of the open-drainage system of the PAD led to a ~28% reduction in the total area of the open-drainage lake area equaling a loss of ~450 km^2 of open-water habitat. The reduction in area of some of the more shallow open-drainage lakes was much more extreme (Dirschl, 1971). The large areas of former lake bottom exposed in 1968 as mud flats transitioned to closed meadow by the summer of 1969, and clear signs of willow encroachment were seen by the summer of 1970 (Dirschl, 1971). The vegetation succession trends were expected to continue with little chance of reversal, based on Dirschl's (1971) perceptions were that water levels of Lake Athabasca and the open-drainage network of the PAD were not expected to improve once the filling of the Williston Reservoir was to be completed in 1971. This forecast was made despite the expectation that Peace River discharge post-1971 was anticipated to be more than double that of the 1968-1971 reservoir filling period of low summer water levels (Dirschl, 1971).

Analysis of the hydrologic controls on Lake Athabasca by Kellerhals (1971) concluded that ~0.6 m of the decline in summer maximum water-levels was due to the hydrologic control of the Bennett Dam and the remainder (~0.9 m) was due to climatic factors. Timoney (2002) noted that Lesser Slave Lake levels (unaffected by the Bennett Dam) underwent a similar drawdown during this period, supporting a regional climatic effect beyond effects of the Bennett Dam on Lake Athabasca during the 1968-1971 reservoir filling period. Kellerhals (1971) also concluded the alteration of the seasonal hydrograph by the Bennett Dam would make this ~0.6 m reduction in summer peak levels permanent and that measures should be sought to counteract this effect. Rock weirs were installed on Rivière des Rochers and Revillon Coupé in 1976 to restrict Lake Athabasca outflow and restore summer minimum water levels of Lake Athabasca and the PAD to pre-regulation levels. The weirs have been reported to be mostly successful towards achieving this goal. But, they have also had the effect of raising winter low water levels above pre-regulation levels, thus reducing the seasonal amplitude of water levels in the PAD and Lake Athabasca (Prowse and Conly, 2002). The rock weirs, while effective at raising minimum and average water levels of the open-drainage portion of the PAD (Lakes Athabasca, Claire, Mamawi and Richardson), did not exert much effect on perched basin lakes (restricted- and closed-drainage) of the PAD (Prowse and Conly, 2002; Timoney, 2002). While not fully appreciated during the 1970s, recharge and flushing of perched basin lakes is primarily achieved during the spring freshet when mechanical breakup of river ice may result in ice-jams on the Peace River. This process has the potential to create very high water levels and flooding of the higher upland areas and perched basins of the PAD (Prowse and Lalonde, 1996; Prowse and Conly, 1998).

Timoney (2002) noted that the paradigm of a dying delta due to hydrological control imposed by the Bennett Dam (1180 km upstream of the PAD) has heavily influenced the early literature (PPADS, 1971, PADPG, 1973; Gill, 1973) and subsequent papers (see Rosenberg *et al*., 1997; Schindler, 1998) of the delta resulting in the *a priori* assumption that all detected changes in the delta are due to the dam and are negative. Furthermore, Timoney (2002) concluded objective investigation of the cause for observed changes was generally lacking. Similarly, variability and timescales of natural processes were often overlooked according to Timoney (2002). Schindler, stated in a synthesis article (Schindler, 1998) that "the… Bennett Dam on the Peace River reduced spring flows to the point at which ice jams no longer occurred on the lower Peace. As a result, spring floods did not rejuvenate the primary successional areas of the Peace-Athabasca Delta." However, while the WAC Bennett Dam was completed in 1968, the PAD did flood extensively due to ice-jams in 1972 and 1974 (PADPG, 1973, MRBC, 1981; Prowse and Lalonde, 1996) and then again in 1996 and 1997 (Prowse and Conly, 2000; Peters *et al*., 2006a). Clearly ice jams and flooding of the PAD have not ceased to occur due to the WAC Bennett Dam. A large part of the controversy over the perceived negative alteration of the natural flood regime and water levels was a lack of knowledge of the natural flood regime and water levels, the range of natural variability and what factors drive the hydrology of the delta.

A history of high water events spanning 1803-1996 for the PAD was developed from historical documents and local Traditional Knowledge (PADTS, 1996). This reconstruction showed that the 21 years without a major flood (1974-96) after installation of the Bennett Dam, while ~double that of the long-term average of ~10-years between major flood events, was not unprecedented. Similarly long periods (1854-1876, 1836-1854) between major floods did occur in the past (PADTS, 1996). More recently, Wolfe *et al*. (2006) reconstructed ~180 and ~300 years of flood history from sedimentary records collected from two oxbow lakes adjacent to major flood distributaries of the Peace River. The flood reconstructions proved highly similar to those developed from Traditional Knowledge and historical sources, and revealed multiple multi-decadal intervals without major flood events during both the 18th and 19th centuries (Wolfe *et al*., 2006). Furthermore, the brief historical record of Lake Athabasca water level shows that it experienced low water levels during 1944-46 (Bennett, 1971; Kellerhals, 1971; Dirschl, 1973) similar to those during the 1968-71 filling period of the Williston Reservoir. Tree-ring based reconstructions of Lake Athabasca water levels (Stockton and Fritts, 1973a,b; Meko, 2006) indicate periods of low inferred water levels have occurred during the past ~200 years similar to those observed during the 1968-71 reservoir filling period.

These multiple and independent lines of evidence demonstrate that the PAD has naturally experienced low water levels and periods of low flood frequency in the absence of human influences. It also indicates that the low water period of 1968-71, while certainly a stress on some communities of the PAD and the people of Fort Chipewyan, was not outside the range of natural variability. While we may expect the modification of the seasonal hydrograph of the Peace River by the Bennett Dam to have some effect on the hydrolimnology of the PAD (Beltaos *et al*., 2006; Prowse *et al*., 2006b), the effect is not as clear or as obviously disruptive of natural deltaic processes as has sometimes been claimed (Rosenberg *et al*., 1997; Schindler, 1998). Timoney (2002) found, following both a quantitative and qualitative assessment of the health of the PAD, it to be largely free of human influences, primarily under the influence of natural processes and predominantly healthy. Based on these findings, Timoney (2002) concluded that the paradigm of the PAD as a dying delta should be discarded and that the new paradigm should be that of the PAD as healthy and largely responding to natural processes and not human impacts.

1.3.2 Climate as a driver of future and past changes in Lake Athabasca water levels and ice-jam flooding of PAD

An emerging concern is anthropogenically induced climate change, which is expected to reduce water flux and alter the timing of river discharge (Rouse *et al*., 1997; Schindler, 2001; Schindler and Donahue, 2006; Wolfe *et al*., 2008a, 2011), factors which likely will lower the likelihood of ice-jam events and flooding of the PAD (Beltaos *et al*., 2006). As mentioned previously, multiple lines of evidence have shown past periods of naturally low water levels and long time intervals between floods (Bennett, 1971; PADTS 1996; Peters and Prowse 2006; Wolfe *et al*., 2008a,b, 2011; Johnston *et al*., 2010). These and other findings have led to the recognition that variations in climate play a strong role in the flood dynamics of the PAD (Peters and Prowse, 2006; Prowse *et al*., 2006a,b; Wolfe *et al*., 2008a, 2011; Timoney, 2009; Hugenholtz *et al*., 2009; Johnston *et al*., 2010).

Reconstructions of past Lake Athabasca water levels (Wolfe *et al*., 2008a, 2011; Johnston *et al*., 2010) have provided some of the most dramatic evidence for the role of headwater climate in regulating the extent of open-drainage habitat in the PAD. Throughout the last thousand years, the highest water levels for Lake Athabasca occurred during the Little Ice Age (LIA; ~1600-1900 CE) and were ~2.3 m above average historical levels (~last 75 years). Since then, water levels have declined with reduction of high elevation glaciers and snowpacks in the Rocky

Mountain headwater region. Over the last ~5200 years, only one other similarly prolonged period of high water levels occurred (~2000-1500 BP, see Wolfe *et al*., 2011). The majority of the 5200 year record infers Lake Athabasca to have been ~2 - 4 m below that of the 20th century water levels. Headwater climate (see Edwards *et al*., 2008) controlling glacier mass and snowpacks is expected to control both the timing and volume of discharge on the Peace and Athabasca rivers, and as a result, the water level of Lake Athabasca (Schindler and Donahue, 2006; Wolfe *et al*., 2008a, 2011; Johnston *et al.*, 2010). With continued decline of Rocky Mountain glaciers and snowpacks (Schindler and Donahue, 2006; DeBeer and Sharp, 2007), we are most likely heading into a period of much reduced water levels, not only in the PAD but likely for much of western North America (Schindler and Donahue, 2006; Edwards *et al*., 2008; Wolfe *et al*., 2008a, 2011; Johnston *et al*., 2010). The striking implications of this reconstruction is that Canadian society developed during a period of higher water availability than has been the norm for the last >5000 years, so may not be prepared for significant reductions in water availability that future conditions will likely provide.

For reconstructing past hydrologic regimes of the PAD, lake sediment records have proven to be an invaluable archive. The paleolimnological approach provides the temporal perspective that has allowed identification of the drivers of change in the PAD (Hall *et al*., 2004; Wolfe *et al*., 2005, 2006; 2008a,b, 2011; Johnston *et al*., 2010; Sinnatamby *et al*., 2010). However, to date, we have been unable to reconstruct flood event records for the elevated perched basin lakes where the magnetic susceptibility method (successfully applied in low-lying oxbow lakes, see Wolfe *et al*. 2006) has not proven effective because of the higher organic content of these sediments. Flood history of the more elevated PAD lakes would be useful in providing additional information on the influence and timing of past ice-jam floods in the more elevated portions of the PAD.

1.3.3 Diatom communities, a potential tool for constructing flood records and bio-monitoring of PAD lakes

While supply of magnetic minerals is low to perched basins, sedimentary diatom remains are plentiful and may effectively record occurrence of past flood events, because floods may deliver river diatoms as well as potentially alter habitat availability based on observed physical, chemical and biological differences between open-drainage and closed-drainage lakes in the PAD. Open-drainage lakes with continuous river inputs are turbid, have lower concentrations of dissolved nutrients and support only sparse growth of macrophytes. Here, diatom communities are dominated by epipsammic taxa that are competitive in low-light environments and by taxa common in river plankton (Hall *et al*., 2004; Sokal *et al*., 2008, 2010). In contrast, closed-drainage lakes have clear water, high concentrations of dissolved nutrients and prolific macrophyte beds. Consequently, diatom assemblages are dominated by epiphytic taxa (Hall *et al*., 2004; Sokal *et al*., 2008, 2010). Paleolimnological studies have exploited these features to reconstruct past changes in lake hydrology, but have been limited to broad-scale interpretations of shifts between more closed-drainage and open-drainage conditions (e.g., Hall *et al*., 2004, Wolfe *et al*., 2005; Johnston *et al*., 2010; Sinnatamby *et al*., 2010). Diatom communities evidently respond to persistent (multi-annual to multi-decadal) differences in lake water conditions. Such gradual (but directional) or sudden state changes in lake hydrology can be characterized as “ramp” or “press” disturbance, while a flood event acts as a “pulse” disturbance (*sensu* Lake, 2000). The effects of a flood-pulse are likely to be limited in duration and more subtle in terms of its effect on average lake conditions than a state change between closed- and open-drainage conditions. Nevertheless, it is hypothesized that a flood-pulse would alter lake water conditions sufficiently to have some recognizable effect on diatom community composition.

At this time, our understanding of the effects and persistence of flood-pulse effects on the limnology and biological communities such as diatoms in PAD lakes remains inadequate for the fine-scale interpretation of discrete flood-events. Consequently, there is a need to develop a bio-monitoring method that can examine concurrent diatom community-environment relations on an intra-annual to annual time period relevant to the timescales of river flood events. Collections of epiphytic diatom community samples representative of both flooded and non-flooded lakes accrued during the pertinent time period could be obtained by the deployment and subsequent collection of submersed artificial substrates. However, there remains some contention on how representative artificial substrates are of natural surfaces (Amireault and Cattaneo, 1992). This issue should be investigated in PAD lakes before a large-scale application of artificial substrates can be used as a research tool in the delta with confidence.

Chapter 2 of this thesis, entitled ***"Epiphytic Diatoms as Flood Indicators",*** serves two major research goals. The first goal of this chapter was to compare epiphytic diatom communities on artificial substrates versus two common macrophyte species and to assess whether artificial substrates sufficiently mimic natural substrates for use as a research and bio-monitoring tool for lakes of the PAD. Artificial substrates could provide advantages for comparing epiphytic communities among lakes (e.g., standardization of colonization time, water depth, and factors that promote host-specificity), relative to sampling diatoms growing on natural (*in situ*) macrophytes. They also greatly increase the ease of obtaining the necessarily large sample mass required for analysis of contaminants. These features would increase the utility of epiphytic algal communities for bio-monitoring programs.

The second objective of this chapter was to test whether epiphytic diatom community composition and abundance differed between lakes that did or did not receive floodwaters. If significant differences in contemporary epiphytic diatom community composition between flooded and non-flooded lakes are found to exist, can we identify diatom indicator taxa that could be used to reconstruct flood history for closed-drainage lakes? Previously, analysis of lake sediment diatom communities have been found useful in the PAD to distinguish changes in lake hydrology (closed- versus more open-drainage conditions; see Hall *et al*., 2004, Wolfe *et al*., 2005; Johnston *et al*., 2010). In contrast,-identification of discrete flood events has been possible using magnetic susceptibility in sediments of restricted-drainage oxbow lakes (Wolfe *et al*., 2005, 2006, 2008a), which has proven an invaluable tool in reconstructing a history of ice-jam flood events, but only from a low elevation area of the PAD adjacent to major distributary channels. If the epiphytic diatom community could be shown to change in predictable ways in response to flooding of closed-drainage lakes, then it may be possible to reconstruct flood histories from lakes which are typically both more remote from distributary channels, and in more elevated portions of the delta. Thus, the second research goal of Chapter 2 is to provide complementary flood history information about the extent and penetration of past flood events into an upland closed-drainage lake (PAD 5).

1.3.4 Hydrolimnology and flooding of PAD lakes

A major gap in our knowledge is the consequences of altered flood frequency on hydrolimnological conditions of lakes in the PAD. As discussed by Timoney (2002), there has been widespread perception that human activities have led to the "death of the delta" due to hydrological modification (PPADS 1971; Rosenberg *et al*., 1997, Schindler, 1998). This perception arose despite the lack of knowledge of what the ecological roles of hydrological processes were, and the spatial and temporal scales of variability affecting these processes in lakes of the PAD. Elsewhere, river flooding has been seen to exert a strong control over the physical, chemical and biological conditions of floodplain lakes (Junk *et al*., 1989; Junk and Wantzen, 2004; Wantzen *et al*., 2008). So, there is the expectation that hydrological gradients will result in marked differences in lake conditions within the PAD. However, little research has been conducted to characterize what the limnological expression of river flooding, or the lack of flooding, is for lakes of the PAD. These aspects need to be considered for a comprehensive understanding of how the PAD landscape evolves over space and time in response to differing hydrologic conditions. The following describes the expectations and observations that previous studies and reports have generated concerning the limnology of PAD lakes and what related research questions this thesis will pursue in Chapter 3.

Fuller and LaRoi (1971) postulated that river flooding of perched basin lakes was required to maintain nutrients and productivity. This was echoed by Dirschl (1972), who stated that the gradient from open- to closed-drainage basins in the PAD is one of decreasing nutrient availability. While neither of these reports provided any data on nutrient concentrations or primary productivity to support these statements, they appear to have established an accepted but untested assumption on how hydrology controls nutrients and aquatic productivity in lakes of the PAD (MRBC, 1981; Prowse *et al*., 2006b; Anisimov *et al*., 2007).

Gallup *et al*. (1971) surveyed zooplankton and phytoplankton in several locations in the open-drainage network (several PAD rivers and lakes: Mamawi, Claire, Richardson and Athabasca) in the summer of 1971. They described the phytoplankton abundance as being "low" and unlikely to be sufficient to support the high zooplankton abundance observed. No data were reported for the restricted- and closed-drainage PAD lakes. While phytoplankton abundance is probably best qualitatively described as "low" in the open-drainage system of the PAD (see Wolfe *et al*., 2007b), the #20 mesh used by Gallup *et al*. (1971) for both phytoplankton and zooplankton collection would have led to substantial underestimation of the phytoplankton abundance in the delta. For example, analysis of sediment collected from Lake Mamawi for diatoms found the diatom community to be heavily dominated by small centric diatoms (~ 10 µm diameter; Hall *et al*., 2004), which the 69-µm mesh (98 µm diagonal; see Evans and Sell, (1985)) used by Gallup (*et al*., 1971) would have been ineffective in sampling. This would explain, at least in part, why Gallup *et al*. (1971) reported only two taxa of phytoplankton in total found across 17 samples from the PAD, and why 15 of those sampled reportedly contained zero phytoplankton. While zooplankton and benthic invertebrates were the main focus of the Gallup *et al*. (1971) study, their report remains the only attempt by the Peace-Athabasca Delta Project Group (PADPG, 1973) to quantify primary producers of PAD lakes.

The first comprehensive limnological survey of PAD lakes that included the restricted- and closed-drainage lakes, as well as the open-drainage system, was carried out by Wolfe *et al*. (2007b) during October of 2000. This comprised a regional survey of water chemistry and water isotope composition in 61 lakes. Closed-drainage lakes (i.e., only rare river connectivity during ice-jam floods) were found to have high concentrations of many dissolved ions, DOC (dissolved organic carbon), and dissolved nitrogen and phosphorous compared to open-drainage lakes (i.e., with continuous river connection). Restricted-drainage lakes (i.e., with periodic river connectivity during spring ice-jam floods) had intermediate concentrations (Wolfe *et al*., 2007b). Consistent with this pattern, analysis of photosynthetic pigment concentrations in the surface sediments found that closed-drainage lakes have higher algal production than lakes that flood more frequently (McGowan *et al*., 2011). The one-time regional survey by Wolfe *et al*. (2007b) was conducted at the end of the ice-free season, and, thus, likely under-represents the influence of important hydrological processes that occur during the spring freshet (i.e., snowmelt and river flooding) on limnological conditions. To improve our ability to anticipate limnological responses to climate- and human-mediated changes in river hydrology of the PAD, knowledge of linkages between hydrological processes and limnological conditions is required over seasonal and inter-annual timescales.

Chapter 3 of this thesis entitled ***"Timescales of hydrolimnological change in floodplain lakes of the Peace-Athabasca Delta, northern Alberta, Canada"*** provides much-needed limnological data concerning the nutrient status, water clarity, chemistry and phytoplankton abundance of lakes in the PAD. The study aims to improve our understanding and knowledge of seasonal and inter-annual patterns of hydrolimnological variation in lakes of the PAD. In this chapter, repeated hydrolimnological measurements over three years (2003–2005) from a series of lakes positioned along the hydrological gradient (open-, restricted- and closed-drainage) and rivers in the PAD were used to examine the role of flooding on seasonal- and inter-annual variations in physical and chemical conditions and phytoplankton standing crop. The results characterize the nature and timescales of hydrolimnological change in PAD lakes in response to flooding and provide knowledge to anticipate hydrolimnological consequences of predicted long-term declines in river discharge and flood frequency (Schindler, 2001; Schindler and Smol, 2006; Wolfe *et al*., 2008a).

1.3.5 The Athabasca oil sands

The rapid rise in Athabasca oil sands development has led to increasing concerns over the potential for downstream impacts at the PAD (Schindler, 2010). The Regional Aquatic Monitoring Program (RAMP) is an industry-funded multiple-stakeholder agency, tasked with monitoring and evaluating the aquatic environment of the Regional Municipality of Wood Buffalo (~63,000 km^2) and communicating effects of resource development (Burn *et al*., 2011). RAMP has faced increasing criticism (Timoney and Lee, 2009, 2011; Kelly *et al*., 2009, 2010; Schindler, 2010) and scientific review panels have found RAMP to be inadequate to meet its objectives (Ayles *et al*., 2004; Burn *et al*., 2011).

Considerable atmospheric deposition of PACs and heavy metals was found within a 50 km radius of bitumen upgrader facilities (Kelly *et al*., 2009, 2010) that was not previously identified by RAMP. These findings, and the independent review of RAMP by the Royal Society of Canada (Gosselin *et al*., 2010), identified further shortcomings in the methodology of RAMP. This has led Environment Canada, in collaboration with the Province of Alberta and many academic researchers, to formulate a new monitoring program for the Alberta oil sands development area, Athabasca River, and regional aquatic and terrestrial ecosystems (Environment Canada, 2011a-e).

One of the very public (Wingrove, 2010) concerns to have arisen is whether oil sands development has led to increasing loadings of polycyclic aromatic compounds (PACs) and heavy metals to the PAD ~200 km downstream of the Athabasca Oil sands (Kelly *et al*., 2009, 2010; Schindler, 2010; Timoney and Lee, 2011). The Athabasca River and several of its tributaries cut into and flow through the McMurray Formation, so some level of natural background erosion and transport of oil-sands-derived PACs and heavy metals downstream exists (Conly *et al*., 2002; Colavecchia *et al*., 2004; Timoney and Lee, 2011). However, monitoring of such river contaminants began well after the onset of oil sands development (Schindler, 2010), and available data are of questionable quality (Burn *et al*., 2011; Timoney and Lee, 2011) or poorly positioned to quantify long-term temporal trends or account for natural variability (Schindler, 2010; Timoney and Lee, 2011). Ultimately, there are no effective data to determine the historical natural PAC loading to the PAD, and whether it has increased with increasing oil sands development and production (Schindler, 2010, Environment Canada, 2011a,b).

Kelly *et al*. (2009) showed there to be substantial aerial deposition of bitumen and related PACs in the snow collected near a bitumen upgrader (site AR6 in Kelly *et al*., 2009). Deposition of PACs declined exponentially with distance from the AR6 sampling site, indicating that the vast majority of the deposition falls within a 50-km radius, equaling ~1700 kg of PACs annually. Kelly *et al*. (2009) also examined dissolved (primarily low molecular weight) PAC concentrations in water from the Athabasca River and six tributaries. Concentrations of dissolved PACs were found to be low within the main stem of the Athabasca River, but rose in concentration as the river traverses the McMurray Formation and the oil sands development projects, and then decreased after passing the confluence with the Firebag River (AR9 in Kelly *et al*., 2009). Kelly *et al*. (2009) postulated that dilution, biodegradation and adsorption onto organic sediment particles in the Athabasca River may be the cause of low dissolved PAC concentrations in the PAD, which were comparable to that found upstream of Fort McMurray and oil sands development.

Based on previous findings of PACs in sediments of the PAD, Kelly *et al*. (2009) suggested that long-range atmospheric and/or fluvial transport of particulate-bound bitumen PACs to the PAD can be inferred. Furthermore, they suggest fluvial transport of such PACs may be heavily weighted to the spring freshet period. Such a pattern has previously been documented for other contaminants in the Athabasca River and elsewhere (Scrimgeour *et al*., 1994).

Kelly *at al.* (2009) have generated some important findings on the quantity of atmospheric transport of PACs and helped spur further research into an important environmental issue. However, the relative and quantitative contribution of oil sands development versus natural processes to bitumen-related contaminant-transport to the PAD, presently and historically, remains unknown.

Timoney and Lee (2009) provide a useful illustration of the difficulty of assessing whether there is, or is not, a detectable increase in PAC loading due to oil sands development. These authors examined dissolved PAC concentrations from samples collected upstream and downstream of development on the Muskeg River and found an increase in concentration of all reported PACs downstream of development. The complication here is that the Muskeg River traverses the McMurray Formation so an increase in PAC concentrations from upstream to downstream is expected. The question remains: How much of the increase is natural and how much is due to development? Unraveling this issue is confounded by the location of the upstream and downstream sites on the Muskeg River. The upstream site appears to be just on the outer edge of the surface expression of McMurray Formation. The downstream site is not only downstream of development but is located such that the river has now also flowed ~20 km through the surface expression of the McMurray Formation (see Fig 1 in Timoney and Lee, 2011 and Fig 3.2-1, Fig 5.3-1 RAMP, 2007). So the increase in PACs has more than one possible source and may well be a combination of natural river processes, the active industrial site as well as recent land disturbance within the catchment.

Timoney and Lee (2011) examined RAMP data (RAMP 2011) on total PAC concentrations in sediment from monitoring sites at river sites within the Athabasca Delta. They reported a weak increasing trend (R^2=12%) during the 10-year period covered by the data (1999-2009). Additionally, they reported that the concentration of total PACs was positively correlated with sediment organic matter (R^2=34%) and normalizing the data for organic matter content removed the increasing trend with PAC concentration and time. These authors then inferred that industrial activities must be increasing both organic matter and PACs through landscape disturbance upstream. However, due to the propensity of PACs (and most other hydrophobic contaminants) to be scavenged from the water column by fine organic matter (Zhang *et al*., 1993; Johnson *et al*., 2002; Kersten and Smedes, 2002), one would also expect a positive and significant correlation between river sediment fine organic matter content and PACs in the absence of industry and landscape disturbance. I have examined the RAMP data (RAMP, 2011) used by Timoney and Lee (2011) and found sediment concentration of PACs to also be positively correlated to sediment % clay as well as the sediment iron concentrations (see Figure 1.2). The latter is often used to normalize for grain-size effects as it is expected to positively co-vary with the abundance of iron-rich clay minerals (Herbert *et al*., 1989; Loring, 1991). As such, the apparent increasing temporal trend reported by Timoney and Lee (2011) probably reflects differences in sediment grain size between sample years, and is likely an artifact of sample variability in a dynamic riverine system. Small changes in site hydrology, channel migration, and the river reach sampling location chosen by the RAMP field crew could all lead to the retrieved sediment being of significantly different grain size and % organic matter (which tend to co-vary). Another confounding factor noted by Timoney and Lee (2011) was the 4-6 cm deep sediment sample collected within a given year by RAMP was assumed to cover a period of time ranging from 2.4 to 15.6 years (Timoney and Lee, 2011; see their Supplementary Text). For these, and previously described confounding influences, it is uncertain that the RAMP river sediment data can be used to accurately capture temporal trends over a 10-year period. Additionally, since industrial oil sands development began in 1967, the 1999-2009 RAMP sediment data cannot be used to distinguish between natural and anthropogenic loadings of PACs to the PAD.

Because monitoring data are inadequate, a different approach is needed to determine if Athabasca oil sands industry has led to delivery of bitumen-sourced PACs to the PAD above that of natural processes. Chapter 4 of this thesis uses a paleolimnological approach to examine the roles of riverine and atmospheric processes in delivery of bitumen-related and other PACs to lakes of the PAD. The goal is to establish pre-impact contaminant levels, and assess if oil sands development has elevated PAC contaminant levels in the PAD.

In Chapter 4 of this thesis, entitled "***Natural processes dominate the delivery of polycyclic aromatic compounds to the Athabasca Delta downstream of oil sands development***", sediment cores were collected from two lakes in the Athabasca Delta and one from the Peace Delta in order to reconstruct the depositional history of river- and atmospheric-transported PACs to the PAD. This chapter provides much-needed long-term data on downstream transport of McMurray oil-sands derived PACs by the Athabasca River. The methodology employed here is one recommended by the Federal Expert Oil Sands Advisory Panel (Dowdeswell *et al*., 2010) and Environment Canada's proposed integrated oil sands monitoring program (Environment Canada, 2011a). This is the only means available to reconstruct and directly measure PAC concentrations prior to (and since) industrial development of the oil sands, as all monitoring programs and research projects began well after oil sands production was underway (Schindler, 2010). The results of this chapter can be expected to provide useful information to guide effective future monitoring programs of the PAD and Athabasca oil sand development by provincial and federal regulatory agencies.

1.4 Thesis description

The body of this thesis contains three original research chapters as outlined above (Chapters 2, 3, and 4) and a conclusions chapter synthesizing the findings and placing them within context of ongoing concerns in the PAD and other northern deltaic systems. Below is a brief account of each of the three primary research chapters, their publication status and the contributions made by those involved.

1.5 Major contributions of author and others.

Chapter 2. Epiphytic diatoms as flood indicators

Wiklund JA, Bozinovski N, Hall RI, Wolfe BB. 2010. Epiphytic diatoms as flood indicators. **Published in**; *Journal of Paleolimnology* **44**: 25-42. DOI 10.1007/s10933-009-9383-y

Idea + planning: Wiklund JA.

Field work: Wiklund JA, MacDonald C, Köster D

Laboratory analyses: Wiklund JA and Bozinovski N, except water chemistry analyses which were submitted to NLET (Environment Canada's National Laboratory for Environmental Testing; Burlington, ON) for analysis. Additionally, this paper also reanalyzed the data from sedimentary diatom record from PAD 5 (diatoms counted by Karst-Riddoch TL; see Wolfe *et al*., 2005).

Data analysis: Wiklund JA.

Figures: Wiklund JA.

Writing: Wiklund JA (wrote the first draft, refined subsequent drafts), Hall RI and Wolfe BB (comments and contributions to text).

Chapter 3. Timescales of hydrolimnological change in floodplain lakes of the Peace-Athabasca Delta, northern Alberta, Canada.

Wiklund JA, Hall RI, and Wolfe BB. 2012. Timescales of hydrolimnological change in floodplain lakes of the Peace-Athabasca Delta, northern Alberta, Canada. **In Press**; *Ecohydrology* DOI: 10.1002/eco.226

Idea + planning: Wiklund JA, Hall RI, Wolfe BB

Field work: Wiklund JA, MD Falcone, Y Yi, MacDonald C, Köster D, RI Hall, BB Wolfe.

Laboratory analyses: Wiklund JA and work study students supervised by Wiklund JA, except water chemistry analyses which were sent to TAIGA Laboratory (Yellowknife, NWT) and NLET (Environment Canada's National Laboratory for Environmental Testing; Burlington, ON).

Data analysis: Wiklund JA.

Figures: Wiklund JA.

Writing: Wiklund JA (wrote the first draft, refined subsequent drafts), Hall RI and Wolfe BB (comments and contributions to text).

Chapter 4. Natural processes dominate the delivery of polycyclic aromatic compounds to the Athabasca Delta downstream of oil sands development.

Wiklund JA, Hall RI, Wolfe BB, Edwards TWD, Farwell AJ, and Dixon DG. **In Preparation**. Natural processes dominate the delivery of polycyclic aromatic compounds to the Athabasca Delta downstream of oil sands development.

Idea + planning: Hall RI, Wolfe BB, Edwards TWD.

Field work: Hall RI, Wolfe BB, Wiklund JA, Elmes M.

Laboratory analyses: Wiklund JA. Sediment samples were submitted for PAC analysis to ALS Canada Ltd. (Edmonton Alberta)

Data analysis: Wiklund JA, Hall RI, Wolfe BB.

Figures: Wiklund JA.

Writing: Hall RI, Wolfe BB, Wiklund JA, Edwards TWD (main part of the text), Farwell AJ and Dixon DG (comments and contributions to text).

1.6 Figures

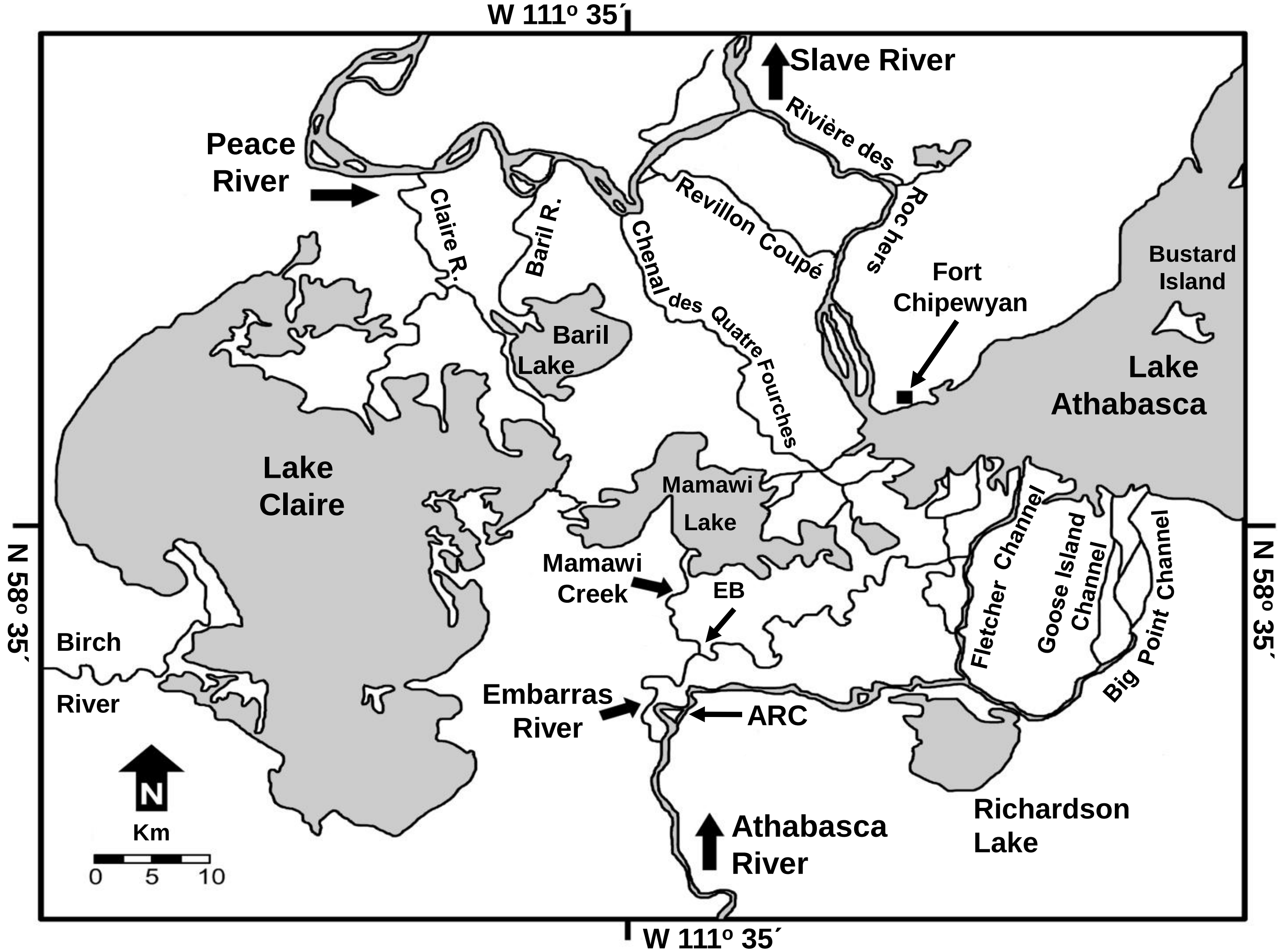

Figure 1.1 Map of the Peace-Athabasca Delta (PAD) showing locations of major lakes, rivers and Fort Chipewyan. Additionally, locations of recent significant hydrogeomorphic changes are shown: the Athabasca River Cut-off (ARC; 1972) and the Embarras River Breakthrough (EB; 1982).

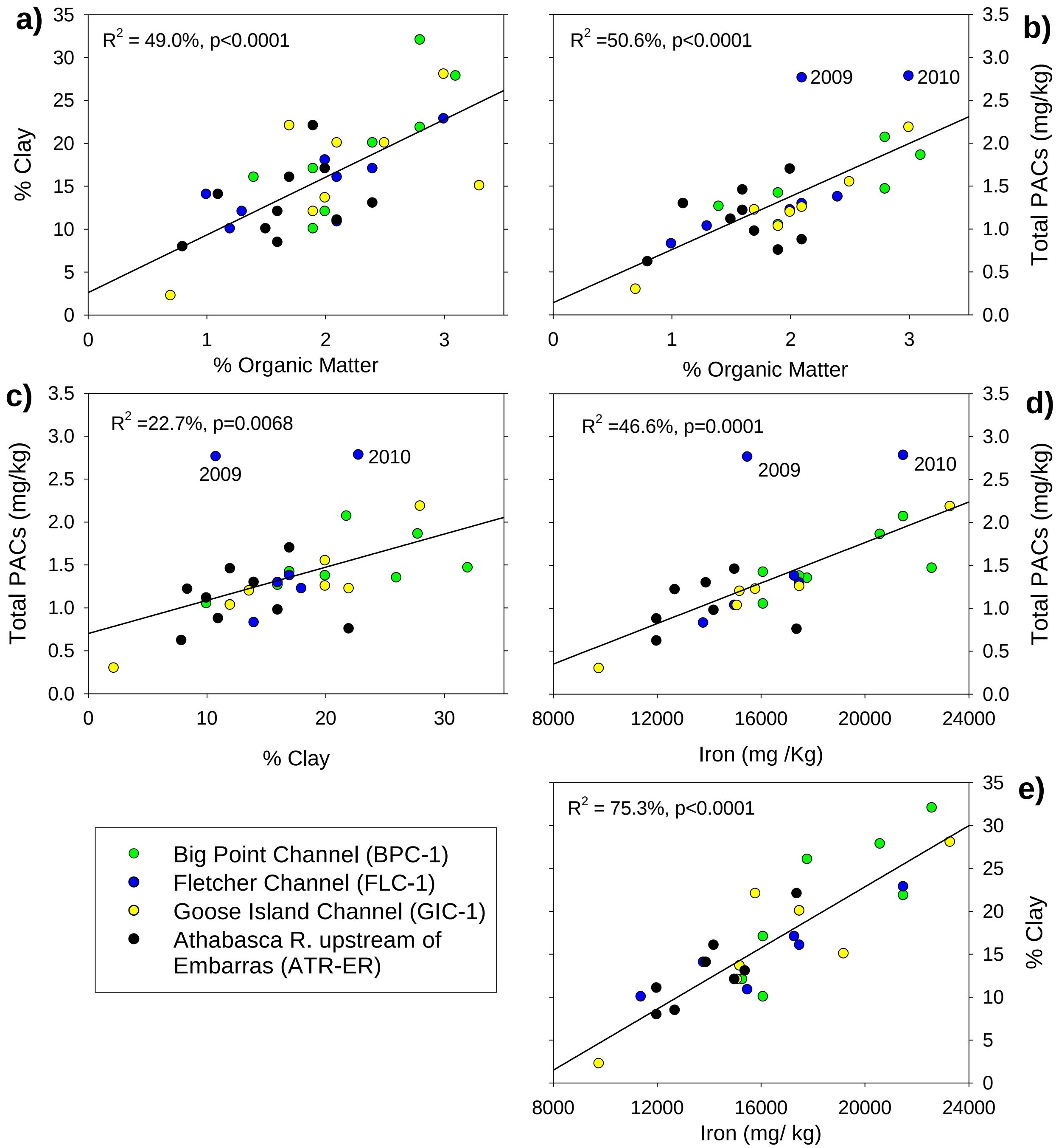

Figure 1.2 Scatter plots and linear regressions showing relationships between pairs of sedimentary constituents measured in Athabasca River Delta sediment samples collected during 1999-2009 and reported by the Regional Aquatics Monitoring Programme (RAMP, 2011). **a)** % clay and % organic matter, **b)** total PACs (mg/kg) and % organic matter, **c)** total PACs (mg/kg) and % clay, **d)** total PACs (mg/kg) and iron concentration and **e)** % clay and iron concentration. The samples obtained from Fletcher Channel in 2009 and 2010 are marked with the year of collection, as they appear as potential outliers in the general trend seen between total PAC concentration and values of the other Athabasca River Delta sediment measurements.

Chapter 2

Epiphytic diatoms as flood indicators

2.1 Summary

The hydroecology of floodplain lakes is strongly regulated by flood events. The threat of climate warming and increasing human activities requires development of scientific methods to quantify changes in the frequency of short-lived flood events, because they remain difficult to identify using conventional paleolimnological and monitoring approaches. We developed an approach to detect floods in sediment records by comparing the abundance and composition of epiphytic diatom communities in flooded and non-flooded ponds of the Peace-Athabasca Delta (PAD), Canada, that grew on submerged macrophytes (*Potamogeton zosteriformis*, *P. perfoliatus*) and an artificial substrate (polypropylene sheets) during the open-water season of 2005. Analysis of similarity tests showed that epiphytic diatom community composition differs significantly between flooded and non-flooded ponds. After accounting for the ‘‘pond effect,’’ paired comparisons of the three substrates determined that variation in community composition between the artificial substrate and macrophytes was similar to that between the macrophyte taxa. Similarity percentage analysis identified diatom taxa that discriminate between flooded and non-flooded ponds. The relative abundance of ‘strong flood indicator taxa’ was used to construct an event-scale flood record spanning the past 180 years using analyses of sedimentary diatom assemblages from a closed-drainage pond (PAD 5). Results were verified by close agreement with an independent paleoflood record from a nearby flood-prone oxbow pond (PAD 54) and historical records. Comparison of epiphytic diatoms in flooded and non-flooded lakes in this study provides a promising approach to detect changes in flood frequency, and may have

applications for reconstructing other pulse-type disturbances such as hurricanes and pollutant spills.

2.2 Introduction

Floodplains are sensitive to changes in temporal and spatial variability of river discharge. Floodwaters exert strong control on floodplains because they provide a primary source of water and redistribute nutrients, suspended and dissolved materials and organisms (Junk *et al*., 1989; Wantzen *et al*., 2008). For the lentic ecosystems (i.e., lakes, ponds, wetlands), periodic floods can be a major driver of water balance (Amoros and Bornette, 2002; Wolfe *et al*., 2007; Wantzen *et al*., 2008), optical (Coops *et al*., 2008; Squires and Lesack, 2003a) and biogeochemical conditions (Forsberg *et al*., 1988; Lesack *et al*., 1998; Wolfe *et al*., 2007), and the structure (Hay *et al*., 1997; van Geest *et al*., 2003; Izaguirre *et al*., 2004) and productivity of biotic communities (Lewis *et al*., 2000; Squires and Lesack, 2003a; Zalocar de Domitrovic, 2003). Changes in hydrology can have profound and varied ecological consequences for floodplains (Sparks, 1995; Lewis *et al*., 2000; Jungwirth *et al*., 2002).

Flow regimes of more than half the world's large rivers have been altered by humans (Nilsson *et al*., 2005), and recent evidence indicates that river flows and flood frequency in northern watersheds are regulated strongly by climate variations (Schindler and Smol, 2006; Wolfe *et al*., 2008b). In the era of climate warming, such findings highlight the need to improve methods to detect and quantify hydrological and ecological changes in floodplain landscapes (Bailey, 1995; Sparks, 1995). A broad array of approaches, including spatial surveys and monitoring programs, process studies, controlled experiments, paleoenvironmental analyses and modeling are needed to understand complex interactions among physical, chemical and biological processes that operate at multiple spatial and temporal scales (Amoros and Bornette, 2002). Environmental assessment and remediation of large river floodplains is further complicated by a lack of hydrological and ecological data of sufficient duration to distinguish human influences from natural variability, or to predict future changes (Brown, 2002; Jungwirth *et al*., 2002; Wolfe *et al*., 2008b). Arctic and sub-arctic regions lack long-term data, but it is in these regions where effects of climate change are expected to be most pronounced (Corell, 2006; Schindler and Smol, 2006).

Environmental monitoring of surface waters has traditionally focused on measurements of chemical and physical variables collected at regular or irregular time intervals. However, most measured variables (e.g. nutrient concentrations, pH, light attenuation) represent ‘snapshot’ values that characterize conditions over shorter time periods (typically hours to weeks) than the duration between sample collections (months to years, or longer). Furthermore, if a main goal of monitoring programs is to detect changes in ecological integrity, then they must include direct assessment of biological communities (Poulickova *et al*., 2004; Lavoie *et al*., 2006). Ideally, both biomonitoring and hydrolimnological monitoring should be carried out concurrently to increase understanding of ecological responses to anthropogenic and natural influences (Stevenson and Smol, 2003). For floodplain ponds and lakes, diatoms are particularly effective biomonitors of hydrolimnological conditions (Hay *et al*., 1997; Sokal *et al*., 2008; Wolfe *et al*., 2008a). Due to the shallow nature of most floodplain ponds and lakes, they support high biomass and surface area of macrophytes (Janauer and Kum, 1996; Squires *et al*., 2002; Sokal *et al*., 2008). Consequently, their diatom floras are often dominated by epiphytic taxa. Thus, bioassessment methods based on epiphytic diatoms may be particularly effective for tracking changes in hydrolimnological conditions of floodplain lakes and ponds.

The Peace-Athabasca Delta (PAD) is an important northern floodplain landscape, much of which has experienced declining flood frequency over the past several decades (Wolfe *et al*., 2006; 2008a, b). The PAD is located at the confluence of the Peace and Athabasca rivers. It has a surface area of 6,000 km^2 and is the world's largest inland freshwater boreal delta (Peters *et al*., 2006). Due to its ecological, historical and cultural significance, the PAD is recognised as a Ramsar Wetland of International Importance and as a UNESCO World Heritage Site. Most of the delta lies within Canada's largest National Park (Wood Buffalo).

We used a field experiment to assess the roles of river flooding and substrate type (two natural macrophyte taxa, one artificial substrate) in regulating the density and composition of epiphytic diatom communities in ponds of the PAD. This was done to develop the use of diatoms for aquatic ecosystem bio-monitoring and to refine reconstructions of past hydrolimnological conditions from changes in sedimentary diatom assemblages obtained from floodplain environments. Our study compared limnological conditions and epiphytic communities from two ponds that flooded during the spring of 2005 with two ponds that did not flood in 2005. Epiphytic diatom samples were obtained in mid-summer from two submerged macrophyte taxa common to all four ponds and from an artificial substrate to determine if the density and composition of epiphytic diatom communities differ between flooded and non-flooded ponds. We used an artificial substrate to explore whether a standardized method could adequately mimic natural macrophytes because it potentially can remove the effects of confounding factors associated with comparing epiphytic diatoms growing on different natural substrates among lakes (e.g., variations in depth, illumination, orientation, colonization time, host-periphyton interactions; Amireault and Cattaneo, 1992). Results from the experiment were used to identify epiphytic diatom taxa indicative of river flooding. Finally, we tested whether the indicator diatom taxa could detect ‘‘pulse disturbances’’ of flood events over the past ~180 years from a previously published diatom record from one of the study sites (Wolfe *et al*., 2005). Our findings indicate that epiphytic diatoms are useful for detecting the occurrence of flood events. Further, we suggest that the experimental approach used in this study may be more effective for assessing other short-lived pulse type disturbances such as hurricanes, chemical spills and drought episodes, than conventional paleolimnological approaches based on ‘training sets’ from lakes situated along environmental gradients, which are designed to track effects of ‘ramp’ (i.e. when the strength of a disturbance increases over time) and ‘press’ (i.e., when the strength of a disturbance increases sharply and reaches a new constant level that is maintained) type disturbances (*sensu* Lake, 2000).

2.3 Methods

2.3.1 Study sites

Four study ponds (PAD 1, 5, 8 and 54) were selected to compare ponds that flooded in 2005 with ponds that did not flood in 2005 (Fig. 2.1). Ponds PAD 1 and PAD 5 are closed-drainage basins which, to our knowledge, have not flooded since at least 1997 (Wolfe *et al*., 2007). In contrast, PAD 8 and PAD 54 are restricted-drainage basins (Wolfe *et al*., 2007) that flood intermittently (i.e., not every year). They received floodwaters from the Peace River in early May 2005 due to a river ice-jam. Physical attributes of PAD 1, 5, 8, and 54 are listed in Table 2.1.

2.3.2 Water sampling and limnological analyses

Physical and chemical variables were measured near the centre of each lake and the Peace River at Rocky Point during late-May (spring), late July/early August (summer) and mid-September (fall) of 2005. Pond water pH, temperature, dissolved oxygen, and specific conductivity were recorded at 10-cm depth intervals from the surface using a YSI 600QS multi-meter and the mean of the upper 50 cm was used to characterize the water body. The light extinction coefficient of photosynthetically active radiation (Kd-par) was calculated from measurements taken using an Apogee Instruments Quantum meter (Model QMSS-SUN) at ~10 depth intervals per site, spanning a 90% reduction in incident light where water-column depth permitted. Three PAR values were recorded at each depth interval and the mean was natural log-transformed and regressed versus depth (m). The slope of the relationship was used to estimate Kd-par.

Water samples were collected from ~10 to 20 cm water depth for determination of alkalinity, and concentrations of total suspended solids (TSS), inorganic suspended solids (ISS), organic suspended solids (OSS), chlorophyll *a* (Chl *a*), total phosphorus (TP), dissolved P (DP), total nitrogen (TN), nitrate, ammonia, dissolved reactive silica (DSi), major dissolved ions (Ca, Cl, Mg, Na, K, SO4), DOC and DIC. All samples for chemical analysis were kept at 4ºC until analyzed at Environment Canada's National Laboratory for Environmental Testing, Burlington, Ontario. For analysis of suspended solids, pond water was filtered through pre-ashed (1 hr at 550ºC), pre-weighed Whatman GF/C filters (0.7 µm pore size). Filters were dried at 90ºC and weighed for determination of TSS, then ashed at 550ºC for 1 h and weighed for determination of ISS. OSS was calculated as the difference between TSS and ISS. For Chl *a* analysis, material in a measured volume of pond water was filtered onto a Whatman GF/F filter (0.4 µm pore size) and frozen until analysis. Extraction and quantification of Chl *a* concentration was performed using standard fluorescence techniques (Stainton *et al*., 1977).

2.3.3 Sampling and analysis of epiphytic diatoms

Epiphytic diatom samples were collected from an artificial substrate and from two macrophyte taxa (*Potamogeton zosteriformis* Fern. and *Potamogeton perfoliatus* L. var. *richardsonii* AR. Bennett) at three locations within each pond. These locations were selected to be spatially distant and to represent within-pond variability (e.g., PAD 8 has three connected basins and an artificial substrate station was deployed in each). At each location, we deployed an artificial substrate station consisting of 10 polypropylene sheets (each sheet = 5 cm wide x 14 cm long) secured between plastic bookbinders. The polypropylene sheets were suspended vertically at a water depth of 40 cm (from top of artificial substrate) using a wooden float (60 x 2.5 x 5 cm) anchored to the pond bottom. Artificial substrate stations were deployed in May and collected in late July or early August, which provided ~10 weeks for colonization at each site. During collection, the polypropylene sheets were rolled and placed into plastic scintillation vials, which were frozen upon return to base camp. Leaves from the two common aquatic macrophyte taxa present in all four study ponds were collected near each artificial substrate station. A 12 mm diameter cork borer was used to collect 7–12 leaf discs per sample (5 samples per station) from *P. perfoliatus* var. *richardsonii*. For the lanceolate leaves of *P. zosteriformis*, 4–6 leaves were collected per sample (five samples per station) and the dimensions of each leaf were measured using a ruler and recorded before being placed in scintillation vials and frozen. The study design provided spatial within-pond replication (three locations in each pond) and within-site replication (five samples from each location) for each of the three substrates, at each of the four ponds. We intended to count diatoms from two samples from each of the three substrates, at each of the three locations within each of the four ponds (=18 samples/pond, or 72 samples total). One artificial substrate station was lost from PAD 1 due to beaver activity, and both macrophyte taxa were not always present near the artificial substrate stations in PAD 5 and PAD 54. Consequently, diatoms were enumerated in 59 samples.

For preparation of microscope slides for diatom enumeration, samples of artificial substrate and macrophyte leaves were placed into beakers (250 ml) and digested in hot (90ºC) 30% H_2O_2 for 3 h to remove organic matter, followed by addition of 3 ml of 10% HCl to remove carbonates. Acid residues were removed from the diatom slurries by repeatedly allowing diatoms to settle for 24 h, discarding the supernatant and replacing it with deionized water (Hall and Smol, 1996). A known number of microspheres were then added to each sample to determine the density of epiphytic diatoms (# diatom valves cm^{-2} of substrate), following methods of Battarbee and Kneen (1982). Diatom slurries were then dried onto circular coverslips (18 mm diameter) and mounted onto microscope slides using Napthrax™. Diatom slides were analyzed using a Zeiss Axioskop II Plus compound light microscope at 1000X magnification under oil immersion (numerical aperture = 1.30). A minimum of 300 valves per sample was identified in each sample. Diatom taxonomy followed Krammer and Lange-Bertalot (1986–1991). Diatom data were expressed as density and relative abundances of the total diatom sum.

2.3.4 Data analysis

Principal components analysis (PCA) was used to explore the major differences in the physical and chemical conditions between flooded and non-flooded ponds, and to compare conditions in the ponds with those in the river samples. All data were ln(x + 1)-transformed prior to analysis (except pH and Kd-par) to improve normality and equalize variances. Scaling was focused on inter-variable distances and variables were divided by their standard deviation prior to ordination and centered and standardized by variable. PCA ordination was computed using CANOCO version 4.5 (ter Braak and Šmilauer, 2002).

A two-way ANOVA was used to determine if density of epiphytic diatoms differs between flooded and non-flooded lakes (independent of differences among substrates) and among the three substrates (independent of differences between flooded and non-flooded ponds). ANOVA tests were computed using SYSTAT version 10.2.05, and, where appropriate, post-hoc tests with Tukey's test statistic were run to provide pairwise comparisons.

Multi-dimensional scaling (MDS) and statistical tests (analysis of similarities-ANOSIM) were used to assess variation in composition of epiphytic diatom communities among ponds, between flooded versus non-flooded pond classes and among the three substrates. Diatom taxa with percent abundance ≥1% in at least three samples were retained for analysis of community composition. Percent abundances of these 33 diatom taxa were square-root transformed prior to calculating the Bray-Curtis similarity coefficients used in the MDS ordinations and ANOSIM tests. MDS was used to explore the influence of flooding (flooded vs. non-flooded lakes) and substrate type (artificial substrate, *P. zosteriformis* and *P. perfoliatus* var. *richardsonii*) on the composition of epiphytic diatom communities among the four study ponds. A series of one-way ANOSIM tests assessed the significance and relative strength of factors that account for variation in the epiphytic community (Clarke and Warwick, 2001). Two-way crossed ANOSIM tests were performed to determine if community composition differed: (1) among individual ponds independent of the effects of the different substrates, and among the substrates independent of effects of differences among ponds, and (2) between flooded and non-flooded pond classes independent of the effects of the different substrates, and among the substrates independent of effects of differences between flooded and non-flooded pond classes. The ANOSIM test statistic (global R) reflects the observed differences between groups of samples contrasted with the differences among replicates within each group and ranges from 0 to 1. A value of 0 indicates that the similarity between and within groups is the same on average. A value of 1 indicates that replicates within a group are more similar to each other than to all other replicates of other groups (Clarke and Warwick, 2001). A *p*-value was computed by comparing the distribution of within- and across-group rank Bray-Curtis similarities (9999 computations) to the initial rank similarity, as reported by the global R value (Clarke and Gorley, 2006; Clarke and Warwick, 2001). For all tests, we set alpha = 0.05.

Similarity of percentages (SIMPER) analysis was used to identify ‘indicator’ epiphytic diatom taxa that discriminate flooded from non-flooded ponds. Specifically, SIMPER was used to determine to what extent diatom taxa contribute to % similarity within a group (e.g., flooded ponds) and to % dissimilarity between groups (i.e., flooded versus non-flooded ponds). Taxa that contributed >2% of the average within-group similarity (for either flooded or non-flooded ponds) and >2% of the between-group dissimilarity were identified as having indicator value, following criteria used by Sokal *et al*. (2008). We used the following criteria to distinguish four ‘indicator groups’ of epiphytic diatom taxa, strong flood indicators, moderate flood indicators, strong non-flood indicators and moderate non-flood indicators. The strong flood indicator taxa were those that contributed >2% to the dissimilarity between flooded and non-flooded ponds, and contributed >2% similarity within flooded ponds, but <2% similarity to within non-flooded ponds. These taxa were consistent members of flooded ponds and rare or absent from non-flooded ponds. The moderate flood indicator taxa were those that contributed >2% to within-group similarity for both flooded and non-flooded ponds, while also contributing >2% to between-group dissimilarity (flooded versus non-flooded pond). These are taxa that were found in both flooded and non-flooded ponds, but were consistently more abundant in the flooded ponds. The strong non-flood indicator taxa and the moderate non-flood indicator taxa were determined using analogous criteria as detailed above for the flood indicator taxa, but as appropriate for the non-flood situation. Analyses by MDS, ANOSIM and SIMPER used the software PRIMER, version 6.1.5 (Clarke and Gorley, 2006; Clarke and Warwick, 2001).

2.3.5 Epiphytic diatom-inferred flood reconstruction

We used the four categories of flood indicator taxa, identified by the above SIMPER analysis, and diatom assemblages in a sediment core from one of our study sites (PAD 5), to assess if this new approach can identify flood events in the stratigraphic record. Previous paleolimnological interpretations derived from analysis of diatoms and several other sediment proxy variables did not identify individual flood events at PAD 5, but instead identified marked decadal-scale variability of hydro-limnological conditions over the past 300 years in response to climatic changes (Wolfe *et al*., 2005).

Sediments incorporate diatom taxa from all habitats within a basin. In contrast, the indicator epiphytic diatom taxa identified from the artificial substrate and macrophytes in our ‘natural experiment’ likely under-represent diatom taxa that occupy mainly benthic, planktonic and epipelic habitats. To account for these differences and allow comparisons between sample types (sediment assemblages vs. epiphyte assemblages), the percent abundance of the indicator epiphytic diatom taxa present in the sediment samples from the PAD 5 core were re-calculated after excluding non-epiphytic taxa from the diatom sum. This was done conservatively, as we excluded only taxa that we know are non-epiphytic, primarily benthic Fragilariaceae and planktonic centric taxa.

The summed percent abundance of the epiphytic diatom taxa in the ‘strong flood indicator’ group was converted to Z-scores to identify samples with a high abundance of flood indicators and which are, thus, likely indicative of flooding. In the absence of objective criteria, we explored the possibility that sediment core samples with a Z-score >1 are 'highly likely' to indicate a flood and samples with a Z-score between 0.5 and 1 are 'likely' to indicate a flood. The chronology of the core from PAD 5 was determined by ^{210}Pb dating and the CRS model (core KB-3 from Spruce Island Lake in Wolfe *et al*., 2005) and indicates the contiguous 0.5-cm-thick sediment intervals span ~4 years on average.

A relict, or flood-activated channel that runs east–west ~350 m to the north of PAD 5 is the most likely source of flood waters to PAD 5, as all other areas of the catchment are surrounded by elevated bedrock with mature forest. This relict channel traverses a low-lying area and connects to the vicinity of a flood-prone oxbow lake (local name Horseshoe Slough, or 'PAD 54' in Wolfe *et al*., 2006, 2007; Fig. 1). With this landscape configuration, floods of magnitude sufficient to overflow the relict channel and enter PAD 5 must also flood into PAD 54, but not all floods that enter PAD 54 will flood into PAD 5. This allows us to compare flood events inferred from the abundance of the strong flood indicator taxa at PAD 5 with the record of flood events at PAD 54 inferred from magnetic susceptibility measurements for the period CE 1820–2001 (Wolfe *et al*., 2006). The comparison provides a way to assess if the experimentally derived flood indicator taxa can identify previously undetected flood events at PAD 5 (Wolfe *et al*., 2005). Additionally, we used an historical record of major flood events compiled from a collection of written sources and traditional knowledge to assess accuracy of floods identified at PAD 5 (PADTS, 1996).

For the paleo-flood record at PAD 54, Wolfe *et al*. (2006) used a magnetic susceptibility peak associated with 1974, the year of the largest recorded ice-jam flood that inundated much of the PAD (Peters *et al*., 2006), as a threshold for identifying other major ice-jam flood events. The high sedimentation rate of PAD 54, combined with 2-mm resolution of the magnetic susceptibility record, provides sub-annual temporal resolution (Wolfe *et al*., 2006). For verifying the PAD 5 flood dates, flood events inferred from indicator diatom taxa in sediment samples from PAD 5 were considered to be in agreement with the PAD 54 record if the time span of the PAD 5 sample matched a major flood event identified by a magnetic susceptibility peak at PAD 54 within ±4 years. Although we would like to be more discriminating, we must account for potential age inaccuracies in both the PAD 5 (^{210}Pb) and PAD 54 (^{137}Cs) sediment core chronologies. The ±4-year age error was chosen, in part, because the largest documented floods in recent times, 1974 and 1965 (PADTS, 1996; Prowse and Conly, 2000), are potentially captured in PAD 5 sediment samples dated to 1971 (1969.6–72.6) and 1962 (1960.2–63.4), implying an approximate 3-year error in dating for events. As the ages of flood events in the PAD 54 record have their own associated chronological uncertainty, we propose a ±4-year window to verify flood events in the PAD 5 record in our comparison of the two records. The ~180-year record from PAD 54 contains evidence of 25 major floods based on magnetic susceptibility values equal to or exceeding that of the 1974 flood. Given the lower temporal resolution of the PAD 5 record (~4 years per sediment slice), only 15 major floods should be identifiable because there were several instances when multiple floods were recorded within 4-year intervals in the PAD 54 magnetic susceptibility record.

2.4 Results and interpretation

2.4.1 Limnological differences among ponds

Principal components analysis (PCA) indicated that limnological conditions differed markedly between flooded and non-flooded ponds and that the differences persisted throughout the ice-free season of 2005 (Fig. 2.2). The first PCA axis captured 42.2% of the total variation and separated water samples from ponds that flooded from those that did not flood. Sample scores from flooded ponds (PAD 8, 54) were positioned to the right along PCA axis 1, characterized by higher concentrations of sulfate than in non-flooded ponds, and by higher concentrations of DSi, ISS, TSS and Kd-par, primarily in samples collected in spring. Flooded ponds were positioned near samples from the Peace River (R2), indicating strong influence of flood waters on their water chemistry (Fig. 2.2). In contrast, samples from the non-flooded ponds (PAD 1, 5) were positioned to the left along PCA axis 1, characterized by higher DOC, TN, Na, K, Cl, Mg, alkalinity, specific conductivity, DIC, pH, NO3, and DP, than in flooded ponds and rivers. PCA axis 2 accounted for 23.6% of the total variation and captured mainly seasonal variations that occurred within the ponds and the Peace River. Axis 2 was positively correlated with TSS, OSS, ISS, Ca, TP, Kd-par, DIC, specific conductivity and alkalinity, and negatively correlated with pH. Thus, concentrations of suspended sediments, DSi and Ca tended to decline over the growing season in the study ponds, while pH increased. Interestingly, limnological conditions remained distinct between flooded and non-flooded ponds at the end of the growth season. These results indicate that spring flooding imparts strong differences in physical and chemical pond conditions that endure throughout the growth season.

2.4.2 Density of epiphytic diatom communities

Epiphytic diatom density differed among the study ponds, between flooded and non-flooded ponds, and among the three substrates (Fig. 2.3). A two-way ANOVA identified that mean density of epiphytic diatoms was significantly higher in flooded than non-flooded ponds ($F_{1,53}$ = 10.33, p = 2.2 x 10^{-3}) and differed among substrate types ($F_{2,53}$ = 16.57, p =3 x 10^{-6}), with no significant difference due to an interaction between these factors ($F_{2,53}$ = 1.96, p = 0.151). Tukey's post-hoc tests determined that the density did not differ significantly between *P.*

zosteriformis and the artificial substrate, but was significantly lower on both of these substrates than on *P. perfoliatus var. richardsonii* ($p<0.001$).

Higher density of epiphytic diatoms in flooded compared to non-flooded ponds may be a response to greater availability of DSi. Concentrations were on average 3-fold higher in the flooded ponds (Appendix A). Despite higher concentrations of nutrients (dissolved and total N and P) in the non-flooded ponds, these factors did not result in elevated epiphytic diatom density relative to flooded lakes. Instead, mean epiphytic diatom density per cm^2 on all substrates in the flooded ponds was found to be almost twice that in non-flooded ponds (Fig. 2.3). Flooded ponds, however, support less than half as much macrophyte standing crop as non-flooded ponds, and therefore provide less colonizable area of macrophyte substrate per m^2 of pond area. Thus, overall, total epiphytic diatom standing crop in flooded and non-flooded ponds is likely similar when expressed per unit area of pond surface.

2.4.3 Epiphytic diatom community composition

The distribution of samples in a two-dimensional MDS plot (Fig. 2.4) shows that the greatest differences in composition of epiphytic diatom communities occur among ponds. Separation of community composition between samples for flooded and non-flooded ponds is also readily apparent. The spread of sample scores among the different substrates within each pond was small relative to differences among ponds and between flood classes, and the relative position of sample scores from the different substrates was highly inconsistent among the study ponds, suggesting that differences among the substrates exerted weak control on epiphytic diatom communities, with little to no systematic differences among lakes.

A series of one-way ANOSIM tests allowed assessment of the relative importance of each of the individual factors (individual pond, pond flood class, and substrate type) on composition of epiphytic diatom communities, without removing the effects of the other factors. Differences among individual ponds accounted for the greatest amount of variation in epiphytic diatom community composition ($R = 0.784$, $p<0.001$), followed by differences between flooded and non-flooded ponds ($R = 0.332$, $p<0.001$) and then by differences among substrates ($R = 0.081$, $p = 0.01$). Although statistically significant, the values of the R-statistics clearly show that differences in epiphytic diatom community composition among the three substrates are highly overshadowed by differences among the individual ponds and between flooded and non-flooded ponds.

A two-way crossed ANOSIM test of pond and substrate factors on epiphytic diatom community composition resulted in statistically significant differences among the ponds, independent of effects of the substrates (global $R = 0.927$, $p<0.0001$), and among all three substrate types (artificial substrate, the two Potamogeton taxa) within each pond (global $R = 0.570$, $p<0.0001$; Table 2.2). Pair-wise comparisons showed that composition of epiphytic diatom communities differs significantly among all four ponds and among all three of the substrates (all $p<0.0001$; Table 2.2). The difference in epiphytic diatom community composition between *P. perfoliatus* var. *richardsonii* and *P. zosteriformis* ($R = 0.560$) was less than that between *P. perfoliatus* var. *richardsonii* and polypropylene sheets ($R = 0.705$), but was similar to the amount of difference between *P. zosteriformis* and polypropylene sheets ($R = 0.555$). By accounting for the effects of differences among ponds, the two-way crossed ANOSIM test greatly improved the ability to detect the effect of substrate on epiphytic diatom community composition compared to the one-way ANOSIM tests.

A two-way crossed ANOSIM test of the factors flood class (i.e., flooded vs. non-flooded ponds) and substrate type on epiphytic diatom community composition resulted in statistically significant differences between flooded and non-flooded ponds, independent of effects of substrate type (global R = 0.328, p<0.0001), and among the three substrates, independent of the differences between flooded and non-flooded ponds (global R = 0.127, p = 0.009; Table 2.3). Based on values of global R, flooding exerts greater control on epiphytic diatom community composition than do differences among substrates.

Comparison of results from the 1-way and 2-way ANOSIM tests with the factor 'flood class' indicates that accounting for substrate effects did not improve our ability to detect the effect of flooding on epiphytic diatom community composition (1-way ANOSIM without substrate effect removed, R = 0.332, versus 2-way ANOSIM with substrate effect removed, R = 0.328 (Table 2.3). In addition, accounting for differences in community composition between the flooded and non-flooded ponds only modestly improved our ability to detect differences among the three substrates (1-way ANOSIM without effects of flood class removed, R = 0.081, versus 2-way ANOSIM with effects of flood class removed, R = 0.127) (Table 2.3). In contrast, comparison of results from the 1-way and 2-way ANOSIM tests with the factor 'individual pond' indicates that accounting for differences in epiphytic community composition due to pond-specific factors substantially improved the ability to detect differences among the three substrates (1-way ANOSIM with pond effect not removed, R = 0.081, versus 2-way ANOSIM with pond effect removed, R = 0.570) (Table 2.2). Thus, it is only within individual ponds that variation in host substrate acts as a substantial regulator of epiphytic diatom community composition. This finding is important, because it may help reconcile debates that have persisted for many decades among limnologists about whether macrophytes act as neutral substrate or exert differential effects on epiphytic algae (Siver, 1977; Morin, 1986). For example, Pip and Robinson (1984), Blindow (1987) and many others have reported that substrate effects between different macrophyte species account for significant differences in composition of epiphytic communities, but they examined plants only from within an individual waterbody. Our results indicate that within individual basins is the only scale for which considerable substrate effects are apparent. Substrate effects have a very modest influence at larger scales that compare among water bodies, or along environmental gradients. Studies by Reavie and Smol (1997) and Rothfritz *et al*. (1997) support this conclusion.

Results of the ANOSIM tests showed that significant differences exist between the composition of epiphytic diatom communities growing on the artificial substrate compared to those growing on *in situ* macrophytes, but that the magnitude of the differences was comparable to that observed between the two naturally occurring macrophyte taxa. Thus, bias imposed by use of the artificial substrate is apparently no worse than the influence of confounding factors that are introduced when epiphytic samples are compared among different host macrophyte taxa. Our results justify use of artificial substrate because it does not appear to introduce greater uncertainty than that obtained from use of different macrophyte taxa. Furthermore, use of an artificial substrate will likely remove variation due to the confounding effects of factors that are known to control epiphyte communities growing on in situ natural substrates when comparisons are made among ponds and lakes (e.g., substrate age, location within a waterbody, water depth, macrophyte host species; Amireault and Cattaneo, 1992; Sokal, 2007; Table 4).

2.4.4 Epiphytic diatom indicator taxa for the presence or absence of flooding

Using the criteria described in the Methods, SIMPER analysis performed on the epiphytic diatom communities growing on all the substrates (n = 59) identified five taxa that are ‘strong flood indicators’ (*Gomphonema angustum, G. gracile, Rhopalodia gibba, Nitzschia fonticola* and *Cymbella microcephala*). Three taxa (*Epithemia turgida, Navicula cryptocephala* and *Craticula* *halophila*) were identified as ‘strong non-flood indicators’. Six taxa (*Achnanthes minutissima*, *Cocconeis placentula* small (<15µm), *Gomphonema parvulum, Epithemia adnata*, *Nitzschia paleacea* and *Navicula radiosa*) were identified as ‘moderate flood indicators’, and four taxa (*Cocconeis placentula* (>15 µm), *Nitzschia palea*, *Navicula minima*, and *Gomphonema clavatum*) were identified as ‘moderate non-flood indicators.’ In total, the 18 taxa that were allocated to one of the 4 indicator groups for the presence or absence of flooding contributed 78% of the dissimilarity between epiphytic diatom communities of the flooded ponds and non-flooded ponds. The other diatom taxa (15 of 33) that met the criteria for inclusion in our numerical analyses did not show a discernable preference for flooded or non-flooded ponds.

2.4.5 Can epiphytic diatoms be used to detect flood events in a stratigraphic record?

The natural experiment found that (1) composition of epiphytic diatom communities differs significantly between flooded and non-flooded ponds of the PAD, and (2) numerical methods identified indicator diatom taxa associated with the presence or absence of river flooding. A question we can now address is whether this information can be used to identify past flood events in a stratigraphic record. We tested the ability of the indicator taxa to identify flood events in a sediment core from PAD 5 (Wolfe *et al*., 2005) by comparing results to a nearby stratigraphic record where flood events were identified using the magnetic susceptibility measurements (Wolfe *et al*., 2006). Previous interpretation of the stratigraphic changes in diatom assemblages used diatom-environment relationships derived from surface sediment surveys along a hydrolimnological gradient. Although the approach identified marked multi-decadal variations in conditions, it was not able to identify flood events (Wolfe *et al*., 2005).

The sum of the moderate non-flood indicator taxa and moderate flood indicator taxa appears to track long-term (decadal and longer) changes in hydrolimnological conditions at PAD

5 (Fig. 2.5). Percent abundances of the moderate flood indicator taxa were low between ~1835 and 1890 and were replaced by moderate non-flood indicator taxa that maintained high relative abundance until ~1900. After ~1900, relative abundance of the moderate flood indicator taxa increased.

Taxa in the strong flood indicator category accounted for 8–29% of the epiphytic diatom sum in the stratigraphic record from PAD 5. We assessed whether samples with high relative abundance of the strong flood indicator taxa indicate flood events, by converting the % abundance of the strong flood indicator taxa to Z-scores and comparing years with Z-scores >+0.5 and +1.0 to years in which floods were equal to or greater than the 1974 flood, as identified using the magnetic susceptibility record from the PAD 54 core. Of the 46 samples from PAD 5 that encompass the time period covered by the PAD 54 record (~1820–2001 CE), 8 samples had Z-scores >1.0 and 5 samples had Z-scores between 0.5 and 1.0. Of the 8 samples with Z-scores>1.0, 6 matched dates of major floods detected at PAD 54, within a ±4-year span, while 3 of 5 samples with Z-scores between 0.5 and 1.0 also matched dates of major floods. Four flood events detected at PAD 5 (~1986, ~1980, ~1959, and ~1826) did not correspond to major floods in PAD 54 with respect to the 1974 threshold, however all of these events do correspond to lower-magnitude flood events in the PAD 54 record, with respective dates of 1986, 1979, 1958/60, and 1824. There is no historical record of a flood in 1986, although examination of tree scars along the Peace River indicates an ice-jam flood likely occurred in 1986 (Smith, 2003). Although multiple physical and geochemical records in the PAD 54 stratigraphy also support the occurrence of a flood in 1986 (Wolfe *et al*., 2006), these data suggest the magnitude of this event was less than the 1974 flood, in contrast to the evidence from PAD 5. Additional flood records are required to resolve this discrepancy. The remainder of the flood events identified at PAD 5

(~1980, ~1959, and ~1826) are also supported by historical records of high water events that document significant flood activity in 1979, 1958, and 1826 (PADTS 1996). Overall, of the 13 flood events at PAD 5 inferred from our analysis of the epiphyte diatom record, all but 1986 correspond to flood events in the historical record (PADTS, 1996). The majority of them are classified as high magnitude.

Six major flood events identified from the magnetic susceptibility record at PAD 54 (~1949, 1932, 1928, 1905, 1877, 1872) were not detected by the strong flood indicator diatom taxa in sediments from PAD 5. Results suggest floods that strongly affect PAD 54 may not necessarily always penetrate to the more elevated portions of the Peace sector of the delta. The strong flood indicator diatom taxa in sediments from PAD 5 also identify a multi-decadal interval in the mid-1800s absent of major flood events, a finding that is consistent with the PAD 54 record. Overall, high concordance between flood events identified using strong flood indicator diatom taxa in sediments from PAD 5 and the independent paleo-flood record from PAD 54, suggests that flood indicator epiphytic diatom taxa can be used to detect occurrence of past floods in stratigraphic diatom records.

2.5 Discussion

Consistent with evidence from floodplains in other geographic locations (Lewis *et al*., 2000; Squires and Lesack, 2003b; Wantzen *et al*., 2008), this study demonstrated that lentic basins in the Peace-Athabasca Delta are strongly influenced by flood events, which act as ‘pulse’ type disturbances (*sensu* Lake, 2000) that alter physical and chemical conditions for at least a growth season. Although this result is not surprising, we have shown that flood events significantly alter the density and composition of epiphytic diatom communities that grow on natural and artificial substrates relative to communities in non-flooded ponds. Moreover, our methodological approach identified diatom taxa capable of indicating flood events in floodplain ponds in both contemporary and paleolimnological contexts. The findings suggest an effective new tool for environmental scientists and natural resource managers to detect frequency of floods and other short-lived and sharply delineated pulse-type disturbances (e.g., hurricanes, intense drought seasons, chemical spills).

Climate warming and other processes affected by human activities exert great influence on floodplain ponds and lakes by modifying flood frequency (Prowse and Culp, 2006; Schindler and Smol, 2006; Wantzen *et al*., 2008). Changes in frequency of floods and other pulse-type disturbances, however, are hard to discern because paleolimnological and long-term monitoring methods are generally designed to identify ‘ramp’ and ‘press’ disturbances that act over long time periods or generate long-lasting ecological responses (*sensu* Lake, 2000). Long-term monitoring records of sufficient duration to disentangle natural variability from human impacts are rare, and their utility is often compromised by data gaps and inconsistencies. Also, long-term monitoring records often do not include data from bio-indicators. Our results suggest that epiphytic diatoms can provide useful information about pulse disturbance events in lakes if they are incorporated into monitoring protocols. Artificial substrate provides advantages for comparing epiphytic communities among ponds (e.g., standardization of colonization time, water depth, and factors that promote host-specificity), relative to sampling diatoms growing on natural (*in situ*) macrophytes.

2.5.1 A new approach to diatom-based paleolimnological reconstructions

During the past 20 years, paleolimnological studies that use diatoms have increasingly relied upon spatial surveys of contemporary limnological data and diatom assemblages in surficial sediments (top ~1 cm) of lakes and ponds along broad environmental gradients to inform reconstructions of past environmental changes (Hall and Smol, 1996). This training-set approach provides a method to quantify the optima and tolerances of each diatom taxon along gradients of environmental variables, and has proven to be highly effective for detecting and quantifying changes resulting from ‘ramp’ and ‘press’ type disturbances (*sensu* Lake, 2000) such as lake acidification and eutrophication (Simpson and Hall, 2009) and alternate stable-state changes (McGowan *et al*., 2005). Theoretically, the training-set approach is less well suited to determine changes in pulse disturbances than ramp and press disturbances, because it is based on analysis of environmental gradients.

In dynamic floodplain environments like the PAD, year-to-year hydrolimnological variability can be high at many sites. This makes it difficult for a training-set approach to quantify environmental affinities of diatom taxa because measurement of limnological variables in spot water samples does not capture the same time frame and variability reflected by surface-sediment diatom assemblages, which typically accumulated over several years. Sedimentary diatom assemblages in the shallow macrophyte-rich ponds of the PAD are often dominated by epiphytic taxa (Wolfe *et al*., 2005, 2006, 2008a). Simultaneous sampling of the living epiphytic flora and water samples may improve the quantification of species-environment relations for assessing pulse disturbances. Our study benefited from several years of hydrolimnological monitoring that provided essential knowledge for choosing appropriate study sites.

The experimental approach used in this study demonstrated that composition of epiphytic diatom communities differed significantly between flooded and non-flooded ponds of the PAD. Numerical methods enabled identification of indicator diatom taxa that discriminated between flooding and non-flooding conditions. Comparison of the percent abundance of strong flood indicator diatom taxa in a sediment core from closed-drainage pond PAD 5 with an independent paleo-flood record based on magnetic susceptibility measurements from nearby, flood-prone oxbow lake PAD 54 and historical records, demonstrated that our approach shows remarkable promise for obtaining paleo-flood records from sedimentary diatom assemblages. Previous interpretations of diatom profiles that used the conventional training-set approach emphasized longer-term (multi-decadal to centennial), ramp-type responses to climate trends and did not identify pulse events (Wolfe *et al*., 2005). Although limnological factors such as pH, specific conductance, nutrients and light availability are likely directly responsible for differences in epiphytic diatom community composition in the PAD, these factors are mainly driven by flood frequency (Wolfe *et al*., 2007; Sokal *et al*., 2008).

Overall, results of our study suggest that epiphytic diatoms have the potential to assess past changes in flood frequency and other pulse-type disturbances such as droughts, hurricanes and chemical spills. The approach utilizes indicator species and will thus be limited by factors inherent to community-based approaches (Smol, 2008). For example, absence of a flood indicator taxon is probably not sufficient to conclude the absence of a flood event, although the multi-decadal interval of infrequent flooding during the mid-1800s in the PAD 5 epiphytic diatom record was in agreement with the PAD 54 magnetic susceptibility record. Instead, flood indicators should be used to infer the occurrence of a flood. The technique will perform best in lakes with rapid sedimentation rates that allow sediment sampling to achieve temporal resolution of 1 to a few years, the time resolution required to detect short-lived events. Also, paleolimnological studies may lack modern analogues for sedimentary diatom assemblages because the ‘calibration’ data are obtained from short-lived experiments that fail to capture analogous environmental conditions of the past. Further applications and testing of our methods are required to identify the strengths and limitations of this approach.

2.6 Acknowledgments

Corina McDonald, Robert Grandjambe, Dorte Koster and Yi Yi assisted with the fieldwork. We thank Tammy Karst-Riddoch for training JW in diatom taxonomy and for providing data on the chronology and diatom percent abundances of the PAD 5 sediment core. We thank Mike Sokal and other members of our research group for helpful discussions that improved this paper. We thank the staff of Wood Buffalo National Park who provided logistical support for fieldwork. This study was funded by grants from the Natural Sciences and Engineering Research Council of Canada, the Polar Continental Shelf Project, and the Northern Scientific Training Program of Indian and Northern Affairs Canada. The paper benefited from helpful suggestions by two anonymous reviewers and Mark Brenner.

2.7 Figures

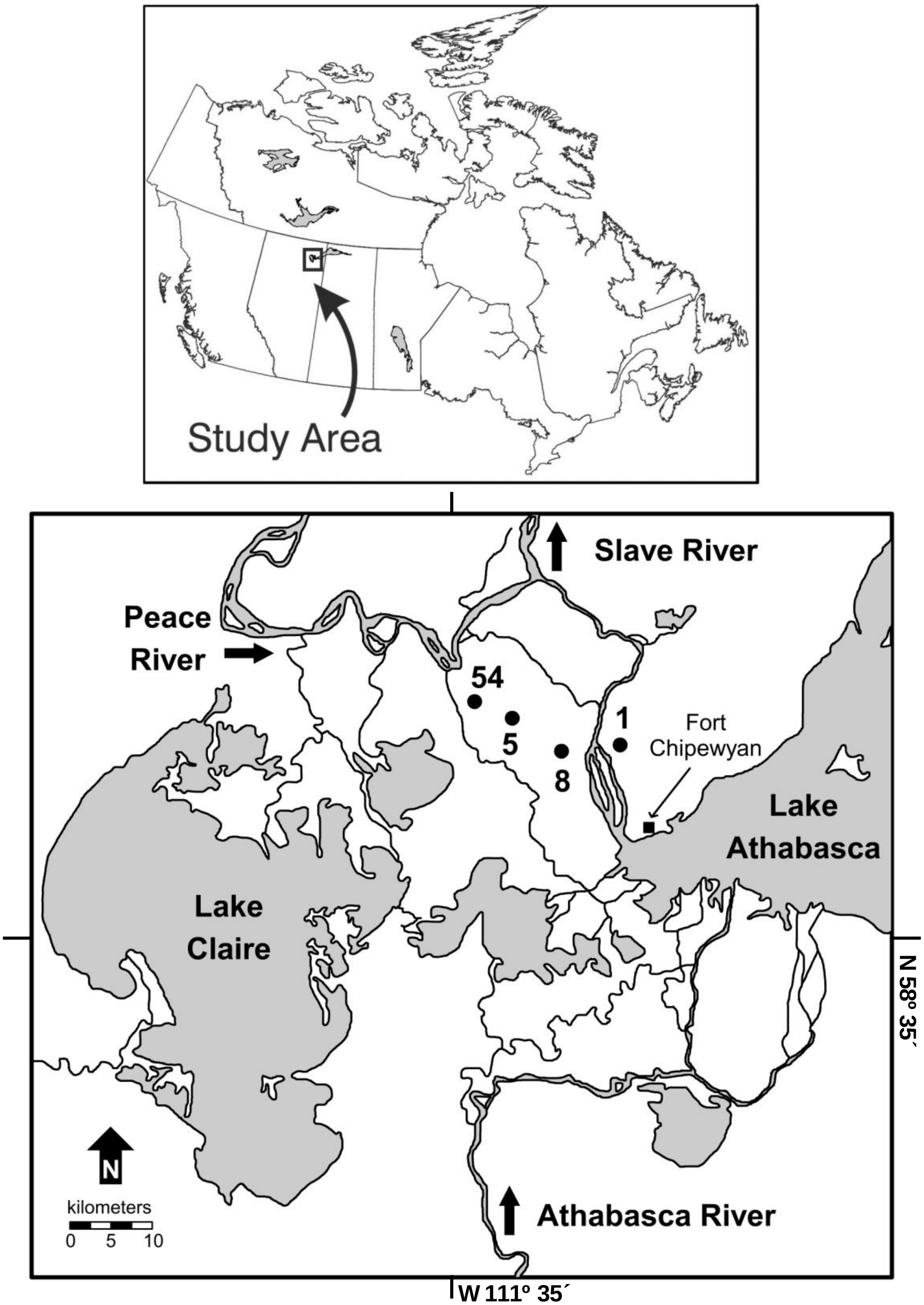

Figure 2.1 Map showing the Peace-Athabasca Delta and location of the study ponds. Ponds PAD 1 and PAD 5 have not flooded since at least 1997, whereas ponds PAD 8 and PAD 54 flooded in 2005.

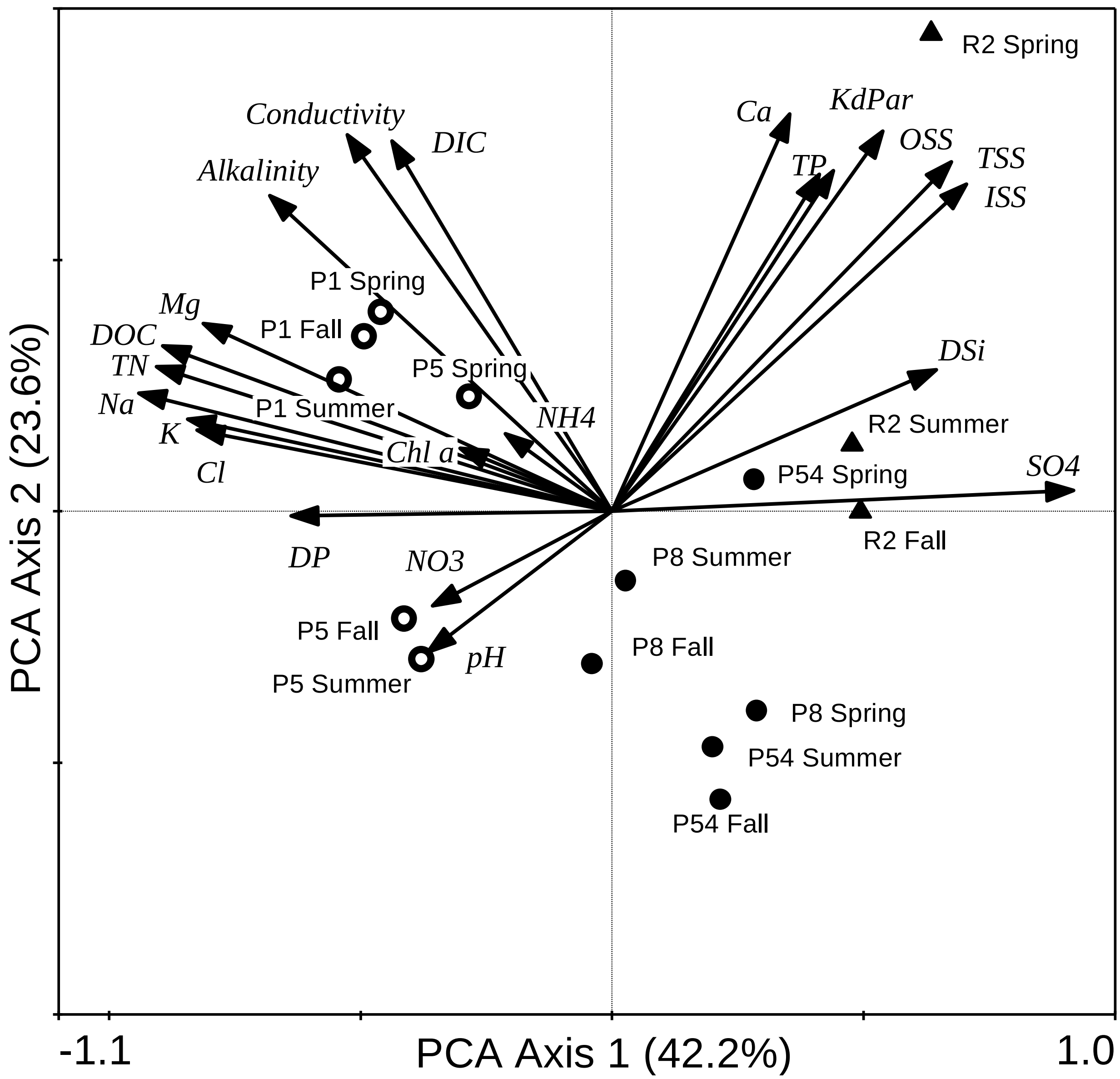

Figure 2.2 Principle components analysis (PCA) biplot of the limnological data obtained from lakes PAD 1, 5, 8 and 54 and the Peace River (R2) during the ice-free season of 2005 showing sample scores as circles and environmental variables as vectors. Ponds PAD 8 and 54 flooded in spring of 2005 (solid circles), likely with Peace River water (solid triangles) whereas ponds PAD 1 and 5 did not flood since at least 1997 (open circles). All variables were natural log (x + 1)-transformed prior to analysis, with the exception of pH and Kd-par. Codes for environmental variables are listed in the ''Methods''.

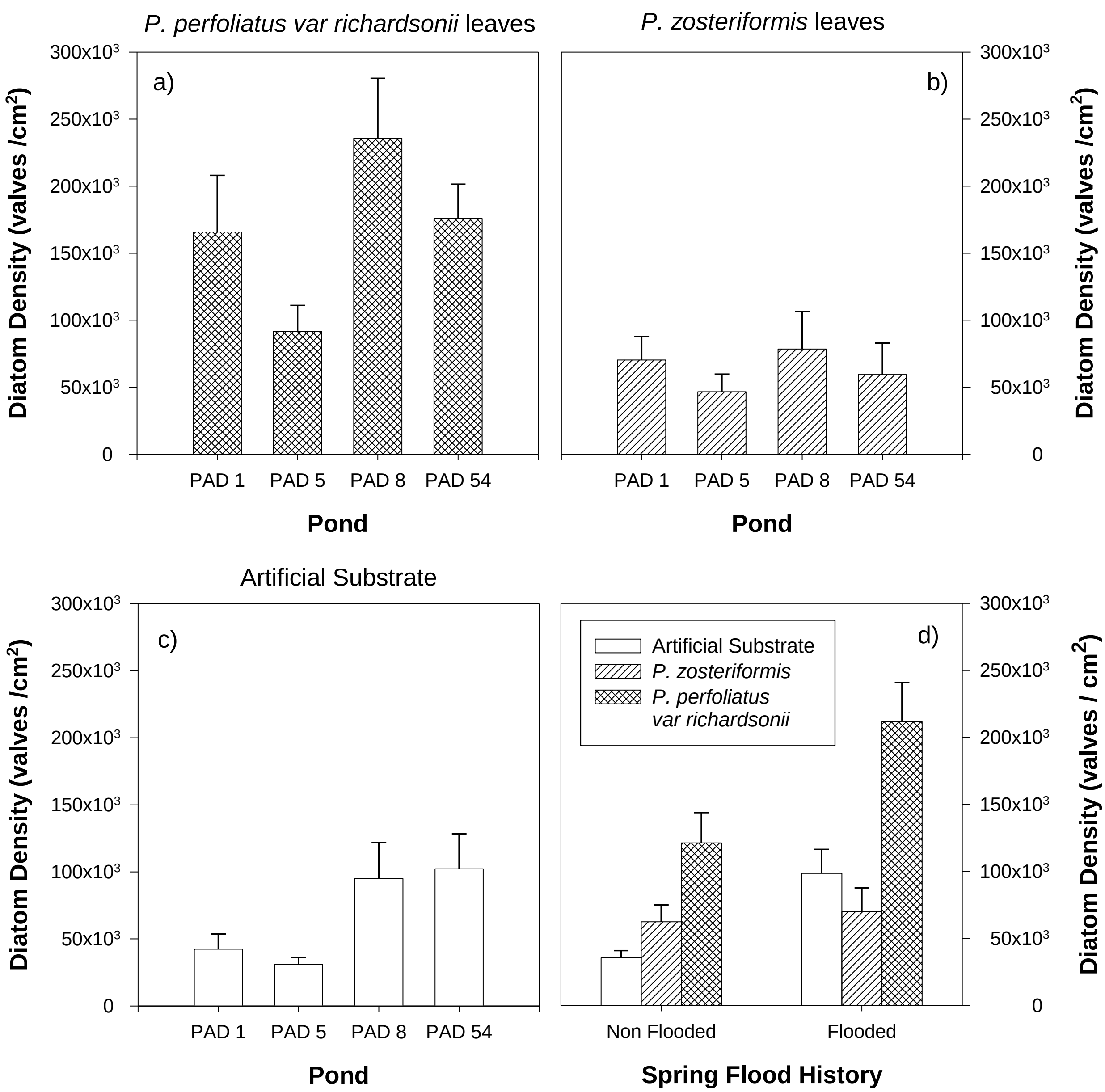

Figure 2.3 Density ± 1 standard error of epiphytic diatoms (No. of valves cm^{-2}) that accrued during the study (2005) in ponds PAD 1, 5, 8 and 54 on substrates **a** *Potamogeton perfoliatus* var. *richardsonii*, **b** *P. zosteriformis*, and **c** artificial substrate **d** contrasts diatom density on samples from flooded and non-flooded ponds pooled for each substrate.

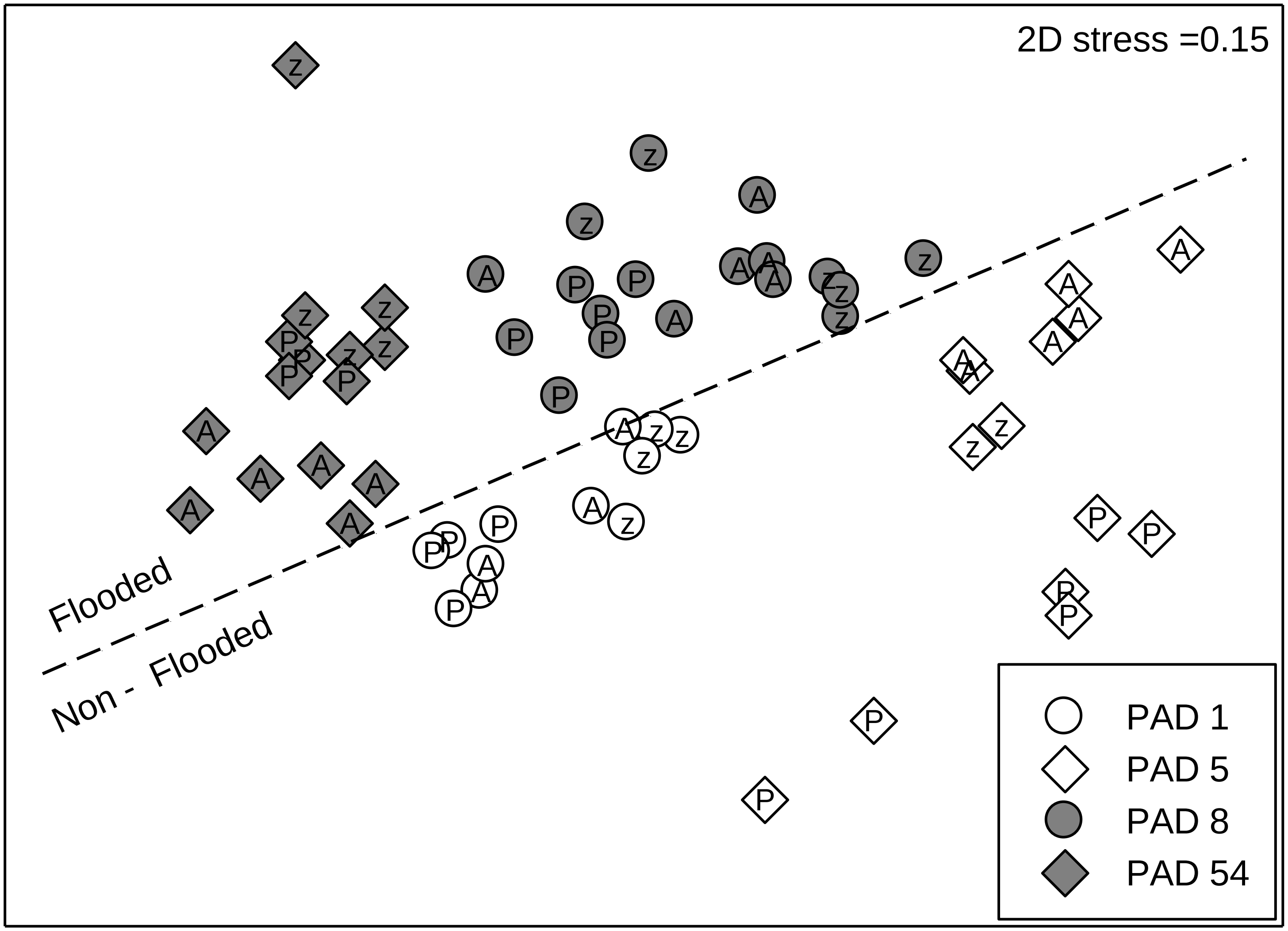

Figure 2.4 Multi-Dimensional Scaling (MDS) plot of sample scores (n = 59) based on epiphytic diatom taxon percent abundances in samples from the four study ponds in the Peace-Athabasca Delta that flooded (PAD 8, 54) and did not flood (PAD 1, 5) in spring of 2005. Within each symbol is a letter code for substrate type: A—polypropylene artificial substrate, Z—*Potamogeton zosteriformis* and P—*P*. *perfoliatus* var. *richardsonii*. The dashed line shows separation of sample scores between the flooded and non-flooded ponds.

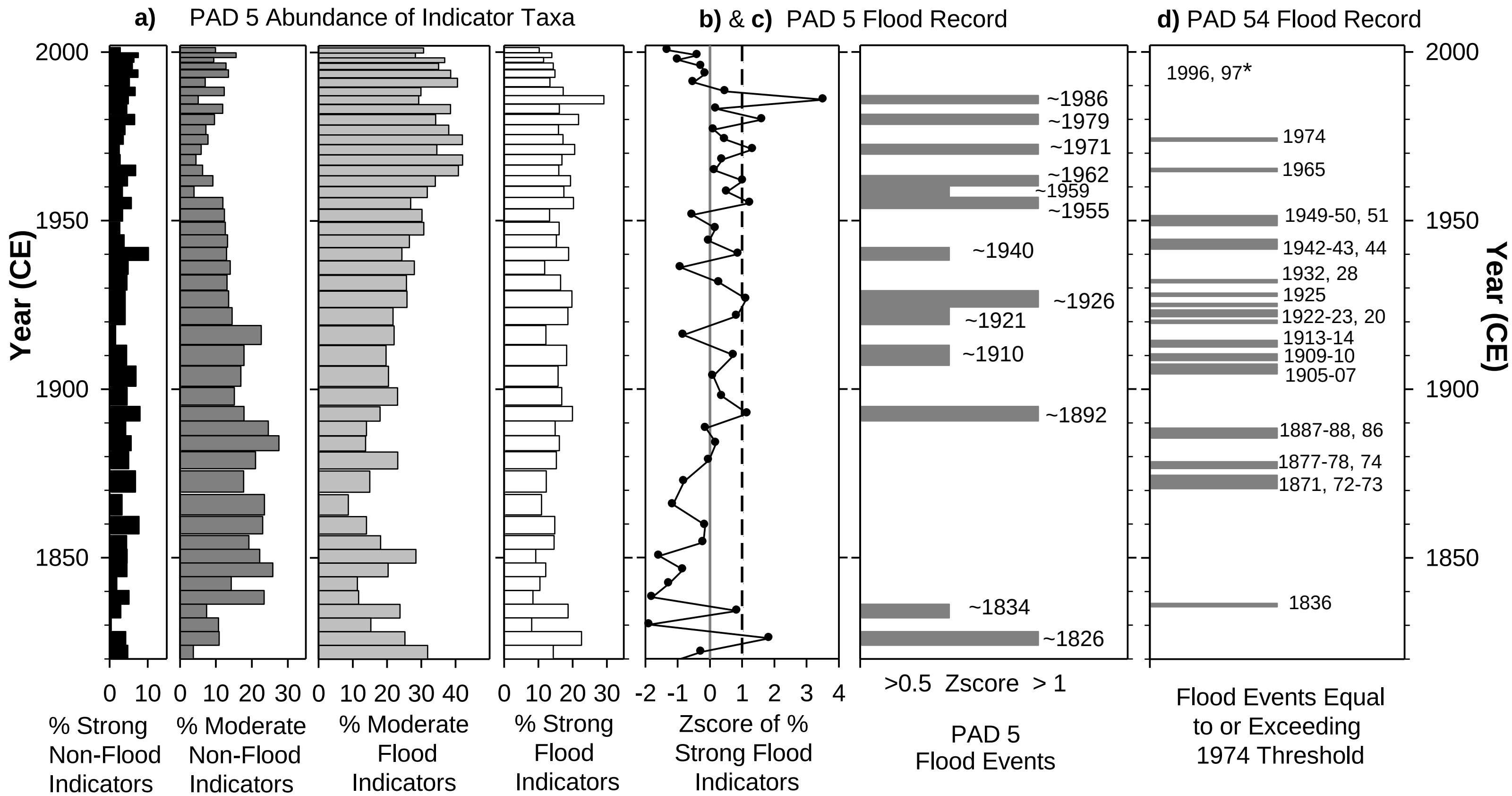

Figure 2.5 a Stratigraphic plot for the PAD 5 sediment core of summed percent abundances of epiphytic diatom taxa, after excluding non-epiphytic taxa from the diatom sum in the sediment samples, of the four categories of flood indicator diatoms identified from four flooded and non-flooded study ponds in the Peace-Athabasca Delta. **b** Z-Scores of the relative abundance of Strong Flood Indicator diatom taxa in the PAD 5 sediment core. **c** Bar graph showing sediment samples from PAD 5 that exceeded Z-scores of the relative abundance of Strong Flood Indicator diatom taxa of 0.5 (short grey bars) and 1 (long grey bars) Z scores from **b**, which likely indicate occurrence of flood events at PAD 5. **d** Bar graph shows flood events during the past ~180 years at nearby oxbow lake PAD 54 that met or exceeded the magnetic susceptibility value associated with the 1974 ice-jam flood event (modified from Wolfe *et al*., 2006) and allows comparison with the PAD 5 flood record based on Z-scores of the relative abundance of Strong Flood Indicator diatom taxa. Years presented along the right side of the graphs are estimated dates of flood events that meet or exceed the magnetic susceptibility associated with the 1974 flood. Note that 1996 and 1997 are known years with major flood events (Prowse and Conly 2000) that were not identified by magnetic susceptibility peaks exceeding the 1974 threshold due to a damping effect of decreasing sediment compaction and increasing water content on magnetic susceptibility values in sediments deposited after ~1975 (see Wolfe *et al*., 2006).

Tables 2.8

Table 2.1 Physical attributes of the Peace-Athabasca Delta study ponds. Depth values are the mean of 2003, 2004 and 2005 summer field survey results. Mean Kd_{-par} is the average of spring, summer and fall measurements obtained in 2005. Values at flooded ponds PAD 8 and 54 were high in spring, but decreased as the season progressed, while values at non-flooded ponds PAD 1 and 5 had the opposite trend. Area, shoreline length, fetch, width, length were measured from air photos taken in September 2004 and provided by Google Earth. Macrophyte biomass data are from summer transect and quadrat (0.5x0.5m) surveys conducted in 2005. Latitude and longitude coordinates are degrees, minutes and decimal fractions of a minute (WGS84).

Variable	units	PAD 1	PAD 5	PAD 8	PAD 54
Latitude	(ºN)	58º 48.351´	58 º 50.788´	58 º 48.688´	58 º 51.859´
Longitude	(ºW)	111 º 14.820´	111 º 28.781´	111 º 21.385´	111 º 33.845´
Area	(ha)	14.27	13.27	17.40	33.23
Mean Depth	(m)	0.67	0.52	1.14	1.78
Max Depth	(m)	0.90	0.85	1.77	4.15
Mean Kd_{-par}	(m^{-1})	2.50	2.34	1.69	1.19
Volume	(m^3)	95,584	69,023	198,344	591,469
Shore Line Length	(m)	1,376	2,121	2,871	6,832
Max Fetch	(m)	508	647	1,154	1,248
Max Width	(m)	398	304	214	108
Max Length	(m)	508	680	1,247	1,495
Shoreline Development Index	(Circle =1)	1.03	1.64	1.94	3.34
Mean Macrophyte Biomass	(g dry wt/ m^2)	346.9	274.1	123.4	115.7

Table 2.2 Results of Two-Way Crossed ANOSIM tests of epiphytic diatom community composition during 2005, testing: 1) no difference between ponds, independent of differences among substrates (Global R of 0.927, p<0.0001), 2) no difference among substrates, independent of differences among ponds (Global R of 0.57, p<0.0001). For all comparisons, 9999 permutations were performed for Monte-Carlo tests of significance.

Pairwise tests: between ponds

Groups	R Statistic	Significance *p*-value	Possible Permutations	# >= Observed
PAD1, PAD5	1.000	<0.0001	661500	0
PAD1, PAD8	0.827	<0.0001	9261000	0
PAD1, PAD54	0.944	<0.0001	926100	0
PAD5, PAD8	0.911	<0.0001	5976432	0
PAD5, PAD54	1.000	<0.0001	2037420	0
PAD8, PAD54	0.983	<0.0001	44823240	0

Pairwise tests: between substrates

Groups	R Statistic	Significance *p*-value	Possible Permutations	# >= Observed
polypropylene, *P. zosteriformis*	0.555	<0.0001	2.09×10^8	0
polypropylene, *P. perfoliatus*	0.705	<0.0001	$>10^9$	0
P. zosteriformis, *P. perfoliatus*	0.560	<0.0001	57047760	0

Table 2.3 Results of Two-Way Crossed ANOSIM tests for analysis of 2005 epiphytic diatom community composition testing: 1) no difference between flooded vs. non-flooded ponds, independent of differences among substrates (Global R of 0.328, p<0.0001), 2) no difference between substrates, independent of differences among ponds (Global R of 0.127, p=0.009). For all comparisons, 9999 permutations were performed for Monte-Carlo tests of significance.

Pairwise test: flooded vs. non-flooded

Groups	R Statistic	Significance *p*-value	Possible Permutations	# >= Observed
flooded, non-flooded	0.328	<0.0001	$>10^9$	0

Pairwise tests: between substrates

Groups	R Statistic	Significance *p*-value	Possible Permutations	# >= Observed
polypropylene, *P. zosteriformis*	0.119	0.042	$>10^9$	418
polypropylene, *P. perfoliatus*	0.175	0.014	$>10^9$	135
P. zosteriformis, *P. perfoliatus*	0.071	0.126	$>10^9$	1255

Table 2.4 Results of Similarity of Percentages (SIMPER) analysis used to identify epiphytic diatom taxa for the presence or absence of flooding at the four study ponds of the Peace-Athabasca Delta in 2005. As described in the Methods, indicator diatom taxa were classified into one of four groups based on criteria for within- and between-group dissimilarity values and average percent abundances in the flooded versus non-flooded ponds.

Epiphytic Diatom Indicator Taxa	Within group similarity (flooded or non-flooded ponds)			Average abundance (%)		Between group dissimilarity (non-flooded vs. flooded ponds)		
	Average similarity	Contrib. %	Cum. %	Non-flooded	Flooded	Average dissimilarity	Contrib. %	Cum. %
Strong flood indicator taxa								
Gomphonema angustum	5.71	9.89	9.89	0.36	5.76	3.00	5.73	5.73
Rhopalodia gibba	2.31	4.00	13.89	0.00	3.17	2.84	5.42	11.15
Nitzschia fonticola	2.25	3.9	17.79	0.90	1.93	2.01	3.85	15.00
Gomphonema gracile	2.10	3.64	21.43	0.28	1.19	1.48	2.83	17.83
Cymbella microcephala	1.77	3.07	24.5	0.03	2.10	2.27	4.33	22.16
Moderate flood indicator taxa								
Achnanthes minutissima	8.97	15.53	15.53	12.25	18.40	1.20	7.92	7.92
Cocconeis placentula small (<15um)	5.69	9.84	25.37	8.41	8.58	1.38	5.85	13.77
Gomphonema parvulum	3.27	5.66	31.03	1.59	3.31	1.32	4.86	18.63
Epithemia adnata	2.82	4.89	35.92	0.72	2.04	1.25	3.18	21.81
Nitzschia paleacea	1.79	3.11	38.03	0.76	1.00	1.23	2.72	24.53
Navicula radiosa	1.15	2.00	40.03	0.02	0.46	1.27	2.01	26.54
Strong non-flood indicator taxa								
Epithemia turgida	2.01	3.74	3.74	1.17	0.72	1.55	2.96	2.96
Navicula cryptocephala	1.45	2.70	6.44	0.86	0.35	1.20	2.29	5.25
Craticula halophila	1.09	2.02	8.46	0.35	0.06	1.03	1.98	7.23
Moderate non-flood indicator taxa								
Cocconeis placentula (>15um)	14.73	27.38	27.38	27.46	13.54	4.81	9.19	9.19
Nitzschia palea	5.36	9.96	37.34	8.41	1.49	3.75	7.16	16.35
Navicula minima	1.10	2.04	39.38	0.88	0.50	1.39	2.65	19.00
Gomphonema clavatum	1.72	3.21	42.59	0.90	0.64	1.21	2.30	21.95

As described in the Methods, indicator diatom taxa were classified into one of four groups based on criteria for within- and between-group dissimilarity values and average percent abundances in the flooded versus non-flooded ponds.

Chapter 3

Timescales of hydrolimnological change in floodplain lakes of the Peace-Athabasca Delta, northern Alberta, Canada

3.1 Summary

Repeated measurements over three years (2003-05) were made on a series of lakes along a hydrological gradient in the Peace-Athabasca Delta (PAD), Canada, to characterize the role of river flooding on limnological conditions of northern floodplain lakes, and to identify the patterns and timescales of limnological change after flooding. River floodwaters elevate concentrations of suspended sediment, total phosphorus (TP), SO_4 and dissolved Si (DSi) and reduce concentrations of total Kjeldahl nitrogen (TKN), DOC and most ions, which leads to increased limnological homogeneity among lakes. After flooding, limnological changes occur at two distinct timescales. In the weeks to months after flooding, water clarity increases as suspended sediments and TP settle out of the water column, but concentrations of DOC, SO_4, TKN and ions do not change appreciably. However, in the absence of flooding for many years to decades, evaporative concentration leads to an increase in most nutrients, DOC and ions. Contrary to a prevailing paradigm, these results suggest that regular flooding is not required to maintain high nutrient concentrations. In light of anticipated declines in river discharge, we predict that limnological conditions in the southern Athabasca sector will become less dominated by the short-term effects of flooding, and resemble nutrient- and solute-rich lakes in the northern Peace sector that are infrequently flooded.

3.2 Introduction

Northern river floodplains are ecologically and culturally important freshwater landscapes that are strongly regulated by floods and variations in river flow (Marsh and Hey, 1989; English *et al*., 1997; Prowse and Conly, 1998; Schindler and Smol, 2006; Wolfe *et al*., 2007a). Seasonal and periodic flood pulses have been shown to play an important role on the water balance, light environment, habitat availability, nutrient supply, productivity and community composition of receiving water bodies (van der Valk and Bliss, 1971; Squires and Lesack 2002; 2003a; Squires *et al*., 2002; 2009; Junk and Wantzen, 2004; Wolfe *et al*., 2007b; Brock *et al*., 2008; Wantzen *et al*., 2008; Sokal *et al*., 2010). Flooding has been recognized as a major hydrological vector for the transport of particulate matter, dissolved organic carbon (DOC), nutrients and biota within river floodplain systems (Tockner *et al*., 1999; Emmerton *et al*., 2007; 2008; Wantzen *et al*., 2008). Alterations to river discharge and flood events due to changing climatic conditions and human activities are, thus, expected to exert strong influence on high-latitude river floodplain systems (Marsh and Lesack, 1996; Rouse *et al*., 1997; Prowse *et al*., 2006; Schindler and Smol, 2006). Yet, our understanding of the effects of both short- and long-term changes in the frequency, magnitude and timing of the flood pulse on biological communities and biogeochemical processes requires further investigation (Junk and Wantzen, 2004), as does our understanding of flood pulses in lake ecosystems (Wantzen and Junk, 2008). This knowledge is crucial to formulate sound strategies for effective stewardship of water resources and aquatic ecosystems.

The Mackenzie River Basin covers 20% of Canada's land mass and is the largest source of freshwater flow from North America to the Arctic Ocean (Rouse *et al*., 2003; Woo and Thorne, 2003). The Mackenzie River drainage basin includes three major floodplains: the

Mackenzie Delta (~68^{o} 30'N), the Slave Delta (~61^{o} 20'N) and the Peace-Athabasca Delta (PAD, ~58^{o} 40'N). A dominant feature of all three deltas is an abundance of shallow, productive, macrophyte-dominated lakes with low to moderate phytoplankton abundance that experience varying degrees of hydrologic connectivity and regularity of river flooding (Marsh and Hey, 1989; Wolfe *et al.*, 2007b, Brock *et al*., 2008; Sokal *et al.*, 2008; Squires *et al.*, 2009). Limnological conditions of floodplain lakes have been examined in the Mackenzie Delta (Fee *et al.*, 1988; Squires and Lesack, 2002; 2003a,b, Squires *et al*., 2002; 2009), the Slave Delta (Brock *et al*., 2007; 2008; 2009; Sokal *et al.*, 2008; 2010) and the PAD (Wolfe *et al.*, 2007b). Studies of lakes in the Mackenzie and Slave deltas have found that flooding reduces water clarity, concentrations of most nutrients in the water column and macrophyte biomass (Squires *et al.*, 2002; 2009; Squires and Lesack, 2003a,b; Sokal *et al.*, 2010). Interestingly, the role of flooding on phytoplankton seems to diverge in lakes of these two deltas. In the Slave Delta, phytoplankton standing crop, measured as chlorophyll *a* concentration (Chl *a*), was highest in lakes that did not flood because water column nutrient concentrations were highest in these lakes (Sokal *et al*., 2008; 2010). In contrast, phytoplankton standing crop in the Mackenzie Delta was highest in lakes characterized by intermediate levels of river connectivity (Fee *et al*., 1988; Squires and Lesack, 2002). In the Mackenzie Delta, Fee *et al*. (1988) proposed that light limited phytoplankton production in lakes with high river connectivity, whereas low nutrient availability reduced growth in lakes with low river connectivity. Subsequent studies by Squires and Lesack (2002) found modest support for this hypothesis, although they suggested that grazing by zooplankton and competition with macrophytes may be the dominant influences on phytoplankton standing crops.

For the Peace-Athabasca Delta in northern Alberta, reduction of river flow due to climate change and human consumptive water uses has the potential to alter the delta's aquatic ecosystems (Prowse and Conly, 1998; Wolfe *et al*., 2008a, b; Johnston *et al*., 2010). Based on a regional survey of water chemistry and water isotope composition in 61 lakes conducted in October 2000, closed-drainage lakes (i.e., without river connectivity) have high concentrations of many dissolved ions, DOC, and dissolved nitrogen and phosphorous compared to open-drainage lakes (i.e., with continuous river connection), while restricted-drainage lakes (i.e., with periodic river connectivity) have intermediate concentrations (Wolfe *et al*., 2007b). Consistent with this pattern, analysis of photosynthetic pigment concentrations in the surface sediments found that closed-drainage lakes have higher algal production than lakes that flood more frequently (McGowan *et al*., 2011). Wolfe *et al*.'s (2007b) one-time regional survey was conducted at the end of the ice-free season, and thus likely under-represents the influence of important hydrological processes that occur during the spring freshet (i.e., snowmelt and river flooding) on limnological conditions. Previous studies have not yet identified the timescales under which limnological conditions respond to hydrological change. To improve our ability to anticipate limnological responses to climate- and human-mediated changes in river hydrology, knowledge of linkages between hydrological processes and limnological conditions is required over seasonal and inter-annual timescales.

In this study, we compare repeated hydro-limnological measurements over three years (2003-05) at lakes and rivers in the PAD to examine the role of flooding on seasonal- and inter-annual variations in physical and chemical conditions and phytoplankton standing crop. The lakes differ widely in the frequency of river flooding, from continuous flooding to an absence of floods for at least the preceding 15 years. Reports by Fuller and La Roi (1971) and MRBC

(1981) have suggested that river flooding stimulates productivity of lakes in the PAD, although they presented no data from measurements of nutrients or aquatic productivity. More recently, Prowse *et al*. (2006) reviewed ongoing and anticipated climate alterations to the hydroecology of high-latitude freshwater ecosystems and concluded that reductions in ice-jam flooding will reduce overall biological diversity and productivity, with the most pronounced effects on floodplain and delta systems. The paradigm that river flooding of PAD lakes is important for maintaining nutrients and aquatic productivity has been often repeated (Fuller and La Roi, 1971; MRBC, 1981; Prowse *et al.*, 2006; Anisimov *et al*., 2007) but is lacking verification. Thus, our study seeks to test if river flooding elevates water column nutrient concentrations and phytoplankton standing crop in flooded lakes compared to lakes that have not flooded for many years to decades. Given the possibility of reduced flooding and increasing water scarcity in the PAD (Wolfe *et al*., 2008a), this knowledge is critical to anticipate limnological changes. Ultimately, our findings provide the basis for identifying timescales of limnological trajectories that can be expected under different flood regimes.

3.3 The Peace-Athabasca Delta

The Peace-Athabasca Delta (PAD) is situated in northern Alberta, Canada, at the confluence of the Peace, Athabasca and Birch rivers (Figure 3.1). The PAD is the world's largest freshwater boreal delta and covers an area of ~6,000 km^2 (Peters *et al*., 2006). The landscape is recognized as a UNESCO World Heritage Site and a Ramsar Wetland of International Importance for its ecological and cultural importance, including that it serves as a key node for four North American flyways used by waterfowl (MRBC, 1981; Prowse and Conly, 2000).

The PAD includes the northern Peace Delta, the southern Athabasca Delta, and a central sector dominated by large, shallow, open-drainage lakes that are in continuous or near-continuous connection with rivers (e.g., lakes Claire, Mamawi, Richardson; Figure 3.1). Except for the elevated river levees, the Athabasca sector has very low topographic relief and floods frequently. In contrast, the Peace sector is a relict delta that has greater topographic relief than the Athabasca sector, with numerous inliers of Precambrian Shield protruding above the fluviodeltaic plain. This feature contrasts with the generally active floodplain landscapes of the Athabasca sector and the Slave and the Mackenzie deltas. Consequently, many lakes in the northern Peace sector receive river floodwaters only during ice-jams that occasionally form on the Peace River (Prowse and Conly, 2000).

The low relief and countless meander scars within the delta have given rise to hundreds of shallow water bodies (hereafter we refer to all water bodies as lakes). The lakes span a broad range of hydrological conditions largely related to the role of river flooding on lake water balance, and they have been functionally categorized as open-, restricted- or closed-drainage basins (Pietroniro *et al*., 1999; Wolfe *et al*., 2007b). Open-drainage lakes are connected to the river network, restricted-drainage lakes periodically receive river water and closed-drainage lakes do not receive any river input except during major flood events. The restricted- and closed-drainage lakes are numerically dominant in the PAD, and most of them are small lakes (~5-50 ha). In contrast, there are only a few open-drainage lakes located in the central region of the PAD and they tend to have very large surface area (>5000 ha). For example, of the 61 lakes surveyed by Wolfe *et al*. (2007b), only lakes PAD 25 (Blanche Lake), PAD 26, PAD 38 (Richardson Lake), PAD 45 (Mamawi Lake), PAD 46 (Otter Lake), and PAD 62 (Lake Claire) were classified as open-drainage lakes based on isotope-inferred evaporation to inflow ratios.

3.3.1 Study lakes

Nine lakes were selected from a set of 61 lakes originally sampled for water chemistry and isotope composition in October 2000, and they include lakes in the open- (PAD 45), restricted- (PAD 8, 15, 31, 54) and closed-drainage (PAD 1, 5, 9, 23) hydrological categories as defined by Wolfe *et al*. (2007*b*) (Figure 3.1, Table 3.1). A total of nine lakes were included in this study because this was the maximum number that our field sampling team and research budget could manage to sample repeatedly over the course of three seasons using boat transportation in a large and remote landscape. The nine lakes were chosen to represent the complete hydrological gradient of lakes in the PAD based on data presented in Wolfe *et al*. (2007b). The lakes were sampled 3-6 times per year for their physical, chemical and biological attributes during the ice-free seasons of 2003, 2004 and 2005. The Peace River, Athabasca River and Mamawi Creek were also sampled to characterize the water isotope signatures and physical and chemical characteristics of floodwater sources.

The closed-drainage lakes did not flood during 2003-05. To our knowledge, PAD 1 and PAD 9 have not flooded since at least the last major ice-jam flood of 1997. PAD 5 likely has not flooded since 1986 (Wiklund *et al*., 2010). PAD 23 did not flood during the three years of monitoring. A single open-drainage lake (PAD 45, or Mamawi Lake) was sampled in this study because lakes in this hydrological class are rare in the PAD and their hydrological and limnological conditions are relatively similar due to strong influence of constant river through-flow compared to restricted- and closed-drainage lakes (Wolfe *et al*., 2007b). Open-drainage lake PAD 45 occupies a large and complex basin. Consequently, three separate sampling sites were used to characterize spatial variability of limnological conditions due to hydrological gradients within the lake. Site PAD 45T1 is a sheltered, macrophyte-rich embayment located ~2 km south of the Mamawi Creek delta and was included to represent a region of the lake with relatively low river influence. Site PAD 45T2 is located between two of the discharge channels of the Mamawi Creek delta and was selected to represent a region of the lake with direct river influence. Site PAD 45 is located near the centre of Mamawi Lake and was selected to represent offshore lake conditions.

For each of the monitoring years, we divided lakes in the restricted-drainage category into two subcategories - those that flooded ('flooded restricted-drainage') and those that did not flood ('non-flooded restricted-drainage'). The flooded restricted-drainage lakes included PAD 8 in all years (2003-05), PAD 15 and 54 in 2003 and 2005, and PAD 31 at all times except spring of 2004 when it did not flood. Non-flooded restricted-drainage lakes included PAD 15 and 54 in 2004 and PAD 31 in spring of 2004 (note: PAD 31 flooded later in the summer of 2004). Flooded lakes were detected by several characteristics. These included direct observation of river inflow, recently formed high-water lines on shorelines and surrounding terrestrial vegetation, abrupt water-level rises recorded by water-level loggers, and measurement of isotopically-depleted lake water and high suspended sediment concentration.

3.4 Methods

3.4.1 Field methods and sample analysis

Water chemistry analysis was conducted on samples collected from each lake and river site in the spring (mid-May to mid-June), summer (late June to early August) and fall (late August to September). Measurements included temperature, hydrogen and oxygen stable isotope composition, pH, alkalinity, specific conductivity, and concentrations of total suspended sediment (TSS), inorganic suspended sediment (ISS), organic suspended sediment (OSS), dissolved oxygen (DO), chlorophyll *a* (Chl *a*), dissolved ions (Ca, Mg, Na, K, Cl, SO_4), dissolved reactive silica (DSi), total Kjeldahl nitrogen (TKN), inorganic nitrogen (NH_4, NO_3, NO_2), total phosphorous (TP), dissolved phosphorous (DP) and dissolved organic carbon (DOC). Water samples were collected mid-lake (or mid-channel) from a depth of ~20 cm and immediately placed in a cooler with ice and refrigerated upon returning to the field base. Oxbow lakes PAD 54 and 15 were sampled at two locations (middle of north and south arms). Water for analysis of TP and TKN was preserved by adding 1 ml of 30% H_2SO_4 to each 250 ml sample.

For Chl *a* analysis, water samples were refrigerated until filtration (usually the same day of collection or the following day) through a Whatman GFF filter (0.4-µm pore size). The filter was then folded in half, wrapped in aluminum foil and frozen until analysis. Chl *a* extraction and quantification were performed on these samples using standard fluorescence techniques described by Stainton *et al*. (1977).

Water chemistry analyses (ions, nutrients, DOC) were performed by Taiga Laboratory (Yellowknife NWT) on samples collected in 2003 and 2004, and by Environment Canada's National Laboratory for Environmental Testing (Burlington, Ontario) on samples collected in 2005. Due to logistical constraints, PAD 15 and 23 were not sampled in 2005 for nutrients and dissolved ions.

To determine concentrations of suspended sediment (TSS, ISS, OSS), water was filtered through pre-combusted (at 550^{o}C for 1 hr) and pre-weighed Whatman GF/C filters (0.7-µm pore size). Filters were folded in half, wrapped in aluminum foil and kept refrigerated until analysis. The filters were dried at 90^{o}C (48 hours) and weighed for determination of TSS concentration, then combusted at 550^{o}C (2 hours) and weighed for determination of ISS concentration. Filters were allowed to cool in a desiccator for several hours prior to weighing. OSS concentration was calculated as the difference between concentrations of TSS and ISS.

Water samples for hydrogen and oxygen stable isotope composition were sealed in 30 ml HDPE bottles and analyzed at the University of Waterloo Environmental Isotope Laboratory using standard methods (Epstein and Mayeda, 1953; Morrison *et al*., 2001). Results are reported in δ values, representing deviations in per mil (‰) from VSMOW on a scale normalized to values of Standard Light Antarctic Precipitation (-55.5 ‰ for $\delta^{18}O$; -428 ‰ for $\delta^{2}H$; Coplen, 1996). Analytical uncertainties are ±0.2 ‰ for $\delta^{18}O$ and ±2.0 ‰ for $\delta^{2}H$.

Temperature, specific conductivity, dissolved oxygen and pH were measured using a YSI 600QS multi-meter (YSI Incorporated, Yellow Springs, Ohio) in 2005, and Hannah Instruments meters (HI 9033, HI 9143M, HI 99101, HI 98128) in 2003 and 2004. Measurements were taken at 2-3 locations within a lake at regular depth intervals spanning the top 1 m of the water column, and the average value was used to represent each site.

The light extinction coefficient of photosynthetically active radiation (Kd-par) was calculated from measurements taken using an Apogee Instruments Quantum meter (Model QMSS-SUN) at ~10 depth intervals per site that spanned a 90% reduction in incident light, where water-column depth permitted. Three PAR values were recorded at each depth interval and the mean value was natural log-transformed and regressed versus depth (m). The resultant slope of the relationship was used to estimate Kd-par. As with other metered measurements, Kd-par values obtained from 2-3 locations were averaged to represent each site. Metered measurements of river sites were performed similarly, but only at one mid-channel location.

3.4.2 Data analysis

Principal components analysis (PCA) was used to explore major differences in the physical and chemical conditions among lakes and the patterns of seasonal variation. The PCA was performed using the software CANOCO version 4.5 (ter Braak and Šmilauer, 2002). All lake sites with complete data were included in the PCA. This included plotting PAD 54 and 15 north- and south-arm sites individually, though for statistical comparisons between hydrological categories (see ANOVAs described below), PAD 54 and 15 were represented as an average of their respective north and south sampling locations to prevent over-representation of these lakes. Scaling focused on inter-sample distances, and variables were divided by their standard deviation prior to ordination and centered by variables. River samples were added passively in the ordination to assess the influence of river flooding on the lakes without affecting the patterns of variation among the lakes. The ratio of TKN/TP was also added passively, because both TKN and TP were included as active variables.

The transparency of water to photosynthetically-active radiation, as measured by Kd-par, can be affected by minerogenic turbidity (estimated as concentration of ISS), suspended organic matter (estimated as concentration of OSS), coloured DOC and phytoplankton (estimated as concentration of Chl *a*) (Cristofor *et al*., 1994). Consequently, we used multiple linear regression analysis (forward and backward selection of variables, performed using the software SYSTAT version 10.5) of the concentrations of ISS, OSS, Chl *a* and DOC to elucidate which factor(s) best explain variation in the underwater light climate (Kd-par) of lakes (n=98) and rivers (n=33), with rivers and lakes analyzed separately. The regression equations (see Table 3.2) were also used to fill in missing Kd-par data for the PCA of the limnological data. TSS was the main factor used to estimate missing Kd-par values and it was highly co-linear with Kd-par, ISS and OSS. Consequently, Kd-par was retained as an active variable in the PCA.

ANOVA tests (at alpha = 0.05) were run to test if limnological variables differed among the hydrological lake categories and among seasons (spring, summer, and fall) using SPSS version 16.0. Two-way ANOVA tests were used to assess if limnological variables differed among the seasons while accounting for the influence of differences among hydrological categories. In contrast, one-way ANOVA tests were used to assess if limnological variables differed among the hydrological lake categories within an individual season. For post-hoc multiple comparisons, Tukey's tests were used, except for variables where variances remained unequal after transformation (TSS, ISS, OSS, Kd-par, Chl *a*, DSi and TP). In these latter cases, Dunnett's T3 post-hoc tests were used because it allows for unequal variances. For the PCA ordination and ANOVA tests, all variables, except pH, were $\log_e(x+1)$-transformed prior to analysis to improve normalcy and equalize variances.

3.5 Results and interpretation

3.5.1 Water balance

Water stable isotope ($\delta^{18}O$ and δ^2H) values differed markedly among the hydrological lake categories due to differences in the relative importance of river flooding and evaporation to the lake water balances (Figure 3.2). The mean isotopic values of river waters showed the least amount of seasonal variation and were closest to mean annual precipitation (δ_P), indicating that evaporation was a small component of river water balance. Mean lake water $\delta^{18}O$ and δ^2H values of the open-drainage lake (PAD 45) were very similar those of the rivers, though slightly more isotopically-enriched, indicating only a small effect of evaporation on the water balance relative to the river inputs. In spring, the mean lake water $\delta^{18}O$ and $\delta^{2}H$ value for flooded restricted-drainage lakes was very similar to that of the open-drainage lake and rivers, identifying the strong influence of river flooding on their water balance during and shortly after the spring freshet. As the season progressed, however, waters became more isotopically enriched in the flooded restricted-drainage lakes than in the open-drainage lake due to the greater influence of evaporation on lake water balance. In spring, mean isotope composition of non-flooded restricted-drainage lakes was enriched compared to that of the flooded restricted-drainage lakes because the former were not flooded. Isotopic signatures of non-flooded restricted drainage lakes and closed-drainage lakes were similar in the spring and were low relative to their values later in the ice-free season, indicating influence of snowmelt on water balance early in the ice-free season. Closed-drainage lakes experienced much greater evaporative enrichment during the summer and fall compared to the non-flooded restricted-drainage lakes, and approached signatures expected for lakes approaching terminal basin steady-state conditions (i.e., δ_{SS}; when inputs = evaporation).

3.5.2 Chemical and physical differences of the Peace and Athabasca River flood waters

The waters that flood lakes in the PAD originates from either the Peace River or the Athabasca River (Figure 3.1). For the two rivers, mean specific conductivity (220±7.8 and 227±8.0 µS/cm; Peace and Athabasca rivers, respectively (as mean ± 1 S.E.)) and alkalinity (93.84 ± 1.84 and 89.96 ± 3.04 mg/L) did not differ significantly based on 1-Way ANOVA tests ($p > 0.05$, d.f.= 22). Similarly, concentrations of Mg and K did not differ significantly between the rivers (Figure 3.3). However, the Athabasca River was significantly higher in concentrations of dissolved sodium ($p < 0.001$), chloride ($p < 0.001$) and DSi ($p = 0.03$), whereas the Peace River had higher concentrations of calcium ($p < 0.001$) and SO_4 ($p = 0.009$) (Figure 3.3).

Based on field observations, turbidity persisted longer in lakes flooded from the Peace River than in lakes flooded by the Athabasca River. For example, PAD 54 and PAD 31 both flooded extensively with river water in the spring of 2003 by the Peace and Athabasca rivers, respectively. The water column of PAD 31 cleared within ~4 weeks after the flood event, but PAD 54 took ~2 months for the sediment load to settle out. One explanation for this observation is that the sediment load in the Peace River was finer-grained and, therefore, took longer to settle out of the water column. Patterns of the rate of change in TSS concentrations support this interpretation. For example, the half-life of TSS in water at PAD 31 following a summer flood event in 2004 was estimated at 2.8 days. This is ~50% shorter than the half-life (5.1 days) calculated for PAD 54 following the 2003 spring flood. These estimates of half-life are based on first-order kinetics, which have previously been used to model sedimentation in lakes (Frisk, 1992) and wetlands (Holland *et al*., 2005). Furthermore, where sufficient data exist, first-order kinetics can be shown to accurately describe the settling of TSS from the water column (Kotz and Purcell, 1991). For example, the logarithm of TSS concentration versus time at PAD 54 (2003) follows a linear decay that spans >2 orders of magnitude of TSS ($R^2 = 99.25\%$, n=4; linear regression not shown).

3.5.3 Comparison of limnological conditions among the hydrological lake categories

The first two axes of the PCA of the physical and chemical data (n=153) explained 54.6% of the variation in limnological conditions among the study lakes and identified distinct limnological differences between flooded lakes and rivers versus the lakes that did not flood

(Figure 3.4). Sample scores from the non-flooded lakes (i.e., closed-drainage and non-flooded restricted-drainage lakes) were positioned to the left along PCA axis 1, indicative of relatively low Kd-par (= high transparency), low concentrations of DSi, Chl *a* and SO_4, and high pH and TKN:TP ratios. Sample scores for rivers and open-drainage lakes were positioned to the right along axis 1, indicating the opposite conditions. Samples from the flooded restricted-drainage lakes showed the greatest amount of variation in the PCA ordination, indicating that they experienced the greatest seasonal limnological changes. Limnological conditions of the flooded restricted-drainage lakes overlapped with those of the rivers and open-drainage lakes during the spring period when they flooded (Figure 3.4b), but rapidly migrated along axis 1 during the summer and fall as they transitioned to conditions that were more typical of the non-flooded restricted-drainage basins (Figure 3.4c, d). Interestingly, sample scores from two of the flooded restricted-drainage lakes (PAD 8 and 31) closely matched those of the river samples throughout the summer and fall, indicating strong influence of continued flood inputs throughout the ice-free season. In contrast, sample scores for PAD 15 and 54 in spring of 2003 and 2005, when they flooded, were similar to those of the rivers, but subsequently diverged during the summer and fall after flooding ceased (Figure 3.4c, d). Limnological conditions at the restricted embayment of Mamawi Lake (site PAD 45T1) were more similar to the flooded restricted-drainage lakes, due to higher pH and lower Kd-par and TP and DSi concentration, than to sites in the open-drainage regions of Mamawi Lake (PAD 45, PAD 45T2). This suggests poor exchange of water between the sheltered embayment and Mamawi Lake during periods of lower river inflow, which commonly occurred during the summer and fall.

Axis 2 of the PCA separated samples from most of the closed-drainage lakes from those of all other hydrological categories (Figure 3.4). Closed-drainage lakes were positioned high on

PCA axis 2, characterized mainly by high alkalinity and conductivity and high concentrations of TKN, DOC, and dissolved ions Mg, Na, K and Cl relative to the other hydrological categories. An exception to these patterns was PAD 23, which possessed physical and chemical characteristics more typical of the non-flooded restricted-drainage lakes due to lower concentration of solutes. For this reason, as well as others discussed below, PAD 23 was categorized together with the non-flooded restricted-drainage lakes in subsequent analyses (see Figures 3.6-3.8). Overall, ordination by PCA illustrates that variations in physical and chemical conditions of lakes that flooded within the previous few years were captured along axis 1 due to control of floodwaters on suspended sediments, water transparency, SO_4 and pH, whereas variations due to the absence of flooding for many years to decades were captured along axis 2 due to evaporative concentration of nutrients and ions.

Time-ordered trajectories of PCA scores from four representative lakes were used to explore further the seasonal and inter-annual patterns of limnological changes within each hydrological category (Figure 3.5). Limnological characteristics of PAD 5 (a closed-drainage lake that has not flooded to our knowledge since 1986) remained distinct from the rivers and did not fluctuate much during 2003-05, as indicated by the relatively tight clustering of sample scores compared to the other lakes and rivers (Figure 3.5a). The sample scores from PAD 5 were positioned in the upper left quadrant of the PCA ordination, associated with high concentrations of TKN, DOC and dissolved ions and high pH. River samples were positioned to the right along PCA axis 1, associated with high Kd-par (low clarity) and high concentrations of suspended sediment, TP, DSi and SO_4, but varied along axis 1 and 2 mainly in response to changes in TP concentration and Kd-par that were associated with seasonal fluctuations in river discharge (Figures 3.6, 3.7).

Limnological conditions of PAD 54, a restricted-drainage oxbow lake, were similar to those of river water during spring of 2003 and 2005 shortly after the lake flooded, as indicated by the overlap with river samples (Figure 3.5b). During these times, the water was turbid (high Kd-par) and had high concentrations of suspended sediment, TP, SO_4 and DSi. After flooding, values of Kd-par, suspended sediment, TP and DSi declined as the season progressed. Sample scores were nearly identical during summer and fall of the two years when the lake flooded in spring (2003, 2005), suggesting that spring flooding exerts important control on seasonal limnological patterns. During 2004, when PAD 54 did not flood, limnological conditions were less variable compared to years when the lake flooded (2003 and 2005). Interestingly, sample scores in summer and fall of the non-flood year (2004) did not differ much from those of summer and fall of years when it flooded (2003, 2005), suggesting that more than one year without flooding is required for limnological conditions to develop towards those of closed-drainage lakes.

Sample scores from PAD 31, a restricted-drainage lake that received pulses of floodwater during the spring of 2003 and 2005 and during the ice-free season of all years, shifted along PCA axis 1 (Figure 3.5c). Whenever the lake flooded, turbidity and concentrations of TP, SO_4 and DSi increased, as indicated by a shift of the sample scores to the right where they overlapped with river samples. After flood events, sample scores moved to the left along axis 1, associated with declines in turbidity and concentration of TP. The sample score from spring of 2004, when PAD 31 did not flood, lies in a unique position compared to all other samples from this lake and was characterized by the lowest Kd-par, TP, SO_4 and DSi. Later in 2004 (June, July and possibly September), PAD 31 flooded and sample scores returned to values more similar to those of the rivers. The more complex path of PAD 31 in PCA space (Fig. 3.5c), in comparison to PAD 54, exemplifies the behaviour of a multi-modal flood pulse (*sensu* Junk and Wantzen, 2004) where limnological conditions are repeatedly influenced by river water within a single ice-free season.

Sample scores from PAD 45, an open-drainage lake that receives constant river inflow, were positioned close to those of the river, indicating continuous strong influence of river water on limnological conditions characterized by high turbidity (high Kd-par) and high TP concentrations (Figure 3.5d). The small offset evident between sample scores from PAD 45 and river water is likely due to settling out of suspended matter between the river mouth and the centre of Mamawi Lake as water velocity declined, which generated values of Kd-par and TP concentration that were lower compared to the rivers.

Use of bar charts and ANOVA tests allowed us to further refine our understanding of the roles of flooding on physical and chemical conditions in the hydrological lake categories of the PAD, as described in the following sections.

<u>3.5.3.1 Suspended sediment and water clarity</u>

Content of suspended sediment (TSS, ISS and OSS) was highest in rivers and decreased along the hydrological gradient from open- to closed-drainage lakes (Figure 3.6a-c). In the lakes that flooded (open-drainage and flooded restricted-drainage), suspended sediment concentrations were highest in the spring and decreased as the ice-free season progressed. This pattern was especially apparent in the flooded restricted-drainage lakes, where TSS and ISS concentrations declined by at least an order of magnitude between spring and fall to values comparable to those of closed-drainage and non-flooded restricted-drainage lakes. The mineral fraction (ISS) dominated TSS in rivers and open-drainage and flooded restricted-drainage lakes at all times. In contrast, suspended sediment content did not vary appreciably over the course of the ice-free season in the non-flooded lakes (closed-drainage and non-flooded restricted-drainage). Also, TSS consisted of a more even mixture of organic (OSS) and mineral (ISS) fractions in the closed-drainage and non-flooded restricted-drainage basins compared to flooded lakes (Figure 3.6).

Differences in water clarity among the hydrological lake classes, as measured by Kd-par, closely followed the trends observed for TSS and ISS, including comparable patterns of seasonal variation (Figure 3.6d). ISS was the dominant factor controlling the aquatic light climate (as Kd-par) in the lakes and in rivers, based on multiple linear regression analysis with ISS, OSS, Chl *a* and DOC concentrations as explanatory variables (n=98 for lakes; n=33 for rivers; Table 3.2). Minerogenic turbidity (ISS) alone explained 66.2% and 86.7% (R^2_{adj}) of the variation in the light climate of lakes and rivers, respectively, similar to findings of Pavelsky and Smith (2009) for rivers of the PAD. OSS concentration was also found to account for significant additional amounts of variation in Kd-par in both lakes and rivers, while Chl *a* concentration only accounted for significant additional amounts of variation in Kd-par in lakes. DOC concentration was not found to explain significant additional variation for predicting the light climate in either lakes or rivers, even though the range of DOC concentration is large (2.6 to 74.7 mg/L and 4.6 to 24.5 mg/L for lakes and rivers, respectively). In fact, DOC concentration showed patterns opposite to those of TSS and Kd-par. DOC concentrations were highest in closed-drainage lakes and comparably low in the other hydrological lake categories and rivers (Figure 3.6). In all lakes, DOC concentrations did not vary appreciably during the ice-free season.

3.5.3.2 Nutrients and chlorophyll *a*

Mean total phosphorous (TP) concentration was consistently higher in rivers compared to lakes (Figure 3.7). Seasonally, TP concentrations in river water were highest in the spring and summer, and decreased in the fall (Figure 3.7a). During the spring period, lakes that flooded (open-drainage and flooded restricted-drainage lakes) had elevated TP concentrations. However, this rise was transitory, and by summer, TP concentrations became comparable to those of the non-flooded lakes — a feature that persisted into the fall.

The concentration of dissolved phosphorous (DP) was often below detection limits for analysis conducted at Taiga Laboratory on samples collected during 2003 and 2004, so a complete set of results for DP is only available from 2005 (Figure 3.7b). These data identify that DP concentration in closed-drainage lakes was double that of the other hydrological lake categories and rivers, which all have comparable values. Also, they identify that most of the TP in river waters is in particulate form, whereas about 50% of the TP in closed-drainage lakes is in dissolved form (DP). In closed-drainage lakes, mean DP concentration ranges 30-50 μg/L, suggesting these systems are not P-limited.

Total Kjeldahl nitrogen (TKN) concentration in closed-drainage lakes was consistently at least double that in lakes of the other hydrological categories, including the rivers (Figure 3.7b). The mass ratio of TKN/TP decreased with increasing river influence (Figure 3.7c). This gradient was most evident during the summer sampling period.

Inorganic nitrogen (NO_2, NO_3, NH_4) concentrations were not available for samples collected during 2003 and 2004. But samples collected in 2005 allowed us to identify that total inorganic nitrogen concentration contributes approximately 5-15% of the total nitrogen present in the lakes and rivers. Total inorganic nitrogen concentration was lowest in rivers and increased with decreasing river connectivity (Figure 3.8e).

Dissolved silica (DSi) concentration was consistently high in the rivers, with little seasonal variation (Figure 3.7d). Concentrations of DSi were higher in flooded lakes (i.e., open-drainage, flooded restricted-drainage) than in non-flooded lakes (Figure 3.7d). Concentrations tended to decline after spring in the flooded lakes, but remained relatively constant in non-flooded restricted-drainage lakes.

Mean water column Chl *a* concentration was highest in the flooded restricted-drainage lakes throughout the ice-free season but only differed significantly from mean values in the other hydrological lake categories during the spring and when values were included for the entire season (Figure 3.8a, b).

3.6 Discussion

During the past century, climate-driven changes in meltwater contributions from glaciers and snowpacks at the headwaters of the Mackenzie River Basin have caused marked reductions in both peak and total river discharge, a pattern that is expected to continue (Wolfe *et al.*, 2008a). Yet, the limnological consequences of reduced river flows and associated frequency and magnitude of flooding downstream in the PAD remain largely unknown. Here we show that river floodwaters exert strong influence on limnological conditions of lakes in the PAD, although their role in supporting nutrient concentrations has been over-estimated, and we identify timescales of limnological trajectories under different flood regimes. As illustrated below, these findings provide knowledge to anticipate the nature of future limnological changes and the timescales at which they are likely to occur.

3.6.1 The effects of flooding on nutrients and phytoplankton

Nutrient concentrations are strongly associated with hydrological conditions of lakes in the PAD. Highest concentrations of several key nutrients (DP, TKN, TIN) occurred in the closed-drainage lakes (Figure 3.7). Rivers have the highest TP concentration, but the majority is in particulate form rather than dissolved form (TP:DP >20:1 on average, see Figure 3.7a). Thus, river waters elevate TP concentration in lakes that are flooded, but concentrations rapidly decline as suspended sediments settle out of the water column. As a consequence, TP concentration of lakes that flooded during spring converged by summer to values typical of closed-drainage lakes. Thus, our data indicate that regular flooding is not required as a source of nutrients to lakes in the PAD because the closed-drainage lakes in our study contain the highest concentrations of bio-available nutrients despite the absence of flooding for at least 6-17 years. This finding is contrary to hypotheses (Fuller and La Roi, 1971; MRBC, 1981; Prowse *et al*., 2006; Anisimov *et al*., 2007) noted previously, which stated that river flooding is necessary to maintain high nutrient concentrations and aquatic productivity. However, our conclusion does agree with results from limnological studies at the Slave (Sokal *et al*., 2008) and Mackenzie deltas (Emmerton *et al*., 2008) downstream of the PAD.

Phytoplankton standing crop is low in lakes of the PAD (generally <4 µg/L). Based on standard relationships between phytoplankton standing crop and water column concentrations of TP and TN (Brown *et al.*, 2000), Chl *a* content is expected to be at least 10-fold higher than we observed in the closed-drainage lakes. This feature is also evident for lakes of the Slave (Sokal *et al*., 2010) and Mackenzie deltas (Fee *et al.*, 1988; Squires and Lesack, 2002). Fee *et al*. (1988) identified that while Chl *a* content was low overall, it was highest in lakes with intermediate river connectivity and hypothesized that this was due to a trade-off between availability of light and nutrients. We investigated this hypothesis in the PAD using multiple linear regression of water column TP concentration and Kd-par on Chl *a* concentration. Results show that Kd-par and TP concentration explain significant amounts of variation in Chl *a* concentration ($p<0.0001$)

and predict a response surface (Figure 3.9, Table 3.3) that is congruent with the light-nutrient hypothesis of Fee *et al*. (1988). However, the relationship has very low predictive ability (R^2 = 10.7%), which is also consistent with findings by Squires and Lesack (2002). The relationship was improved by also including DSi concentration (R^2 = 21.6%; Table 3) but still fails to explain the majority of variation in Chl *a* concentration. Neither water temperature (range 7.05-26.30^{o}C) nor DP (range 7-92 µg/L) explained significant (a < 0.05) additional variation in water column Chl *a* concentration.

While it is attractive to explain the observed maximal Chl *a* concentration at intermediate hydrologic connectivity as a trade-off between light and nutrient availability, other contributing factors are likely the dominant controls on the abundance of phytoplankton in the PAD. Interestingly, Flanagan *et al*. (2003) have noted that the relationship between TP and Chl *a* is much weaker for high latitude (> 60^{o}N) lakes (R^2 =7% for a Log-Log plot) than for mid-latitude lakes, and that nitrogen limitation did not account for this. Instead, they observed a strong negative correlation between Chl *a* concentration and latitude, independent of TP concentration. To explain this, Flanagan *et al*. (2003) hypothesized that the influence of abiotic factors such as light and temperature exert bottom-up control on phytoplankton abundance, or that gradients of biotic factors related to food-web composition exert top-down control. Our data identify weak predictive abilities for TP, Kd-par and DSi for water column Chl *a* (see Figure 3.9, Table 3.3), and non-significant predictive ability of DP and water temperature, a finding that suggests weak bottom-up control. Therefore, we suggest top-down processes are the dominant drivers. In the PAD, phytoplankton face greater competition with macrophytes for space and light and grazing pressure by zooplankton in closed- and non-flooded restricted-drainage lakes compared to flooded restricted-drainage and open-drainage lakes. In short, multiple environmental factors associated with the hydrological gradient (e.g., water clarity, nutrients, macrophytes, zooplankton, and fish) likely contribute to the observed maximal phytoplankton standing crop in the flooded restricted-drainage lakes (Figure 3.8a, b).

3.6.2 Timescales of hydrolimnological change in the PAD

Our results identify that the responses of hydrolimnological conditions to flooding operate at two distinct timescales in lakes of the PAD. This feature is captured by PCA ordination of samples collected during ice-free seasons of three successive years from nine lakes that span the hydrological gradient in the delta (Figure 3.4), and is conceptualized in Figure 3.10.

One timescale involves the short-term responses of lakes over a period of weeks to months after flooding, which is captured by PCA axis 1 (Figure 3.4) and the horizontal axis of Figure 3.10. Floods exchange a substantial volume of water in the shallow floodplain lakes with isotopically-depleted river water that is higher in content of P-rich suspended inorganic sediment and dissolved Si, calcium and SO_4, and lower in pH. The turbid river waters reduce water clarity (increase Kd-par) of flooded lakes. In the weeks to months after a flood, lake water becomes isotopically-enriched due to evaporation, and the supplied sediments settle out of the water column leading to increases in water clarity (reduced Kd-par) and a shift to limnological conditions that resemble those of non-flooded restricted-drainage lakes (Figure 3.5b, 3.10). Restricted-drainage lakes, thus, oscillate along the horizontal axis in response to the rapid exchange with flood waters and move leftwards on the axis in response to evaporation and sedimentation processes that affect concentrations of TSS and TP, and chemical (pH) and nutrient (DSi) factors prone to rapid biological alteration.

In contrast to the relatively rapid, seasonal to inter-annual changes that follow a flood event, the limnological transition from restricted-drainage to closed-drainage hydrological conditions occurs over a much longer timescale of several years to decades, as concentrations of the more conservatively acting ions, refractory organic matter (e.g., DOC) and dissolved nutrients (DP, N) increase. In the absence of flooding, the water balance of closed-drainage lakes is mainly controlled by precipitation and evaporation. Elevated concentrations of DOC, TKN, DP and many dissolved ions in the closed-drainage lakes compared to lakes which have flooded in recent years is consistent with studies of lakes in central Alberta, which show that lakes with longer water residence time have higher conductivity and concentrations of DOC and DON due to the strong role of evaporative concentration (Curtis and Adams, 1995). The process of evaporative concentration operates over years to decades and causes the limnological conditions of closed-drainage lakes to develop along a different trajectory, characterized by increasing concentrations of dissolved nutrients and ions, as illustrated by PCA axis 2 in Figure 3.4 and the vertical axis in Figure 3.10. In a matter of days, a flood event will reset limnological conditions of a closed-drainage lake to that of a flooded restricted-drainage lake (Figure 3.10).

Fortunately, PAD 23 provides an interesting situation that helps to clarify the timescale at which the transition from restricted-drainage to closed-drainage limnological conditions occurs. The isotopically-enriched lake water composition of PAD 23 is consistent with the absence of flooding for several years, but the water chemistry reveals that evaporative concentration of nutrients and ions has not yet fully developed to a limnological state characteristic of the other closed-drainage lakes. Thus, our limnological evidence suggests the lake flooded recently, but prior to the onset of our hydrolimnological monitoring in October 2000. In contrast, the other closed-drainage lakes have not flooded, to our knowledge, since 1986 (PAD 5) and 1997 (PAD

1, PAD 9). Thus, it appears that half a decade or more post-flooding is required for a lake to shift from restricted-drainage to closed-drainage limnological status in comparison to the much more rapid hydrological response which takes ~2 years. Given that the most recent large-scale flood event occurred in 1997, much of the northern Peace sector of the PAD landscape has likely transitioned to closed-drainage limnological conditions.

The broad hydrological gradient that characterizes the PAD has provided the opportunity to define the two timescales of limnological change that occur under different flood regimes. Perhaps unique to this landscape, in comparison to the other Mackenzie River Basin deltas, the relict Peace delta allows us to characterize limnological changes when floods recur at decadal intervals or longer. In contrast, the Slave and Mackenzie delta lakes tend to oscillate along the short-term horizontal axis of Figure 3.10 because they are active floodplain landscapes (Brock *et al*., 2009: Marsh and Lesack 1996; Lesack *et al*., 1998). However, if flood frequency in those landscapes were to decline, we propose that some Slave and Mackenzie Delta lakes will begin to undergo limnological changes along the long-term (vertical) axis of Figure 3.10. Broader transferability of the timescales of limnological change at the PAD to other floodplains is likely dependent on local climate and other factors, and deserves further study.

The variability in flooding strength and extent observed in the three years of our study (see PAD 54; Figure 3.4b) is consistent with the Flood Pulse Concept (Wantzen *et al*., 2008), which states that flood pulse patterns and strength vary among years on inter-annual and inter-decadal timescales. Flood pulses have been previously noted to temporally reset and homogenize limnological conditions of floodplain lakes. After floodwaters subside and lakes become disconnected from the river, limnological conditions will diverge due to local differences in basin and catchment characteristics (Tockner *et al*., 2000; Junk and Wantzen, 2004; Thomaz *et* *al*., 2007). Improved understanding of the impacts of both short- and long-term changes in the frequency, magnitude and timing of the flood pulse on biological communities and biogeochemical processes has previously been identified as an important focus for research (Junk and Wantzen, 2004). This is particularly acute in light of current and anticipated changes in climate which are anticipated to lead to long-term shifts in the hydrologic regime of many river systems (Rouse *et al*., 1997, Prowse *et al*., 2006; Schindler and Smol 2006; Wolfe et al., 2008a; Milner *et al*., 2009). Landscape-scale studies of delta systems can take advantage of existing hydrologic gradients to discern the role of hydro-climatic conditions on the limnological responses to changing flood regimes.

3.7 Conclusions

In a synthesis of studies of tropical and temperate floodplain systems, Thomaz *et al*. (2007) proposed that flooding increases the homogeneity of limnological conditions of river floodplain systems. This occurs because flooding exchanges water, dissolved substances and particulate matter between rivers and lakes, causing limnological conditions of flooded lakes to become more similar to the rivers and each other. During intervals without flooding, however, limnological conditions diverge among floodplain lakes because differences in localized (i.e., lake basin and catchment) biotic and abiotic driving forces diversify limnological and ecological conditions (Junk and Wantzen, 2004; Thomaz *et al*., 2007; Wantzen *et al*., 2008). Our findings from a northern boreal river floodplain are consistent with this concept. For example, flooded lakes in the PAD possess similar physical and chemical conditions due to strong influence of the rivers, although subtle differences between flooded lakes in the Peace and Athabasca sectors can be attributed to the different water chemistry and settling rate of suspended sediment of the

Peace and Athabasca rivers. These findings are also congruent with the Flood Pulse Concept, which predicts that the nutrient status of the floodplain depends on the amount and quality of dissolved and suspended solids of the parent river (Junk and Wantzen, 2004). In the absence of flooding, limnological conditions of the closed-drainage lakes diverge from those of the flooded lakes and rivers.

Building on this conceptual model, findings of this study allow us to characterize the timescales at which limnological conditions of floodplain lakes change after flooding in the PAD (see Figure 3.10). Pulse flood events raise lake-water concentrations of suspended sediments, TP, SO_4 and DSi and reduce water clarity and concentrations of dissolved nutrients, DOC and ions. At a timescale of a few weeks to months after floodwaters subside, suspended sediments rapidly settle out of the water column leading to reduction of TP concentration and increased water clarity. Over this short timescale, concentrations of DOC, SO_4, TKN and ions do not change appreciably. In the absence of flooding over multiple years to decades, within-basin processes dominate that lead to greater limnological heterogeneity broadly characterized by high water clarity and high concentrations of DOC, TKN, bio-available nutrients and ions and low concentrations of suspended sediments and SO_4. In this region of semi-arid climate, concentrations of these variables increase due to evaporation. These conditions define the current limnological status of much of the northern Peace sector of the delta. Given expected trajectories of change in river discharge (Wolfe *et al*., 2008b), we predict that limnological conditions in the southern Athabasca sector will become less dominated by short term (intra- to inter-annual) oscillations along the horizontal axis of Figure 3.10, and become increasingly dominated by longer-term unidirectional progression along the vertical axis. This transition has begun in the more elevated portions of the Athabasca sector, such as observed at PAD 23, and is likely to become more widespread (Wolfe *et al*., 2008a). Based on our study, this transition to increasing hydrologic closure of PAD lakes will be accompanied by an increase in water transparency and bio-available forms of nutrients which will promote primary production, a finding consistent with that of McGowan *et al*. (2011).

3.8 Acknowledgements

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3.9 Figures

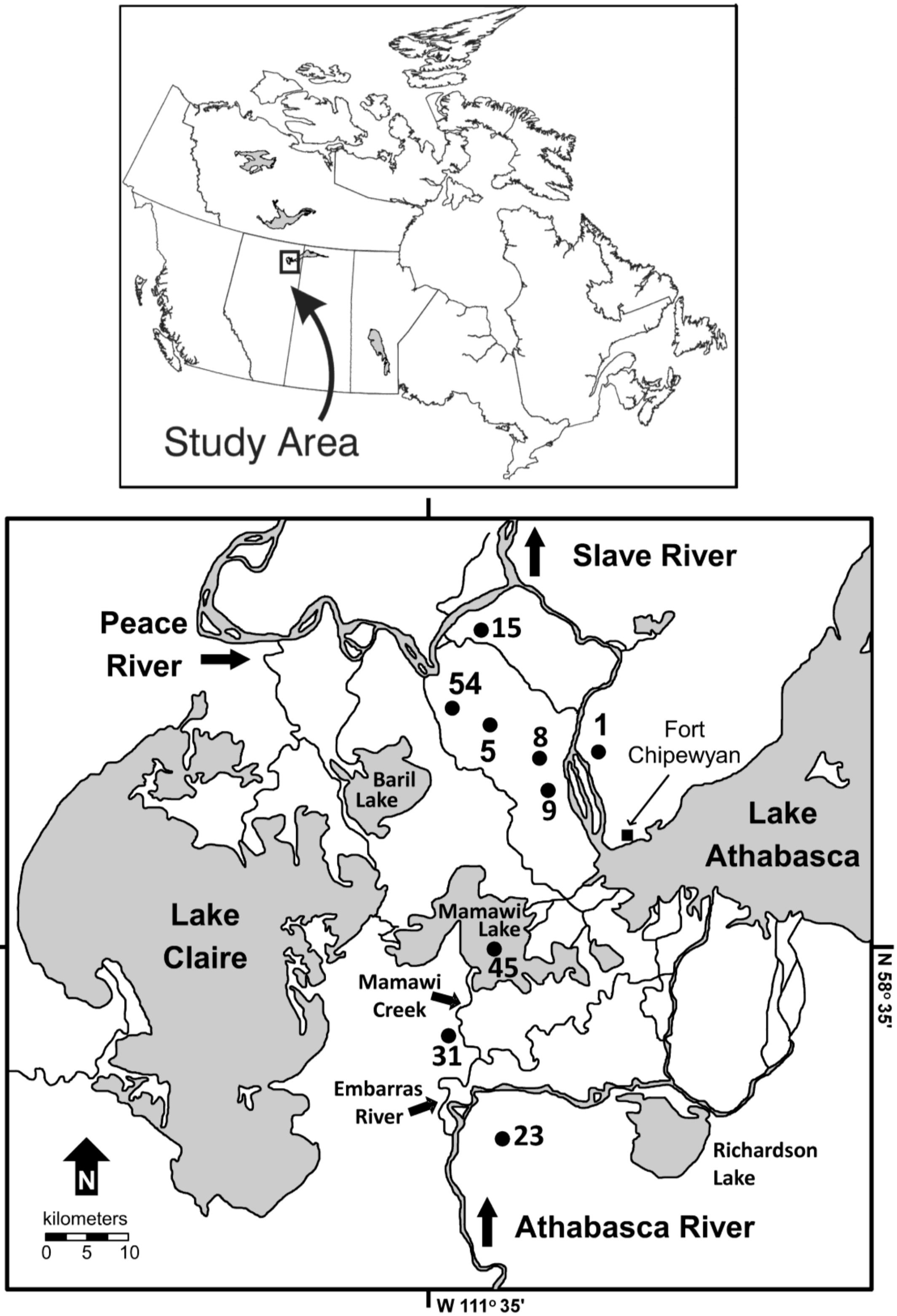

Figure 3.1 Maps showing locations of the Peace-Athabasca Delta (Alberta, Canada) and the study sites.

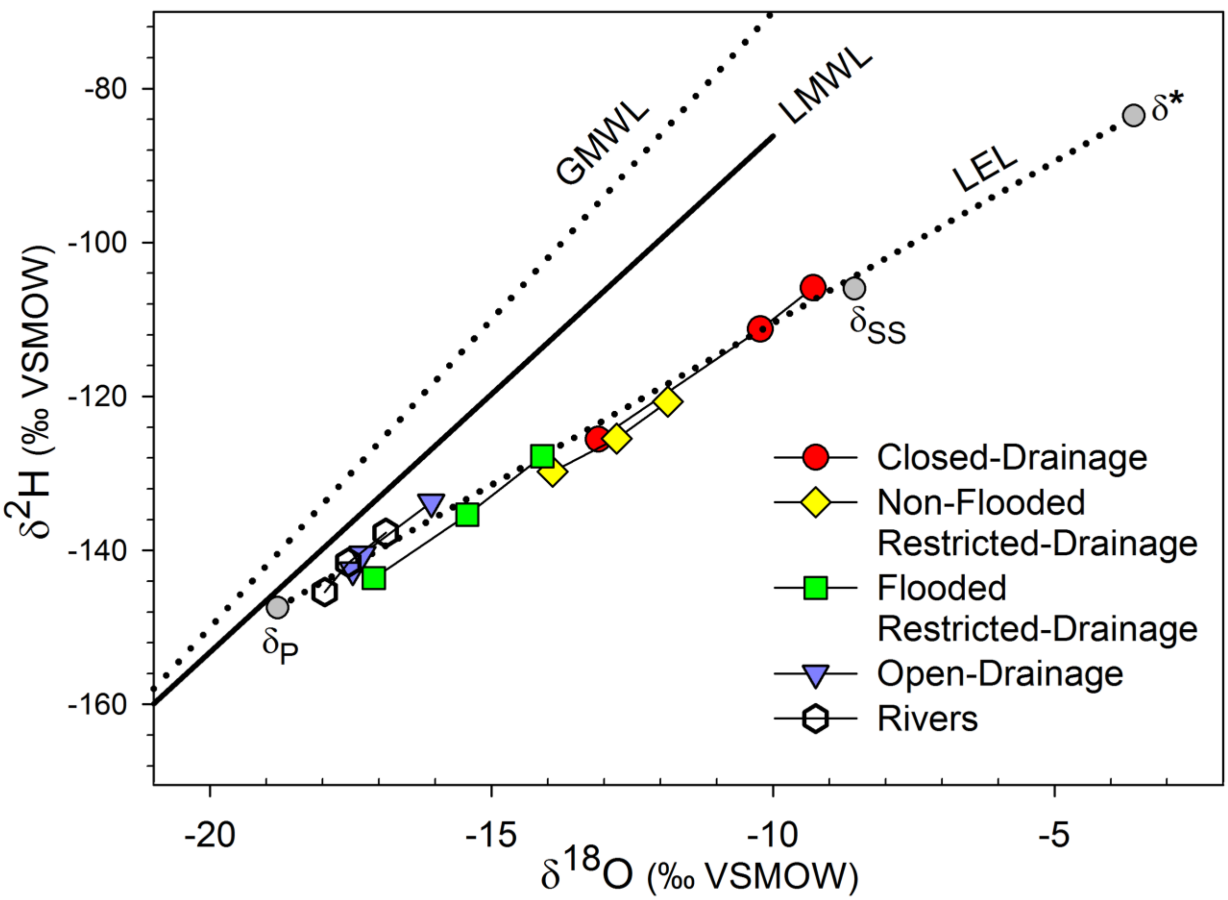

Figure 3.2 Mean isotopic composition of waters from closed-drainage, non-flooded restricted- drainage, flooded restricted-drainage and open-drainage lakes, and rivers during spring (mid-May to mid-June), summer (late June to early August) and fall (late August to September) of the years 2003-2005. Predicted local evaporation line (LEL) for the PAD is shown in relation to the Global Meteoric Water Line (GMWL: Craig, 1961) and the Local Meteoric Water Line (LMWL). δ_{SS} represents the special case of a terminal (i.e., closed-drainage) basin in isotopic and hydrological steady-state fed by waters of mean annual isotopic composition of precipitation (δ_P), and δ^* represents the theoretical limiting isotopic enrichment attainable by a desiccating water body under average thaw season conditions (see Wolfe *et al.*, 2007b for further details).

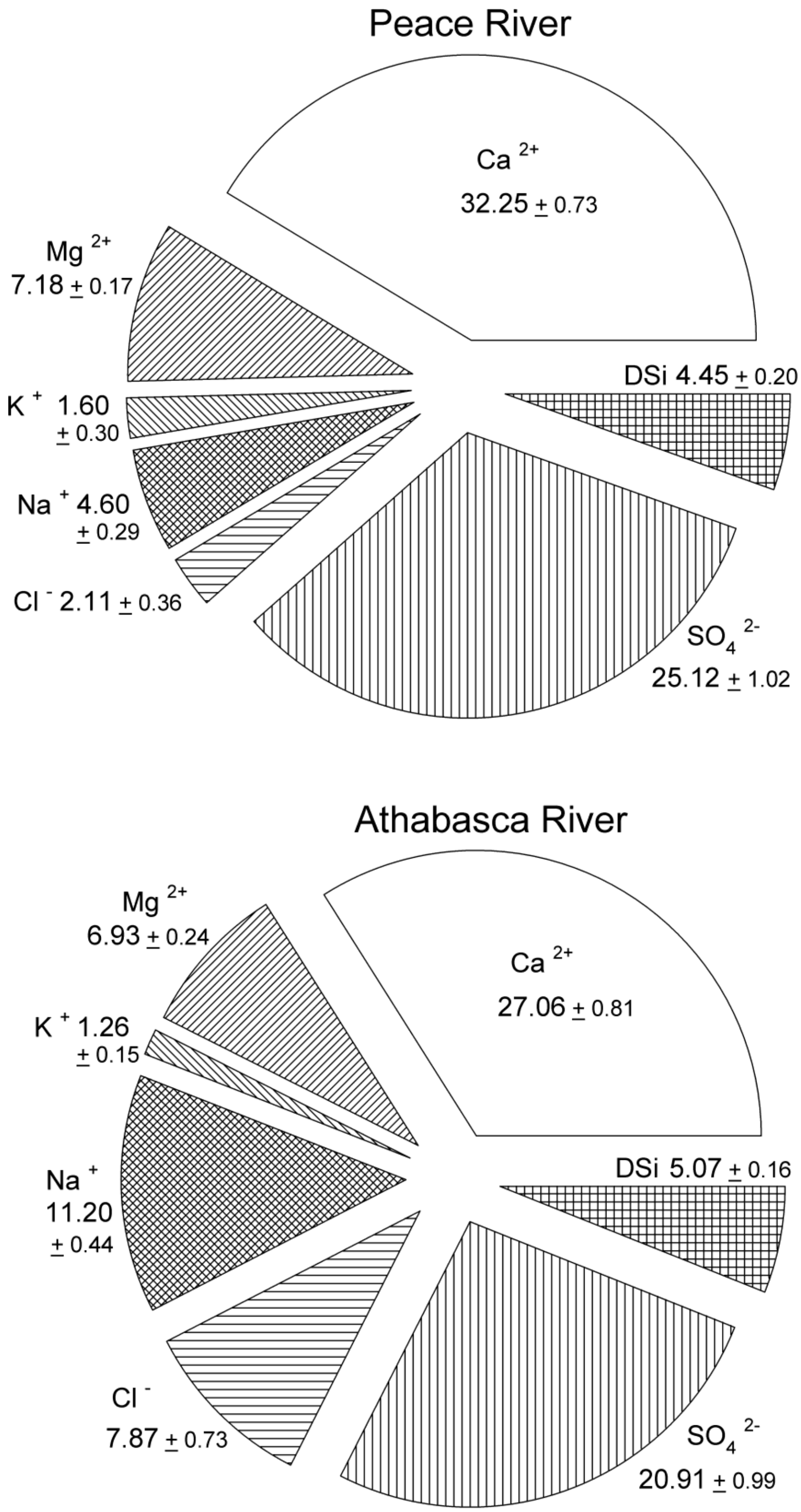

Figure 3.3 Pie chart comparing the mean concentration (mg/L ± 1 standard error) of dissolved ions in the Peace (n=13) and Athabasca (n=10) rivers during the open water seasons of 2003-2005.

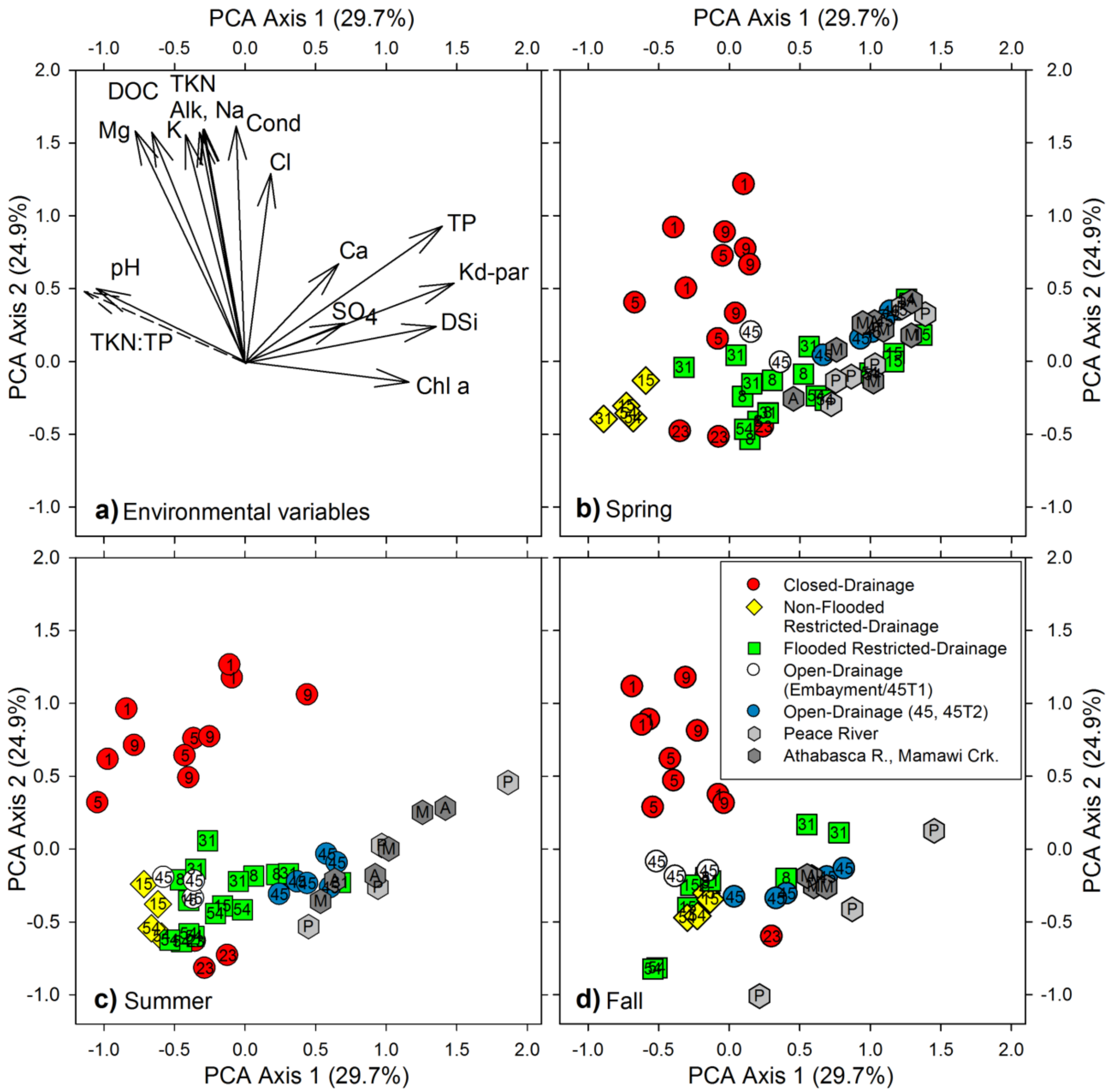

Figure 3.4 Principal Components Analysis (PCA) of physical and chemical data from water samples collected from the study lakes in the Peace-Athabasca Delta in 2003-2005 (n=153). Vectors of the supplied environmental variables are shown in panel **a)**, whereas the other panels show the sample scores for samples collected in **b)** spring (mid-May to mid-June), **c)** summer (late June to early August) and **d)** fall (late August to September). The number within each symbol represents the lake number (i.e. 5 = PAD 5). For rivers, the letter within the symbol represents the Peace (P), Athabasca (A), or Mamawi (M) rivers. The river samples and the nutrient ratio variable TKN:TP were included passively. All variables, except pH, were $\log_e$ (x+1)-transformed prior to analysis.

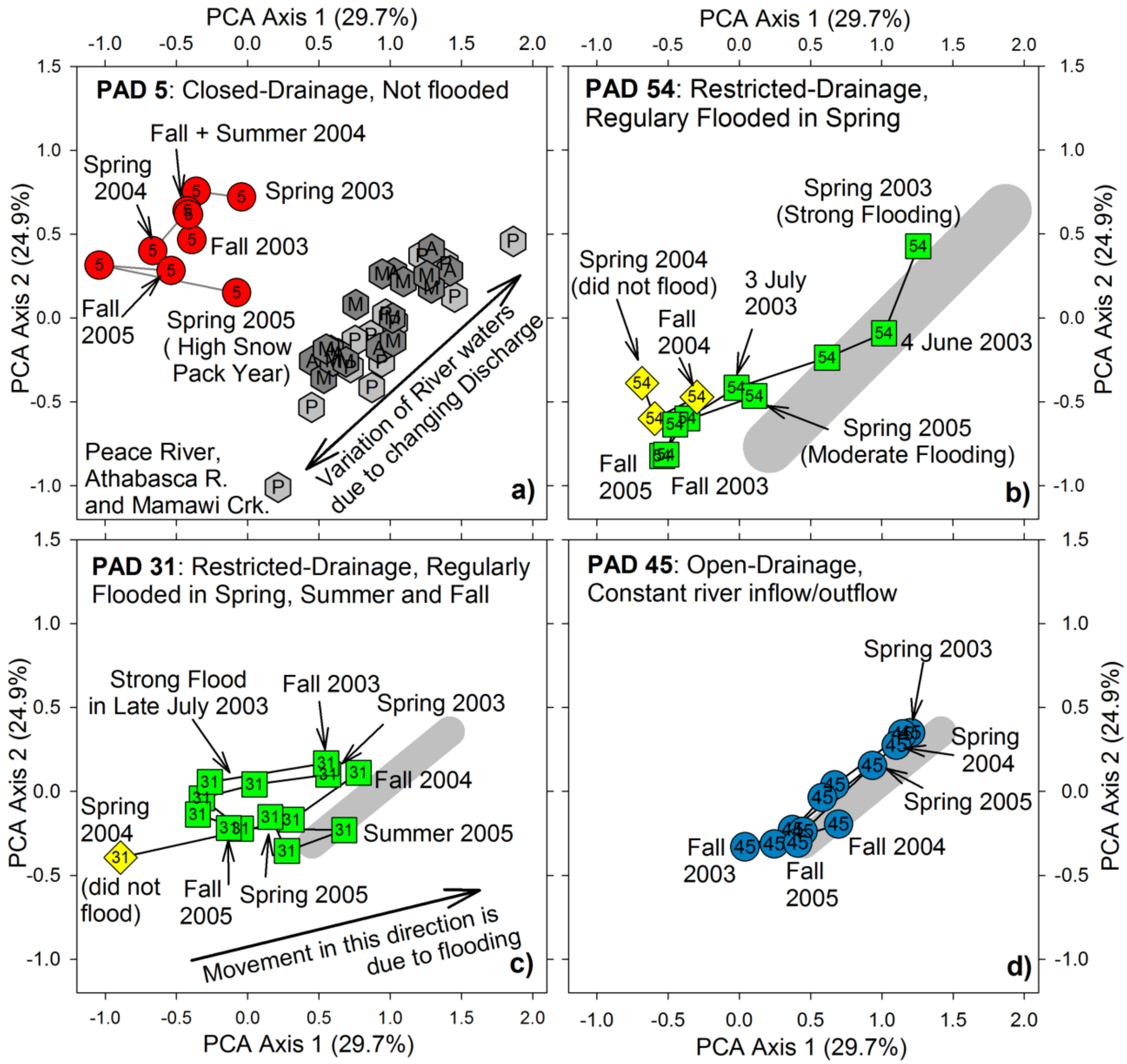

Figure 3.5 Principal Components Analysis (PCA) plots of sample scores to highlight patterns of seasonal and inter-annual trajectories of limnological change in selected study lakes, **a)** PAD 5 and river samples. **b)** PAD 54, **c)** PAD 31 and **d)** PAD 45. Use of symbols and colours are the same as in Fig 4. For panels **b)**, **c)** and **d)**, the sample scores for the river that potentially floods into each lake are depicted by a grey area corresponding to the linear regression of river samples in PCA space [Peace River for panel **b)** (R^2= 83.2%); Athabasca River for panels **c)** and **d)** (R^2= 72.2%)**]**. The width of the grey line is equal to the 95% confidence interval for the linear regression of the respective river data.

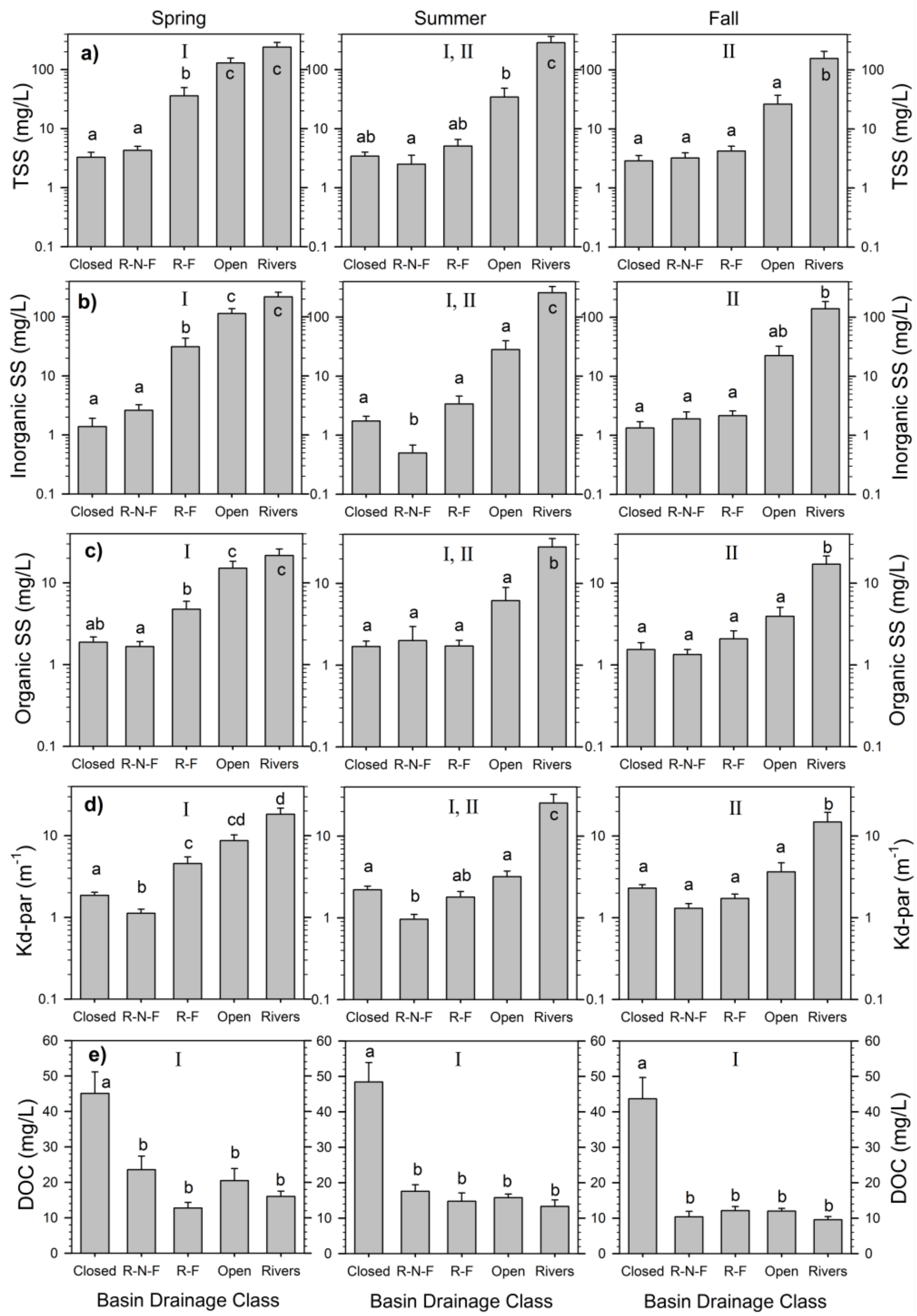

Figure 3.6 Mean concentrations of (**a**) TSS, (**b**) ISS, (**c**) OSS, (**d**) Kd-par and (**e**) DOC in the rivers and hydrological lake categories of the Peace-Athabasca Delta during spring (mid-May to mid- June), summer (late June to early August), early fall (late August to September) of 2003, 2004 and 2005. Error bars = 1 standard error. R-N-F refers to restricted-drainage non-flooded lakes while R-F refers to restricted-drainage flooded lakes.

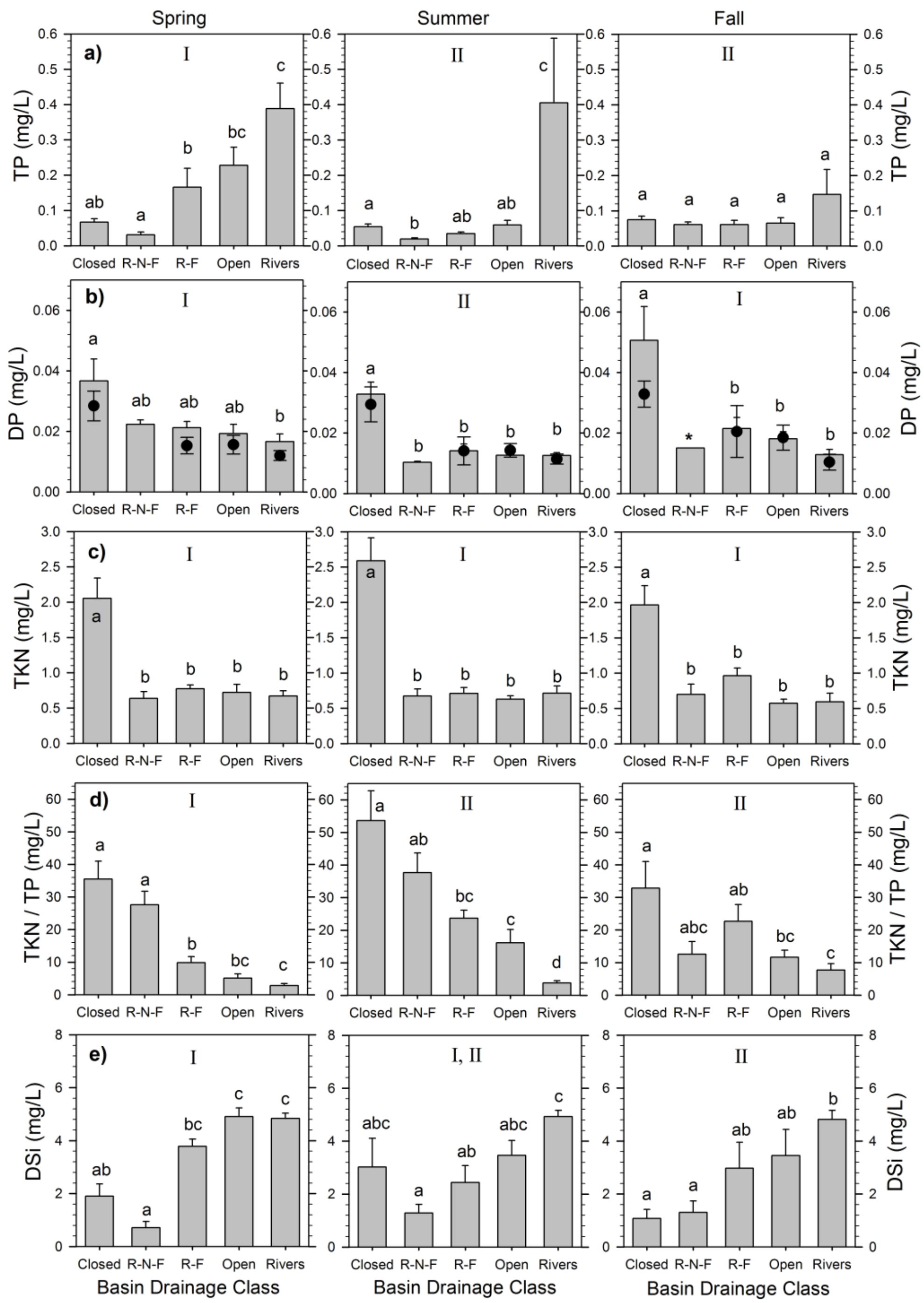

Figure 3.7 Mean concentrations of (**a**) TP, (**b**) DP, (**c**) TKN, (**d**) mass ratio of TKN/TP and (**e**) dissolved reactive silica in the rivers and hydrological lake categories of the Peace-Athabasca Delta during spring (mid-May to mid- June), summer (late June to early August), early fall (late August to September) of 2003, 2004 and 2005. Error bars = 1 standard error. Note that in (**b**), there were several DP values below detection limits for analyses performed at Taiga Laboratory (in 2003 and 2004 data). For comparison, the higher quality 2005 data (NLET) is shown by the solid circles (with error bars = +/- 1 standard error). ANOVA tests were performed on all available data. *****Non-flooded restricted drainage category was excluded from the fall pairwise comparison as only one datum exists above the detection limit for this category. There are no DP data for the non-flooded restricted-drainage category for 2005.

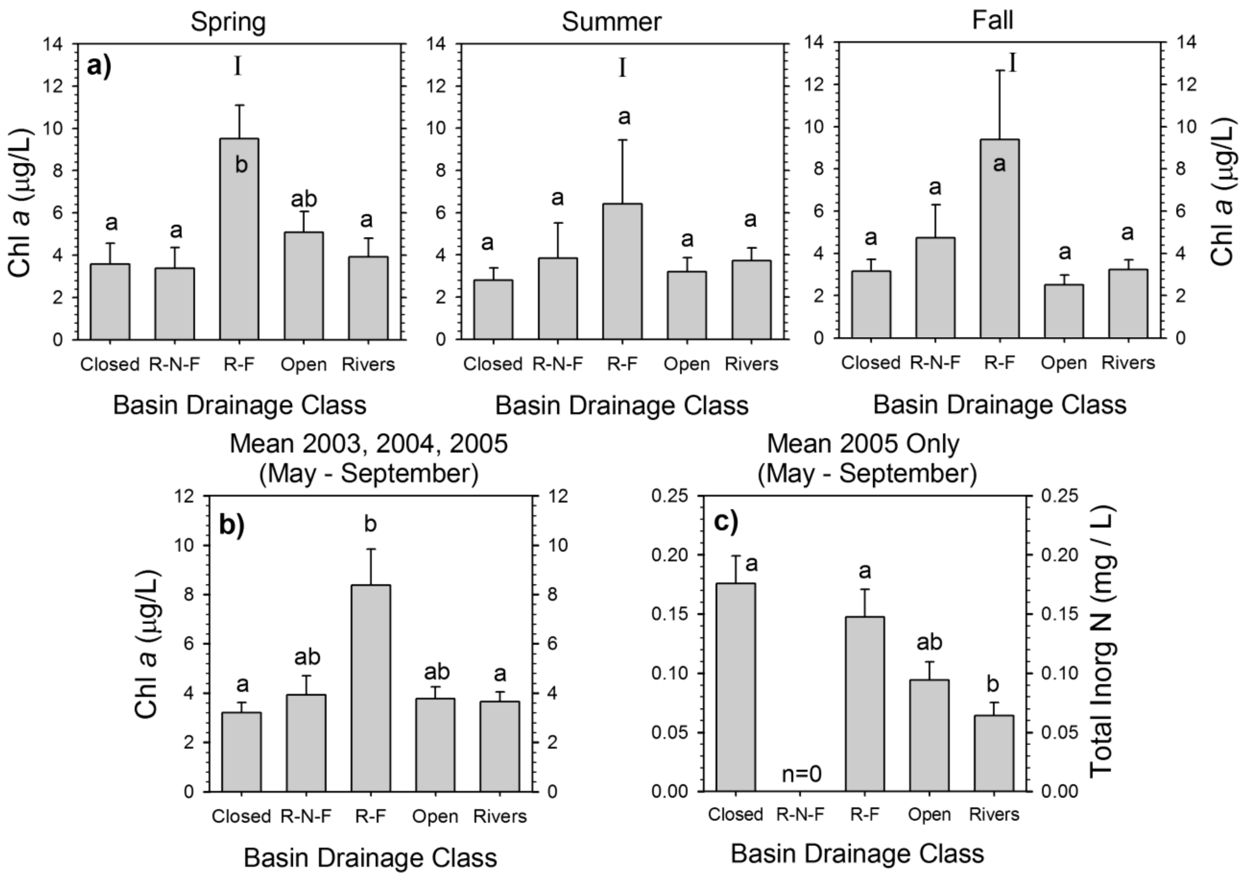

Figure 3.8 a) Mean chlorophyll *a* (Chl *a*) concentration by hydrological lake class for each season, **b)** mean water column Chl *a* concentration for each hydrological class averaged for all seasons and **c)** mean total inorganic nitrogen concentration (sum of nitrate, nitrite and ammonia in mg N/L) for each hydrological class averaged for 2005. R-N-F refers to restricted-drainage non-flooded lakes while R-F refers to restricted-drainage flooded lakes.

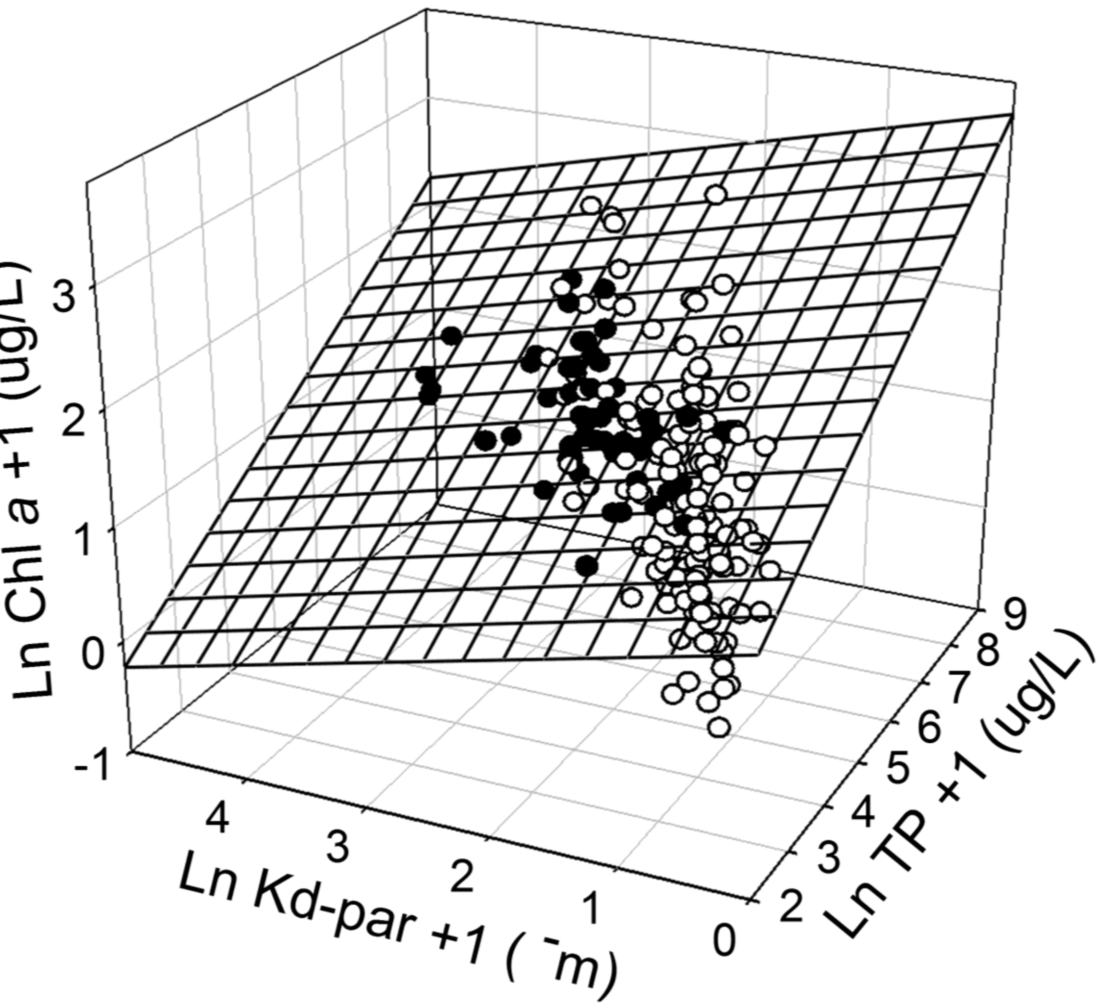

Figure 3.9 Three-dimensional linear regression analysis of total phosphorus concentration (TP) and Kd-par as explanatory variables for water column Chl *a* concentration (see Table 3 for regression details). All sample data (2003-2005) were used and include river samples from the identified sample locations (Mamawi Creek, Peace and Athabasca rivers) plus additional river sites [Chenal des Quatre Fourches, Claire River, Baril River, Revillon Coupé, Fletcher Channel, Rivière des Roches, Chilloney Creek and Embarras River; see Wolfe *et al*. (2007b) for their locations]. Lake samples are indicated as open circles, whereas river samples are indicated as closed circles.

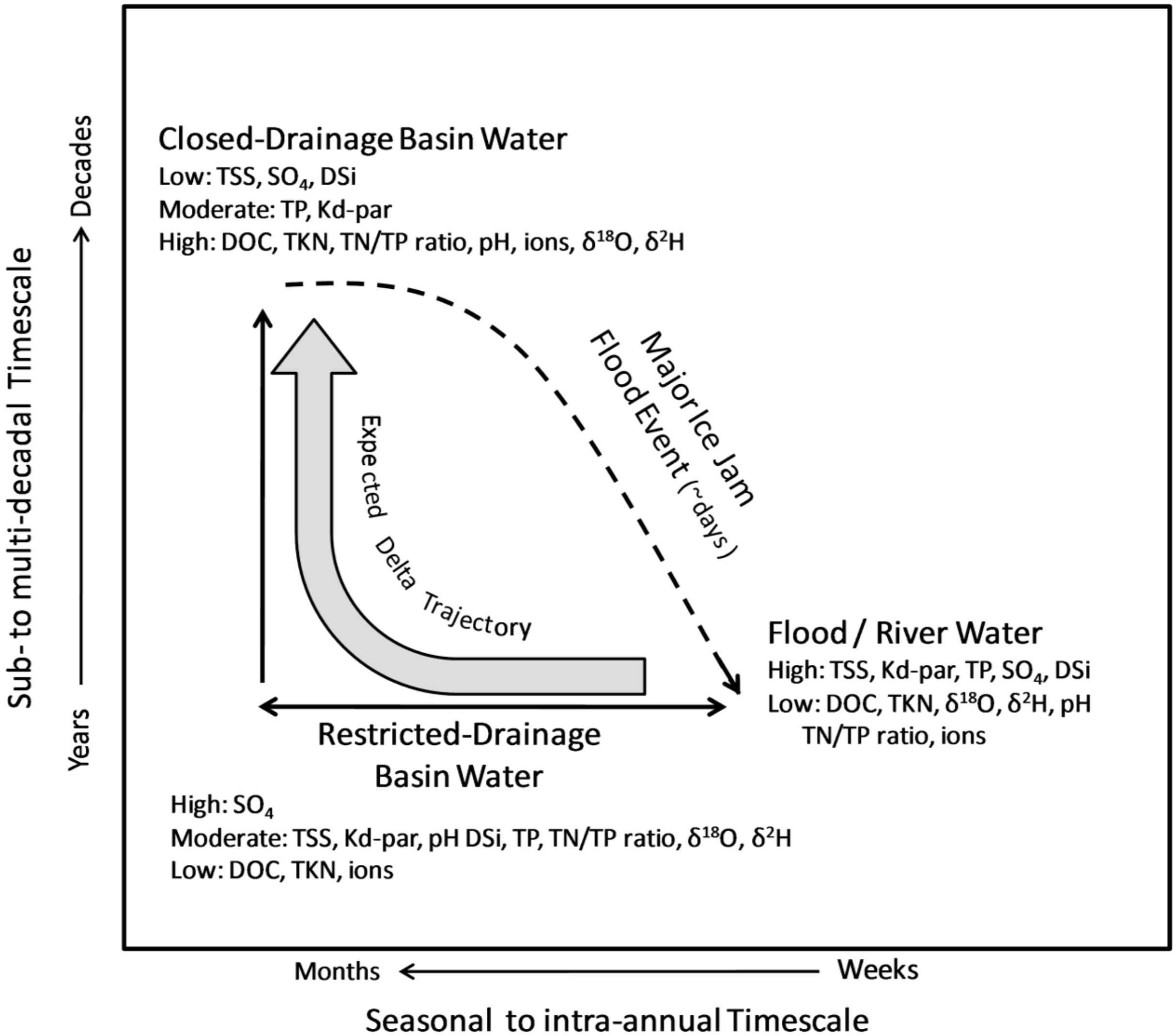

Figure 3.10 Schematic diagram illustrating the two different timescales of limnological change in response to periodic, but variable, flooding of floodplain lakes in the Peace-Athabasca Delta (based on information provided by the Principal Components Analysis (Figures 4 and 5)). The horizontal axis (modeled after PCA axis 1 in Figures 4 and 5) captures relatively short-term changes in limnological conditions due to influence of periodic flooding and processes that ensue after flooding ceases. The vertical axis (modeled after PCA axis 2 in Figures 4 and 5) captures longer-term limnological changes when lakes do not flood for many years to decades. Flooding of either a closed-drainage or restricted-drainage lake resets the limnological properties of the lake to those of river water (lower right corner). The large curving arrow illustrates the expected delta trajectory in coming decades in response to continued decline in river discharge, ice-jam flood events and increasing human consumptive uses of river water that will ultimately lead to an increase in the proportion of PAD lakes that have closed-drainage hydrological and limnological conditions.

3.10 Tables

Table 3.1 Location of surveyed lakes and rivers, hydrologic classification and basin morphometry. All measurements of area and basin dimensions (excluding depth) are from Sept 2004 air photos accessed Jan 2009 from GoogleEarth TM.

Site ID (PAD #)	Name	Hydrologic Class	Latitude (WGS84) N	Longitude W	Area (ha)	Mean depth (m)	Max * depth (m)	Shore line length (m)	Max fetch (m)
1	Devils Gate	Closed	58 48.351'	111 14.820'	14.27	0.67	0.9	1376.5	508
5	Spruce Island	Closed	58 50.788'	111 28.781'	13.27	0.52	0.85	2121.1	647
8	Chillowey's	Restricted	58 48.688'	111 21.385'	17.40	1.14	1.77	2871.1	1155
9		Closed	58 46.491'	111 19.641'	5.85	0.33	0.68	1437.2	490
15	Pete's Creek	Restricted	58 56.660'	111 29.403'	29.74	0.83	1.95	6518.5	1094
23		Closed	58 23.458'	111 26.705'	23.10	1.14	1.75	2364.8	831
31	Johnny Cabin Pond	Restricted	58 29.863'	111 31.105'	33.88	0.98	1.28	2430.6	826
45	Lake Mamawi	Open	58 36.373'	111 27.137'	10814.85	1.32**	?	72382.6	15400
45T1	Clear Water Embayment	Open	58 34.578'	111 28.930'	38.37	0.79	0.92	2923.6	1030 ***(6600)
45T2	Lake Mamawi Creek Delta Site	Open	58 35.625’	111 28.210’	10814.85	0.82	1.36	N.A.	10450
54	Horseshoe Slough	Restricted	58 51.859'	111 33.845'	33.23	1.78	4.15	6831.9	1248
R2	Peace River	River	58 54.526'	111 34.999'	N.A.	N.A.	N.A.	N.A.	N.A.
R4	Athabasca River	River	58 33.811'	111 30.491'	N.A.	N.A.	N.A.	N.A.	N.A.
R7	Mamawi Creek	River	58 21.157'	111 32.438'	N.A.	N.A.	N.A.	N.A.	N.A.

* Mean of maximum depth recorded during summer surveys (2003-2005).
** Mean of repeated sampling of one mid-lake location (2003-2005).
*** 1st value is for the embayment only; the 2nd value is maximum fetch of embayment including Lake Mamawi.
N.A. =Not Applicable.

Table 3.2 Results of stepwise multiple regression analysis of factors contributing to the light extinction coefficient (Kd-par) for PAD lakes and rivers. Forwards and backwards stepwise regression produced identical results.

Dependent Variable		Constant	DOC	Chl *a*	ISS	OSS	R^2_{adj}
Kd-par (lakes)	Coefficient	1.599	N.S.	0.089	0.086	-0.214	76.71%
n=98	p-value	<0.00001		0.0002	<0.00001	<0.00001	<0.000001
Kd-par (rivers)	Coefficient	1.606	N.S.	N.S.	0.099	-0.2111	89.76%
n=33	p-value	0.06341			<0.00001	0.00332	<0.000001

N.S. = not significant.

Table 3.3 Results of multiple linear regression of factors contributing to variation in water column chlorophyll a (Chl *a*) concentration. Concentrations are in ug/L and all variables were Log_e (x+1)-transformed prior to performing regression. Water temperature and dissolved phosphorus (DP) concentration were also investigated as independent variables but were not found to contribute additional significant ($p<0.05$) explanation of water column Chl *a* variation.

Dependent Variable		Constant	TP	Kd-par	DSi	R^2	R^2_{adj}
Chl *a* (lakes+ rivers)	Coefficient	0.3411	0.3547	-0.2560	N.I.	10.68	9.76%
n=198	p-value	0.1780	0.0001	0.0310			<0.0001
Chl *a* (lakes+ rivers)	Coefficient	-1.111	0.328	-0.426	0.238	21.6%	20.4%
n=198	p-value	0.003	<0.001	<0.001	<0.001		<0.0001

N.I. = not included.

Chapter 4

Natural processes dominate the delivery of polycyclic aromatic compounds to the Athabasca Delta downstream of oil sands development

4.1 Summary

The extent to which Athabasca oil sands mining and upgrading operations may have enhanced the delivery of bitumen-derived contaminants downstream to the Peace-Athabasca Delta is a pivotal question that has generated national and international concern. Accounts of rare health disorders in residents of Fort Chipewyan and deformed fish in the downstream delta and Lake Athabasca have provided impetus for a number of recent expert-panel assessments regarding the societal and environmental consequences of this multi-billion-dollar industry. Here, based on analyses of lake sediment cores, we provide evidence suggesting that the Athabasca Delta, located ~200 km downstream of the oil sands development, has been a natural depository of polycyclic aromatic compounds (PACs) derived from the McMurray Formation carried by the Athabasca River for at least the past two centuries. Furthermore, we detect no measureable differences in the proportion or concentration of river-transported indicator PACs in sediments deposited in a flood-prone lake pre-1940s versus post-1982. Findings suggest that natural erosion of exposed bitumen along the banks of the Athabasca River and its tributaries is the main process delivering PACs to the Athabasca Delta, and that the spring freshet is a key period for contaminant mobilization and transport. Such key baseline environmental information is essential for informed management of natural resources and human-health concerns by provincial and federal regulatory agencies and industry, and for designing effective long-term

monitoring and surveillance programs for the lower Athabasca River watershed in the face of future oil sands development.

4.2 Introduction

Industrial development of the Athabasca oil sands deposits in northern Alberta, Canada, has grown rapidly during the past few decades. Production is projected to reach >3.3 million barrels/day by 2020 (Schindler, 2010) and generate $300 billion in tax revenue over the next 25 years (Government of Alberta). The economic and oil-security benefits are undeniable, but public concerns continue to grow over the potential downstream cumulative environmental effects of the oil sands industry on the lower Athabasca River watershed and its mainly-Aboriginal communities. Debate has become polarized in response to the accelerating pace of development. This has led to numerous recent reports by expert review panels that conclude current monitoring programs are inadequate to address the growing concerns (Dowdeswell *et al*., 2010; Gosselin *et al*., 2010; Office of the Auditor General. 2010).

Recent studies have claimed that oil sands activities substantially elevate concentrations of polycyclic aromatic compounds (PACs) and metals in the Athabasca River (Kelly *et al*., 2009; 2010; Timoney and Lee, 2011). These findings have re-ignited controversy over the relative contributions of natural versus industrial contaminant loads, and they have escalated concerns about downstream environmental impacts and human health (Schindler, 2010).

Disentangling industrial from natural loads is difficult, and it remains a scientific challenge because the Athabasca River and its tributaries flow through bitumen deposits associated with the mined McMurray Formation (Dowdeswell *et al*., 2010). Also, the importance of river and ice processes during the spring freshet for downstream contaminant transport remains poorly characterized by prior monitoring and research because equipment and personnel cannot safely retrieve samples when river ice is moving. Yet, the spring freshet may be a key annual event that erodes and transports river and bank sediment, and associated contaminants, because ice-scour is substantial and flow velocity is relatively high.

Focal points of concern are reportedly high rates of rare cancers in the downstream community of Fort Chipewyan and deformities in fish in Lake Athabasca and the Peace-Athabasca Delta (PAD; Figure 4.1) (Timoney 2007; Timoney and Lee, 2009; Schindler, 2010). There, First Nation and Métis residents value a traditional way of life and many believe that contaminants emitted from the oil sands industry are responsible for higher-than-expected cancer rates (Timoney, 2007). Of particular concern are PACs, because many PACs in bitumen are known or suspected human carcinogens (Irwin, 1997) and have been associated with toxicological effects in fish (Colavecchia *et al*., 2006). Recent studies have identified that concentrations of some PACs and metals are elevated in snowpack and river water within 50 km of the oil sands development, and concentrations of some metals remain greater in river water at the PAD than upstream of development (Kelly *et al*., 2009; 2010). Yet, other lines of evidence point to the delta as a natural depository of contaminants. For instance, in Lake Athabasca and Richardson Lake, which continuously receive inflow from the Athabasca River, PAC concentrations are high and comparable in sediments deposited pre- and post-development (Evans *et al*., 2002). Black, bitumen-rich sediment in strata deposited during the early 1800s in oxbow lakes of the PAD prone to floods from the Peace River, which passes through unexploited surficial deposits of oil sands, has also been reported (Wolfe *et al*., 2006). These findings provide evidence that natural fluvial processes deposit contaminants downstream in lakes of the PAD, but relative contributions of contaminants from natural versus industrial causes remain unknown.

Discriminating natural versus industrial contributions of PACs from Athabasca oil sands mining and upgrading operations to downstream locations is challenging because PACs are a diverse group of organic compounds created by natural processes as well as human activities (Irwin 1997; Yunker *et al*., 2003). Also, the Athabasca River and its tributaries traverse surface deposits of the bitumen-rich McMurray Formation in the same area where surface mining and processing occurs, so natural sources confound attempts to attribute differences between upstream and downstream levels of contaminants to industrial activity (Schindler, 2010).

To date, monitoring programs have been unable to establish baseline reference conditions of natural contaminant loading to the delta, a situation identified as “almost unique in monitoring for toxic compounds” by the Federal Expert Oil Sands Advisory Panel (Dowdeswell *et al*., 2010). Based on attempts to analyze PAC data of the Regional Aquatics Monitoring Program (RAMP) from annual collections of bulk river sediment, Timoney and Lee (2011) recently suggested that downstream PAC concentrations increased during 1999-2009, which they attributed to increased oil sands development. However, these results are based on periodic collection of samples of the upper 4-6 cm of river sediment. As acknowledged by the authors, uncertainty regarding the time interval represented by these samples is substantial, with individual samples potentially encompassing time periods that approach the entire decade of sample collection. These data are further complicated by the possibility of sediment remobilization and loss given the dynamic nature of fluvial depositional environments (Garcia-Aragon *et al*., 2011). In fact, the sampling approach has been identified as problematic (Ayles *et al*., 2004; Dowdeswell *et al*., 2010; Schindler, 2010), in part because these factors are likely sufficient to mask any meaningful temporal trends. Thus, the suggestion that industrial activity has caused measureable enhancement of pollutant fluxes to the delta remains a testable hypothesis, rather than a certainty. Unfortunately, RAMP monitoring and other scientific studies began after industrial development of the oil sands, so they cannot readily identify nor distinguish any additional contaminant loading due to industry beyond what is contributed by natural processes (Dowdeswell *et al*., 2010). And, they have not adequately characterized contaminant transport during the spring freshet, an erosive annual event when natural contaminant dispersal occurs in northern rivers (Yunker *et al*., 1993; Scrimgeour *et al*., 2004). Without such knowledge, concerns about contaminant delivery to the delta will inevitably increase as oil sands development expands.

Here, we utilize analyses of precisely-dated lake sediment cores to establish baseline, predevelopment, reference conditions for PAC deposition in the PAD. This represents the only method available to measure PAC concentrations prior to industrial development of the oil sands and to characterize the role of natural riverbank erosion as a vector for downstream deposition of PACs – indeed, it is an approach recommended by the Federal Expert Oil Sands Advisory Panel (Dowdeswell *et al*., 2010) and soon to be adopted by Environment Canada's Phase 2 monitoring program (Environment Canada 2011). We assess whether the Athabasca River and its tributaries have been important vectors for PAC accumulation in the downstream Athabasca Delta over the past ~200 years. We then address the question: Is there evidence to indicate that industry has measurably altered the composition and concentration of PACs in lake sediments at the Athabasca Delta from that provided by natural supplies due to riverbank erosion and subsequent downstream transport by the Athabasca River? We also use our findings to test the hypothesis

(Kelly *et al*., 2009) that oil sands development has altered sedimentary composition and concentration of PACS due to regional atmospheric transport to the delta.

4.3 Material and methods

4.3.1 Study design

Our study design capitalizes on knowledge of past hydrological conditions that we have gained from previous field-based studies in the PAD, which is essential for informed interpretation of stratigraphic records of PACs given the hydrological complexity of the delta over space and time (Hall *et al*., 2004; Wolfe *et al*., 2005, 2006, 2007, 2008ab, 2011; Yi *et al*., 2008; Johnston *et al*., 2010; McGowan *et al*., 2011). Three previously studied lakes were selected for stratigraphic analyses of PACs (Figure 4.1). Lakes 'PAD 23' and 'PAD 31' are located in the southern Athabasca sector, but have markedly different flood histories during the latter part of the 20th century (Wolfe *et al*., 2008b). PAD 23 was prone to flooding until the engineered Athabasca River Cutoff of 1972 allowed flow to bypass a bend in the river where ice-jams had previously formed and routed floodwaters towards PAD 23 (Wolfe *et al*., 2008b). Thus, samples deposited before 1972 were designated as flood-prone, whereas sediments deposited afterwards were designated as not flood-prone. For graphical display of PAC composition in sediments from PAD 23 (Figure 5b), the pre-1972 flood-prone period was further divided into two periods, pre- and post-1900. Sediments deposited pre-1900 were characterized by lower organic matter (OM) content, lower cellulose-inferred lake water $\delta^{18}O$ values and near-absence of macrofossils from the submerged moss *Drepanocladus,* compared to post-1900 sediments, suggesting stronger river influence pre-1900 (Hall *et al*., 2004). In contrast, during the past >200 years, PAD 31 has experienced three distinct periods of differing hydrological conditions. PAD

31 was designated as flood-prone from the base of the core (pre-1800) to 1940 when it was frequently flooded and inundated under a former highstand of Lake Athabasca, as identified by low sediment OM content and abundant open-drainage indicator diatom taxa Hall *et al*., 2004; Johnston *et al*., 2010). During 1940 to 1982, PAD 31 was not flood-prone and existed as an isolated closed-drainage lake due to declining Lake Athabasca water levels, as identified by declining relative abundance of open drainage indicator diatom taxa and a shift to dominance by taxa indicative of closed-drainage conditions in previously analyzed cores from PAD 31, as also occurred in other delta lakes around 1940 (see Fig. 7 in Johnston *et al*., 2010). PAD 31 became flood-prone for a second time after the 1982 Embarras Breakthrough event, a natural avulsion that diverted substantial flow from the Athabasca and Embarras rivers into Cree and Mamawi creeks and towards PAD 31, as identified by a visible contact between darker organic-rich sediment pre-Breakthrough and lighter mineral-rich sediments afterwards (Figure 4.4), a sharp decline in OM content (Figure 4.3), and changes in other sedimentary variables (Wolfe *et al*., 2008b). With knowledge of these site-specific hydrological changes, analyses of PACs in lake sediment cores from PAD 23 and PAD 31 provide data to identify the role of the Athabasca River as a source of contaminant loading to the PAD. In contrast, 'PAD 18', an elevated (214.3 m a.s.l.) closed-drainage lake located in the northern Peace sector in a bedrock basin, has not flooded for at least the past 100 years (Hall *et al*., 2004; Yi *et al*., 2008). Consequently, all sediment samples were defined as not flood-prone. To assess influence of Athabasca oil sands exploration on atmospheric deposition of PACs, the PAD 18 sediment record was divided into pre- and post-1967 onset of oil sands mining activity for presentation in Figure 4.5c. Also, we obtained two samples of flood-deposited river sediment from the ground surface at two locations between Mamawi Creek and PAD 31 (approximately mid-way and 50 m from PAD 31) shortly

after an ice-jam flood event along the Athabasca River in 2007. These sediments, hereafter referred to as the '2007 Athabasca Delta flood deposit', provided reference materials to assess the composition and concentration of PACs supplied to PAD lakes by Athabasca River floodwaters.

4.3.2 Field sampling and laboratory analyses

In September 2010, four sediment cores, 27-53 cm in length, were retrieved from each of PAD 18, 23, 31 using a gravity corer (Glew, 1989) and transported to the field base in Fort Chipewyan where they were sectioned vertically into 1-cm stratigraphic intervals. Samples were kept refrigerated (4^{o}C) in the dark prior to lab analyses. Sequential loss-on-ignition (LOI) analyses were performed on ~0.5 g subsamples of wet sediment from all core slices to provide profiles of water- (post 90^{o}C for 24 hours), OM (post 550^{o}C for 1 hour) and carbonate- (post 950^{o}C for 1 hour) content, following standard methods (Dean, 1974). The OM content profiles were used to transfer the sediment core chronology developed from a single dated core per lake to a second core that was analyzed for the composition and concentration of PACs (Figure 4.2, 4.3).

4.3.3 ^{210}Pb dating of sediment cores

One sediment core per lake (Figure 4.1) was selected for dating by gamma ray spectrometric determination of ^{210}Pb activity at contiguous 1-cm intervals. A measured mass of ~2-4 g of dry sediment was packed into pre-weighed tubes (SARSTEDT product No. 55.524) to a uniform height of 35 mm and a TFA Silicone Septa (Supelco®) was placed overtop the sediment, followed by 1 cc of 2 Ton Clear Epoxy (Devcon® product No. 14310). Three weeks were allowed for ^{222}Rn and its decay products to reach equilibrium with ^{226}Ra (parent isotope) prior to quantifying ^{210}Pb, ^{214}Bi and ^{214}Pb activity. Activities of the radioisotopes were measured in an Ortec co-axial HPGe Digital Gamma Ray Spectrometer (Ortec GWL-120-15) interfaced with Maestro 32 software (version 5.32) at the University of Waterloo's WATER Lab. Sample count time ranged from 23-95 hours per sample, and varied so that net ^{210}Pb counts were >10x the standard deviation of the net counts of a well-defined machine blank to ensure precision (Currie, 1968). Calibration of detector energy efficiency for the radioisotopes was previously established for our gamma ray spectrometers using a similarly prepared known standard (3.012 g of IAEA 300, see Ballestra *et al*., 1994). Detection efficiency values were determined from the mean of three sample runs performed using the IAEA-300 standard. ^{210}Pb activities were decay corrected to the coring date for each lake and the ^{210}Pb activity was density-corrected as described by Schelske *et al*. (1994).

The Constant Rate of Supply (CRS) model (Robbins, 1978; Appleby, 2001) was used to develop the sediment core chronologies (Figure 4.2). The CRS model requires an estimation of supported ^{210}Pb activity, which was determined from activity of ^{214}Bi and ^{214}Pb. Results showed that supported ^{210}Pb activity is variable over time in the sediment cores (Figure 4.2). To reduce influence of this temporal variability, a five-point running mean of ^{214}Pb and ^{214}Bi activity was used as an estimate of the supported ^{210}Pb activity for a given interval. The core depth where total ^{210}Pb activity equals supported ^{210}Pb activity was determined using standard methods (Binford, 1990).

The sediment chronology for the ^{210}Pb-dated core was transferred to the core analyzed for polycyclic aromatic compounds (PACs) based on alignment of OM content profiles in both cores determined by loss-on-ignition (LOI) analysis (Figure 4.3). Slight depth offsets in the OM content profiles of cores from PAD 23 and PAD 31 were adjusted using a constant depth multiplier (+6% and -11.5 %, respectively, for PAD 31 GC-2 and PAD 23 GC-1). This approach preserved sample-to-sample variability in the sedimentation rate determined for the dated core. The CRS chronology was then applied to the modified depth interval of the core analysed for PACs by a straight linear interpolation of the nearest neighbour dates (depth-wise) of the ^{210}Pb-dated core (e.g., if 10 and 11 cm-depth in the ^{210}Pb-dated core corresponded to 2000 and 1998.5 respectively, then a modified sample depth of 10.6 cm depth in the core analyzed for PACs equates to 1999.1). Results are consistent with cores we have previously analyzed for these lakes (Hall *et al*., 2004; Wolfe *et al*., 2008). Also, the stratigraphic contact at 18 cm depth marking the 1982 Embarras Breakthrough was used to confirm alignment of cores from PAD 31, and it provided an independent date marker to assess the accuracy of the sediment chronology for PAD 31 provided by ^{210}Pb dating methods (Figure 4.4).

4.3.4 PAC analyses

Samples from one core from each of the study lakes were analyzed for PACs at ALS Canada Ltd. (Edmonton). Using knowledge of the water content derived from LOI analysis, an amount of wet sediment equivalent to ≥2 g dry sediment (mean = 4.6 g dry mass) was placed into amber glass jars with Teflon lid-liners that were pre-washed with acid (5% HCl) and rinsed with solvent (dichloromethane). We combined adjacent sediment intervals for the uppermost water-rich samples in cores from PAD 18 and PAD 23 to obtain sufficient sample mass. Additionally, sediment was collected in the spring of 2007 from recently deposited Athabasca River flood sediment shortly after floodwaters from Mamawi Creek had receded from PAD 31. Two samples of this ‘2007 Athabasca Delta flood deposit’ were collected and analyzed, one from approximately halfway along the floodpath between Mamawi Creek and PAD 31 and the other within ~50 m of the shore of the flooded PAD 31. These flood deposit samples were kept refrigerated since collection and were similarly prepared and shipped with the other sediment core samples to ALS for analysis of 52 PACs and alkylated PACs using US Environmental Protection Agency method EPA 3540/8270-GC/MS.

Identification and quantification of individual PACs had good repeatability based on analyses of replicate subsamples (mean precision: ±12.5% of PAC concentration averaged across all replicate analyses). Where repeated measurements of a sample were available, the average value was used for data analysis and display. In a few instances, an individual PAC was below detection limit (e.g., <0.040 mg/kg) in one replicate but slightly above the detection limit (e.g., 0.042 mg/kg) in the other replicate for a given sediment interval (e.g., FLPY2 in the sample at 35-36 cm from PAD 18). In these cases, a random number between zero and the detection limit was generated for the first replicate below the detection limit, and then averaged with the value obtained for the second replicate to avoid underweighting the PAC concentration. For situations where all measurements for a given PAC in a sediment interval were below the analytical detection limit, the PAC measurement was treated as having a concentration of zero.

4.3.5 Numerical analyses

A one-way Analysis of Similarities (ANOSIM) test, a nonparametric and multivariate approximate analogue of analysis of variance (ANOVA) tests (Clarke and Gorley, 2006), was performed on the relative abundances (expressed as proportions of the PAC sum) of the quantified PACs in all sediment core samples from the three study lakes ($n = 127$) to determine if composition of PACs differs between flood-prone versus not flood-prone intervals, based on assignment of stratigraphic intervals as described above. ANOSIM tests are commonly, and increasingly, applied to determine differences in biological community composition among site-categories, (Clarke and Gorley, 2006) and they are now being used for analysis of contaminant composition (Jones, 2010). It is common practice to remove rarely encountered species from multivariate analysis and transform the data to up-weight or down-weight uncommon species, depending upon research goals (Clarke and Gorley, 2006). We opted not to remove rare PACs for this study to avoid the possibility of dismissing historically-rare compounds that could have become recently deposited in the PAD due to anthropogenic activities or other processes. Our intent was to analyze the full PAC dataset with as little manipulation as possible. Consequently, the data were not transformed prior to calculating Bray-Curtis similarity coefficients used by ANOSIM computations. The '2007 Athabasca Delta flood deposit' samples were not used in the ANOSIM test or the SIMPER analysis described below. Instead, they served as an independent benchmark to help identify river-transported PACs in the stratigraphic records. The test statistic (global R) computed by the ANOSIM test reflects the observed differences between samples in the two categories (flood-prone *versus* not flood-prone) contrasted with the differences among replicates within each group, and it ranges from 0 to 1. A value of 0 indicates that the similarity between and within groups is the same on average. A value of 1 indicates that replicates within a group are more similar to each other than to all other replicates of other groups (Clarke and Gorley, 2006). A p-value was computed by comparing the distribution of within- and across-group rank Bray-Curtis similarities (999999 computations) to the initial rank similarity, as reported by the global R value (Clarke and Warwick, 2001; Clarke and Gorley, 2006). For all tests, we set alpha = 0.05.

A one-way Similarity of Percentages (SIMPER; Clarke and Warwick, 2001) analysis was performed on the full, untransformed relative abundance PAC data to identify which of the 43 detected PACs best discriminated between samples deposited during flood-prone versus not flood-prone intervals. As detailed below (see section 4.4.2 Identification of river-transported indicator PACs), this provided a method to select PACs indicative of a bitumen origin and transport by Athabasca River floodwaters versus those that are more abundant due to other processes. ANOSIM and SIMPER analyses were performed using the software PRIMER, version 6.1.5 (Clarke and Warwick, 2001; Clarke and Gorley, 2006).

4.4 Results

To determine the importance of the Athabasca River and atmospheric transport as vectors of PACs to the delta, interpretation of the composition and concentration of PACs in sediment cores from the three study lakes were informed by knowledge of their past hydrological conditions (Hall *et al*., 2004; Wolfe *et al*., 2005, 2008a; Johnston *et al*., 2010), as summarized above. We used this information, plus other evidence in the cores collected for this study, to identify stratigraphic intervals as 'flood-prone' or 'not flood-prone'. To assess influence of Athabasca oil sands development on atmospheric deposition of PACs, the PAD 18 sediment record was divided into pre- and post-onset of oil sands mining activity, with the threshold set at 1967, the year when major commercial operations began (Gosselin *et al*., 2010; Schindler, 2010).

4.4.1 PAC composition

The composition of PACs in the 2007 Athabasca Delta flood deposit (Figure 4.6c) closely matches ‘reference’ compositions reported for oil sands samples within the oil sands region (Figure 4.6a) (Kelly *et al*., 2009), and for sediments in the Athabasca River and two tributaries downstream of riverbank deposits of bitumen in areas unaffected by industrial development (Figure 4.6b) Colavecchia *et al*., 2004). The oil sands samples and the natural oil sands region river sediments originate from sites located ~200 km upstream of the Athabasca

Delta (Colavecchia *et al*., 2004; Kelly *et al*., 2009). Based on geochemical fingerprinting, the main source of the PACs in the river sediments is bitumen-rich material in the riverbanks (Headley *et al*., 2001). Similar to the oil sands samples and the reference river sediments, the 2007 Athabasca Delta flood deposit was dominated by alkyl-substituted PACs, including C4 naphthalenes (N4), C2- through C3-fluorenes (F2-F3), C2- through C4-dibenzothiophenes (D2-D4), C1- through C4-phenanthrenes/anthracenes (P1-P4), C2- through C4-fluoranthenes/pyrenes (FLPY2-FLPY4) and C1- through C4-benzo[a]anthracenes/chrysenes (BAC1-BAC4) (Figure 4.6c). C1- through C3-naphthalenes (N1-N3) were also common in the 2007 Athabasca Delta flood deposit. Levels of D2-D4 in the 2007 Athabasca Delta flood deposit could not be compared with the natural bitumen-rich Athabasca River sediments because dibenzothiophenes were not analyzed by Colavecchia *et al*. (2004), (Figure 4.6b), but they are a major component of the oil sands samples (Figure 4.6a) (Kelly *et al*., 2009). Except for perylene, unsubstituted (parent) PACs were absent or rare in the 2007 Athabasca Delta flood deposit. Perylene is formed naturally by metabolic decomposition of plant matter by bacteria and fungi (Wakeham *et al*., 1980) and is associated with transport of terrestrial materials from watersheds and with in-situ generation in aquatic systems (Tolosa *et al*., 1996; Itoh *et al*., 2010), suggesting that the Athabasca River transports PACs of terrestrial vegetation origin to the Athabasca Delta. However, the predominance of alkyl-substituted PACs over unsubstituted PACs in both the 2007 Athabasca Delta flood deposit and reference oil sands samples and river sediments (Figure 4.6) (Headley *et al*., 2001; Colavecchia *et al*., 2004; Kelly *et al*., 2009) identify that a major component of the sediment-associated PACs transported downstream and to the PAD by the Athabasca River derive from a common petrogenic origin – namely, bitumen from exposures of the McMurray Formation along the riverbanks in the oil sands area.

The average composition of PACs in sediments deposited in PAD 31 during the two periods when the lake was flood-prone (pre-1940 and post-1982) closely matches that of the 2007 Athabasca Delta flood deposit (Figure 4.5a, panels 1, 2, 4), which has a similar PAC composition to bitumen measured in natural deposits located upstream (see Figure 4.6) (Colavecchia *et al*., 2004; Kelly *et al*., 2009; Yang *et al*., 2011). PACs in these sediments contain high proportions of the alkyl-substituted forms C2- through C4-naphthalenes (N2-N4), C2- through C3-fluorenes (F2-F3), C2- through C4-dibenzothiophenes (D2-D4), C1- through C4-phenanthrenes/anthracenes (P1-P4), C2- through C4-fluoranthenes/pyrenes (FLPY2- FLPY4) and C1- through C4-benzo[a]anthracenes/chrysenes (BAC1-BAC4). Other relatively abundant PACs are retene (R) and perylene (PLY). Retene is associated with combustion of plant material (Ramdahl, 1983; Gabos *et al*., 2001). Perylene is formed naturally by metabolic decomposition of plant matter by bacteria and fungi (Wakeham *et al*., 1980; Grice *et al*., 2007) and is associated with transport of terrestrial materials from watersheds and with in-situ generation in aquatic systems (Grice *et al*., 2007; Itoh *et al*., 2010). Only minor differences occur between sediments deposited in PAD 31 when it was flood-prone and the 2007 Athabasca Delta flood deposit. Specifically, naphthalene (N) is absent in the 2007 Athabasca Delta flood deposit, but is present in low proportions in PAD 31 sediments deposited post-1982 (<1%) and pre-1940 (<4%). Also, only subtle differences occur in PAD 31 sediments deposited during the two flood-prone periods, with slightly lower proportions of F2-F3, BAC1-BAC3 and R, and a slightly higher proportion of N in sediments deposited pre-1940 compared to post-1982. Clearly, the sediment record from PAD 31 identifies that bitumen-derived PACs carried by the Athabasca River are deposited in lakes of the PAD when they receive river floodwaters, and that this has occurred both before and since onset of industrial development of the oil sands.

By contrast, the average composition of PACs in sediments from PAD 31 when the lake was not flood-prone (1940-1982; Figure 4.5a, panel 3) differed notably from that of the 2007 Athabasca Delta flood deposit, as well as sediments deposited in PAD 31 during the two flood-prone periods (pre-1940, post-1982). Specifically, sedimentary proportions of F3, D2-D4, FLPY2-FLPY4 and BAC1-BAC3 were markedly lower when PAD 31 was not flood-prone (1940-1982), and proportions of N, C1-naphthalenes (N-1), biphenyl (B) and fluorene (F) were more than double. Overall, the data show that composition of PACs in PAD 31 sediments differ detectably between periods of frequent *versus* infrequent flooding. During flood-prone periods, PAC composition closely matches that of river-transported sediment originating from bitumen deposits of the McMurray Formation exposed along the riverbanks (Figure 4.5a, 4.6). During periods of reduced flood frequency, higher proportions of unsubstituted PACs (notably N, B, F) identify greater influence of hydrocarbons from fire and catchment vegetation (Wakeham *et al*., 1980; Gabos *et al*., 2001; Vergnoux *et al*., 2011).

At PAD 23, the average composition of PACs in sediments deposited post-Cutoff (post-1972), when flood frequency at the lake dropped precipitously (Wolfe *et al*., 2008b), is very different from that of the 2007 Athabasca Delta flood deposit (Figure 4.5b, panels 1, 2). Many of the alkylated PACs abundant in the flood deposit (D2- D4, FLPY2-FLPY4, BAC1-BAC4) were absent in post-Cutoff sediments at PAD 23. Also, N and N-1 dominated the PACs in post-Cutoff sediments at PAD 23, but these compounds are absent or in low relative abundance, respectively, in the flood deposit. The high proportions of unsubstituted N, F and PLY, and R in PAD 23 sediments during this ‘not flood-prone’ period suggest the PACs originate from a pyrogenic source (e.g., forest fires) as well as biodegradation products from plant materials (Ramdahl, 1983; Grice *et al*., 2007; Vergnoux *et al*., 2011; Yang *et al*., 2011).

Composition of PACs in sediments deposited at PAD 23 prior to the Cutoff (1972), when the lake was prone to flooding from the Athabasca River, (Wolfe *et al*., 2008b) is notably different compared to the post-Cutoff period of reduced flood frequency. During the pre-Cutoff sedimentation period, N, N1 and F were relatively less abundant on average, and several of the alkylated PACs common in the 2007 Athabasca Delta flood deposit (D2-D3, FLPY2-FLPY4, BAC2) were more abundant (Figure 4.5b, panels 3, 4). Interestingly, this pattern was more strongly apparent during the earliest portion of the flood-prone period (1843-1899), when paleohydrological data identify greatest influence of flooding at PAD 23 (Hall *et al*., 2004). Also, PAC composition during the flood-prone periods at PAD 23 shows some similarities with the subsequent period of reduced flood frequency (post-Cutoff), with generally higher relative abundance of N, N1 and P2-P4 than in the 2007 Athabasca Delta flood deposit. This suggests a mixture of PACs from both petrogenic sources supplied by river floodwaters and pyrogenic sources due to the lake's proximity to forests subject to periodic fires.

Based on data obtained previously, PAD 18 has not received floodwaters for at least the past century (Hall *et al*., 2004). The composition of PACs in sediments from this lake, during both pre- and post-oil sands development periods, is markedly different than that of the 2007 Athabasca Delta flood deposit, the natural oil sands region river sediments and sediments deposited during flood-prone periods in the other two study lakes (Figure 4.5c, panels 2, 3; Figure 4.6). PACs in sediments from PAD 18 are overwhelmingly dominated by N, N1 and R. And, the alkylated PACs characteristic of river-transported bitumen in the 2007 Athabasca Delta flood deposit and during flood-prone periods at PAD 31 and PAD 23 (notably, F2-F3, D2-D4, FLPY3-FLPY4, BAC1-BAC3) are absent at PAD 18. Only FLPY2 was detected, but at low relative abundance (3-5%) and only in five samples deposited pre-1900. Thus, PACs in sediments at PAD 18 are characteristic of mainly pyrogenic and vegetation sources, with little to no inputs from PACs of petrogenic origin.

4.4.2 Identification of river-transported indicator PACs

Based on results of a one-way analysis of similarities (ANOSIM) test, performed on the relative abundance of the PACs in sediment core samples from the three study lakes (Figure 4.5), PAC composition differs significantly between flood-prone versus not flood-prone periods (R-statistic = 0.495, $P<1.0 \times 10^{-6}$, n = 127). This finding confirms a strong influence of river floodwaters on the composition of PACs deposited in lakes of the PAD.

Subsequent similarities percentages (SIMPER) analysis was used to identify the 'indicator' PAC compounds that most strongly contribute to differences in PAC composition between the flood-prone and not flood-prone periods of the study lakes. Ten of the 43 PACs were found to have good indicator qualities: seven for flood-prone sediment intervals (D2- D4, FLPY2-FLPY4 and BAC2) and three for not flood-prone sediment intervals (N, N1 and R) (Table 4.1). Collectively, these ten PACs accounted for >50% of the total dissimilarity between samples deposited during flood-prone and not flood-prone intervals. We sought to identify compounds that were consistently more abundant in either the flood-prone or not flood-prone samples and that strongly contribute to the within-group similarity of one sample-type (but not both).

This selection criterion was met for the PACs indicative of flood-prone intervals. For example, the seven PAC indicators of flood-prone status (D2- D4, FLPY2-FLPY4 and BAC2) had higher relative abundances (proportionally >2x) in sediments deposited during flood-prone intervals and contributed consistently to the between-group (flood-prone versus not flood-prone) dissimilarity (dissimilarity / std. dev. >1, contribute >1% to dissimilarity; Table 4.1). They also contributed substantially to the within-group similarity of flood-prone samples (>1%), but not to the within-group similarity of the not flood-prone samples (<0.1%). These 'river-transported indicator PACs' (coloured blue in Figure 4.5, 4.6) contributed 20.8% to the total between-group dissimilarity for flood-prone versus not flood-prone samples, and 19.6% to the total within-group similarity of the flood-prone samples. They contributed only 0.6% to the total within-group similarity of not flood-prone samples (Table 4.1). They averaged 19% of the total PACs present in sediments in the flood-prone samples, but were <1% of the total PACs present in the not flood-prone samples. These river-transported indicator PACs, based on our independent statistical analysis, are in agreement with PACs previously identified as characteristic of bitumen-rich materials associated with the oil sands of the McMurray Formation (Figure 4.6) (Headley *et al*., 2001; Colavecchia *et al*., 2004; Kelly *et al*., 2009; Yang *et al*., 2011). In fact, these seven river-transported indicator PACs account for 51% of the total PACs in oil sands samples reported by Kelly *et al*. (2009).

Using the same criteria, SIMPER analysis identified three PACs indicative of sediments deposited during not flood-prone intervals (N, N1 and R; Table 1). These three indicator PACs were consistently found at higher relative abundances in sediments deposited during the not flood-prone intervals (proportionally >2x), contributed consistently to the between-group (flood-prone versus not flood-prone) dissimilarity (dissimilarity / std. dev. ≥ 0.8), and contributed considerably more to the within-group similarity of the not flood-prone samples than that of the flood-prone samples. These 'not flood-prone indicator PACs' (coloured red in Figure 4.5, 4.6) contributed 30.4% to the total dissimilarity between flood-prone and not flood prone-samples and 46.2% to the total within-group similarity of the not flood-prone samples (Table 4.1). They contributed 10.5% to the total within-group similarity of flood-prone samples. On average, they comprised 40% of the total PACs found in the not flood-prone samples compared with 12% for flood-prone samples. The indicator PACs for sediments deposited during not flood-prone periods are rare or absent in oil sands bitumen (Meyers and Ishiwatari, 1993; Colavecchia *et al*., 2004; Kelly *et al*., 2009) and are often associated with a pyrogenic source such as forest fires (Ramdahl, 1983; Gabos *et al*., 2001; Yunker *et al*., 2003). However, they also occurred in sediments deposited during flood-prone intervals, suggesting that these PACs are most strongly associated with delivery to PAD lakes by non-river sources and vectors, such as atmospheric transport of PACs produced by fires and from biological degradation of vegetation within the catchment. But, river floodwaters may also acquire these compounds from terrestrial landscapes and deliver them downstream to the delta (Headley *et al*., 2002).

Phenenthrene/Anthracene homologues (P1-P4) were not identified by SIMPER analysis as indicator PACs because they were common in all sediment samples (Figure 4.5, 4.6). Indeed, P1-P4 are common in river sediments both upstream and downstream of Athabasca oil sands deposits (Colavecchia *et al*., 2004), as well as in river sediments draining unburned and burned forests of northern Alberta in areas outside the Athabasca oil sands region (Gabos *et al*., 2001).

4.4.3 PAC profiles in sediment cores

Summing the seven PAC compounds identified by the SIMPER analysis as indicative of flood-prone conditions provided an approach to quantify changes over time in the proportion and concentration of bitumen-associated, river-transported PACs to the three study lakes, as described below.

At PAD 31, equivalent proportions of the river-transported indicator PACs occur in sediments deposited since the Embarras Breakthrough in 1982 (when the lake became frequently and increasingly flooded by channelized flow of Athabasca River-sourced water along Mamawi

Creek) as there are in sediments deposited pre-1940 when PAD 31 was frequently inundated by Lake Athabasca (Figure 4.7a, top panel). A similar pattern is evident when the summed river-transported indicator-PACs are expressed as concentrations, with values falling close to that of the 2007 Athabasca Delta flood deposit (Figure 4.7b, top panel). Indeed, the average concentration during 1983-2010 [0.476 mg/kg ± 0.165 (1 SD)] does not differ significantly (independent-samples t-test, P = 0.821, d.f. = 31) from that of the pre-1940 interval (0.466 mg/kg ± 0.065). Peak concentration occurred in 2007, the year when ice-jam flooding delivered the reference Athabasca Delta flood deposit. The two other concentration peaks post-1982 correspond with high open-water flow on the Athabasca River (1990) and ice-jam floods (1996-97), (Peters *et al*., 2006; Schindler and Donahue, 2006). Consistent with this evidence of strong regulation of sediment PACs by river flooding, the sum of the river-transported indicator PACs (expressed as both proportion and concentration) declined to very low levels during 1940-1982 when PAD 31 was not flood-prone (except for two peaks within this period that correspond to ice-jam flood years of 1963-64 and 1974 (Peters *et al*., 2006). These data provide evidence that the proportion and concentration of accumulated river-transported indicator PACs has not changed measurably since onset of oil sands development.

At PAD 23, highest amounts of river-transported indicator PACs were deposited in sediments before ~1900 (middle panels in Figure 4.7a,b), when prior research shows strongest flooding (Hall *et al*., 2004). The long-term 20th century decline in proportions and concentrations of river-transported indicator PACs likely reflects declining susceptibility of this basin to floods (Wolfe *et al*., 2008b). Except for a brief rise in the sample that includes 1974, the year of a known major ice-jam flood event (Peters *et al*., 2006), and in the top-most sample, possibly representing a recent unrecorded flood event, river-transported indicator PACs have been virtually absent in sediments deposited in PAD 23 since the Athabasca River Cutoff (1972). These findings highlight that natural erosion and transport via the Athabasca River are the main processes delivering these contaminants. Further verification that these compounds are transported by the river is provided by the statistically significant, strong negative relation between river-transported indicator PAC concentration and organic matter content in the sediments of PAD 23 and PAD 31 ($R^2 = 0.63$, $P < 0.0001$, d.f. = 60), which vary inversely in response to hydrological conditions (see PAC Concentration versus Sediment Organic Matter Content in Figure 4.8).

At PAD 18, where floods have been absent for the last century (Hall *et al*., 2004), river-transported PACs were not detected, except for very low concentrations (0.032 – 0.057 mg/kg) of FLPY2 during the early- to mid-1800s (bottom panels in Figure 4.7a,b). Clearly, the river-transported PACs are not supplied in substantial amounts to lakes in the absence of flooding, but their presence in a few samples suggests that PAD 18 may have received a few floods during this time. Interestingly, total PAC concentration shows a gradually declining trend throughout the sediment core, except for an increase in the uppermost sample to values more typical of the late 1700s (Figure 4.7c). PACs in the uppermost sample are dominated by N, N1 and R, identified by our analyses as supplied by non-flood vectors, and by P2-P4, which are the major PACs in sediments of surface waters in areas affected by wildfires in northern Alberta (Gabos *et al*., 2001). Consistently lowest total PAC concentrations occurred ~1975-1995, a result that indicates oil sands activities are not elevating sedimentary concentrations of atmospherically deposited PACs in the delta.

4.4.4 Total sedimentary PAC concentration profiles

Total sedimentary PAC concentrations ranged from 0.053 to 3.008 mg/kg at PAD 23, from 0.837 to 2.234 mg/kg at PAD 31 and from 0.0271 to 1.596 mg/kg at PAD 18 (Figure 4.9). Concentrations of total PACs and the seven river-transported indicator PACs are markedly higher during the flood-prone versus not flood-prone periods (Figure 4.9). Analyses of sediment cores from PAD 31 and PAD 23 identified transient increases in total and river-transported indictor PAC concentrations in samples dating to 1974, a year of widespread flooding that inundated both lakes despite their not flood-prone status. At PAD 31, three distinct peaks occur in total PAC concentration during the post-1983 flood-prone period (~1990, the late 1990s and 2007), which correspond to major floods of summer 1990, combined ice-jam flood years of 1996 and 1997, and the ice-jam flood of 2007, respectively. At PAD 23, average total PAC concentration during the post-1972 'not flood-prone' period is less than half that of the pre-1972 average. High total PAC concentration in the uppermost sample (2010) at PAD 23 is due mainly to increases in retene and C2- through C4 phenathrenes/anthacenes, which are elevated in river sediments near forest fires in northern Alberta (Gabos *et al*., 2001) and elsewhere (Ramdahl, 1983) and common in sediments of the Athabasca River and its tributaries both upstream and downstream of oil sands deposits (Colavecchia *et al*., 2004; Kelly *et al*., 2009). At PAD 18, total PAC concentration is elevated in the uppermost sample (2010), where PAC composition is dominated by the parent compounds fluorene (F), fluoranthene (Fl), naphthalene (N), phenanthrene (P), perylene (PLY), and other PACs that do not have a unique association with bitumen or oil sands production (C1-biphenyls, C1- to C4 naphthalenes (N1-N4)) (Colavecchia *et al*., 2004; Kelly *et al*., 2009). The absence of rise in oil sands-associated PACs and retene (a marker of conifer fire) (Ramdahl, 1983; Gabos *et al*., 2001) in the uppermost sample suggests oil sands development and fire cannot be the underlying cause. Instead, the rapid down-core decline in concentration of most parent PACs between the uppermost two sediment samples suggests that degradation by biological, chemical or physical processes (i.e., diagenesis) could account for the pattern. Consistent with this interpretation, several compounds only attain values above the detection limits in the uppermost core sample from PAD 18 (perylene, fluorene, fluoranthene, C1-biphenyls, C4-naphthalenes).

4.4.5 PAC concentration *versus* sediment organic matter content

Two distinct trends are evident when comparing river-transported indicator PAC concentrations in river and lake sediments in the Athabasca Delta versus organic matter content (Figure 4.8). Data obtained from RAMP (2011) show that the organic content of river bottom sediments is much lower than that of lake sediments. Also, concentrations of indicator PACs in river sediment are positively correlated with organic matter content of bottom sediments obtained in the Athabasca River and distributaries within the delta ($R^2 = 0.35$, $P = 0.0004$, d.f. = 30; Figure 4.8). This positive association probably derives mainly from variations in grain size distribution and composition of river sediment (see Figure 1.2), because the finer grained fraction possesses higher organic matter content and higher affinity for hydrophobic contaminants, such as PACs (Kersten and Smedes, 2002), than coarser grained fractions.

In contrast to the sediments of the Athabasca River and distributaries, river-transported indicator PAC concentrations in the lake sediment records of PAD 23 and PAD 31 are significantly and negatively correlated with organic matter content ($R^2 = 0.63$, $P < 0.0001$, d.f. = 60). This relation reflects periodic inoculation of the lakes with river-borne sediments that are relatively low in organic matter content, but relatively high in PAC concentration. Under non-flood conditions, PAC concentrations in the lake sediments are diluted by in-lake aquatic productivity that increases organic matter content. A similar pattern has been reported for sediments of floodplain lakes in the Mackenzie Delta (Headley *et al*., 2002). The presence of higher concentrations of PACs in PAD 31 (and correspondingly lower organic matter content) compared to PAD 23 is consistent with the more proximal location of PAD 31 to river floodwaters. Notably, high PAC concentrations in the 2007 flood deposits obtained near PAD 31 lie close to the intersection of the two relations, confirming that flood events deposit river sediment and associated PACs directly into PAD 31.

4.5 Discussion

Records from sediment cores of three lakes in the PAD provide distinctly different profiles of PAC deposition over the past >200 years. Prior paleohydrological reconstructions of the study lakes were critical to inform accurate interpretations of the PAC stratigraphic records. Without paleohydrological knowledge, entirely conflicting conclusions could readily have been drawn from the PAD 31 and PAD 23 records, whose profiles show increasing and decreasing supply of river-transported indicator PACs over the past few decades, respectively (Figure 4.7). These trends clearly reflect natural and engineered geomorphic changes in the flow of the Athabasca River that have led to both increasing (PAD 31) and decreasing (PAD 23) flood frequency in recent decades. Results from these two sites identify that flooding from the Athabasca River is an important vector that naturally supplies bitumen-sourced PACs to the delta.

Predictable responses of sedimentary PAC composition and concentration to changing hydrological conditions confirm that the sources and trends of these contaminants can be determined effectively from analyses of sediment cores from lakes in the PAD, an approach recommended by the Federal Expert Oil Sands Advisory Panel to assess environmental impacts of oil sands development (Dowdeswell *et al*., 2010) and proposed for the new federal Phase 2 monitoring program (Environment Canada 2011). Here, we demonstrate these methods yield informative results, but that knowledge of hydrological variations is essential because shifting hydrological conditions at the study lakes complicates blind comparison of sedimentary PAC characteristics between stratigraphic intervals representing pre- and post-1967 development of the oil sands. Consequently, the PAC record from PAD 23 cannot be used to evaluate whether additional industrial loading of PACs has occurred, because the lake has received river floodwaters less frequently during the period since oil sands development than it did pre-development. The stratigraphic record at PAD 23 does show, however, that natural river processes, in particular ice-jam floods, have been an important source of PAC delivery to the lake in the recent past. In contrast, the increase in flood frequency at PAD 31 that has occurred since the Embarras Breakthrough in 1982 can be used to evaluate the role of industrial contributions of PACs by comparing results from this stratigraphic interval to the pre-1940 frequently-flooded interval (Figure 4.5a, 4.7). This comparison identifies that natural processes responsible for delivering bitumen from along the banks of the Athabasca River and its tributaries can account for the PACs most associated with a bitumen origin in the post-1982 sediments of PAD 31. Thus, despite rapid growth of oil sands development during the past 25 years (Schindler, 2010), the data reveal no measurable increase in recent downstream PAC concentration or proportion of river-transported indicator PACs.

We carefully considered multiple ways to present these data, including in flux units (e.g., as mass of PACs per unit area per unit time) to directly assess if industrial activity is accelerating the rate of delivery of PACs to the delta. But, this was not possible based on the experimental design of this study, because at PAD 31 sedimentation rates increased (Figure 4.2) when the lake became more susceptible to flooding following the Embarrass Breakthrough (Wolfe *et al*., 2008b). As a consequence, it is not possible to distinguish natural hydrological causes of changes in PAC *fluxes* from those potentially due to industrial activities because they are confounded in time. Rather, we contend that if industry has substantially enhanced PAC loads to the delta, then the likelihood of doing so with the same sedimentary *concentration* and *composition* of PACs that has occurred naturally due to erosion of the Athabasca River would seem highly unlikely, but remains to be tested at additional sites. However, we note that Timoney and Lee (2011) have concluded that oil sands industrial activity is related to increasing sedimentary PCA *concentration* in the Athabasca River.

Although we fully recognize that our conclusions of no post-industrial increase in the sedimentary composition and concentration of bitumen-associated and river-transported PACs is based on only one lake record, PAD 31 is located at the upstream front of the Athabasca Delta where river floodwaters spread out over the delta (Wolfe *et al*., 2005, 2008a,b) and it is frequently and easily flooded, both during high-water events in the spring due to ice-jams and rain events in summer (Wolfe *et al*., 2008b; Wiklund *et al*., 2012). Thus, PAD 31 should be a particularly sensitive recorder of changes in river-borne PAC transport, and is well positioned for continued monitoring of bitumen-derived PACs from flooding of the Athabasca River. Notably, conclusions we have drawn from the sediment record at PAD 31 are consistent with a previous study (Evans *et al*., 2002) showing that concentrations of most PACs were similar in sediments deposited during the 1950s and the late 1990s at Lake Athabasca and Richardson Lake, lakes that continuously receive Athabasca River water. From data at these two time points, Evans *et al*. (2002) concluded that there was little evidence of a temporal increase in PAC concentrations due to the oil sands industry. Moreover, sedimentary concentrations of the compounds we have identified as indicative of transport by the river (D, FLPY, BAC) are similar in sediments from the PAD 31 post-1982 strata and samples in Richardson Lake from the 1950s and late 1990s (Evans *et al*., 2002). Agreement of findings at these sites suggests that high-flow (flood) events on the Athabasca River are the main vector for PAC-transport to the delta, as occurs downstream in the lower Mackenzie River basin (Yunker *et al*., 1993; Headley *et al*., 2002). This conclusion is also supported by equivalent PAC concentrations in flood deposits of PAD 31 and the upper range of concentrations in Athabasca River sediment measured by RAMP and reported in Timoney and Lee (2011) (see Figure 4.8;). Given the importance of natural processes during river flood stages, monitoring and research programs must begin to sample at locations and times that capture contaminant dispersal during flood events. We propose that a network consisting of a larger number of monitoring sites is critically needed to further evaluate spatial and temporal distributions of PACs in the delta and their potential toxicity to biota. Such a monitoring network would serve as an early warning signal for any future changes in PAC delivery by the Athabasca River.

Results also reveal no evidence that industrial activity has contributed measurably to the sedimentary concentration of PACs supplied by long-range atmospheric transport and deposition in the vicinity of the PAD. Dominance of PACs supplied by atmospheric transport in sediments from PAD 18 (Figure 4.5) reflects pyrogenic-sourced PACs typically produced by forest fires (Gabos *et al*., 2001; Vergnoux *et al*., 2011), and the total PAC profile (Figure 4.7c) indicates that this has been a decreasing source of PACs since the mid-1700s. Maximum pyrogenic-sourced PACs during the 1700s at PAD 18 may reflect more frequent or larger fires during the regionally arid climatic conditions that prevailed in elevated regions of the PAD during the Little Ice Age

(Wolfe *et al*., 2005, 2008a) These baseline data on PAC concentrations at PAD 18 can be used for continued monitoring of sediment PAC composition and concentration at this site to track changes in atmospheric PAC deposition to the delta as oil sands development expands.

Our findings add new dimensions to conclusions developed by recent studies that have assessed oil sands industrial contributions to downstream PAC fluxes (Kelly *et al*., 2009; Timoney and Lee, 2011). For example, Kelly *et al*. (2009) identified that, during the non-breakup period, *dissolved* PAC concentrations at sites in the Athabasca River adjacent to and immediately downstream of the oil sands mining area were significantly greater than concentrations at upstream sites. However, because PACs are strongly hydrophobic, PAC loads to the Athabasca Delta should be dominated by the *particulate* fraction that is archived in the sediments of floodplain lakes. The study by Timoney and Lee (2011) did attempt to track changes in particulate PAC loads to the Athabasca Delta using river bottom sediment samples collected by RAMP during 1999-2009, yet this sampling design has been identified as problematic (Ayles *et al*., 2004; Dowdeswell *et al*., 2010), in part because of the shifting nature of fluvial sedimentary environments (Garcia-Aragon *et al*., 2011) and the short sampling interval. Our experimental methods, on the other hand, offer an alternative approach to address concerns related to the possible effects of oil sands industrial activities. An important advantage is that analyses of floodplain lake sediment profiles provide the hydrological and temporal context required to define pre-development baseline conditions and decipher trends over time due to natural versus anthropogenic processes. The unique perspective offered by the lake sediment core records described here indicates that the PAD has been a natural depository of PAC-laden sediment carried by the Athabasca River for the past >200 years (and likely millennia).

As we demonstrate in this and other studies (Wolfe *et al*., 2006), ice-jam floods are associated with peak proportions and concentrations of river-transported PACs both prior to and since onset of oil sands development. This occurs because moving river-ice and high river flow velocities can mobilize and transport naturally occurring bitumen-rich materials in the riverbanks downstream to the delta. Similarly, studies at the Mackenzie Delta have identified that naturally occurring petrogenic PACs eroded from the mainstem of the Mackenzie River are carried with the sediment loads during the spring freshet (Yunker *et al*., 1993) and that concentrations of PACs in floodplain-lake sediments are positively related to flood frequency (Headley *et al*., 2002).

Ironically, flood events, which have long been considered a crucial natural process for maintaining hydrological and ecological integrity of the delta (Timoney, 2002), are also the main vector supplying organic contaminants. Consequently, our findings identify that the design of monitoring and research studies must adequately capture contaminant transport and deposition during the influential spring freshet and other periods of river flood stage in order to account for the substantial natural PAC loads to the Athabasca River and its distributaries. Additional lakes should be cored and analyzed to verify if these findings are representative of other parts of the delta and upstream along the Athabasca River floodplain, and to provide further critically-needed baseline information of PAC deposition over space and time.

4.6 Acknowledgement

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4.7 Figures

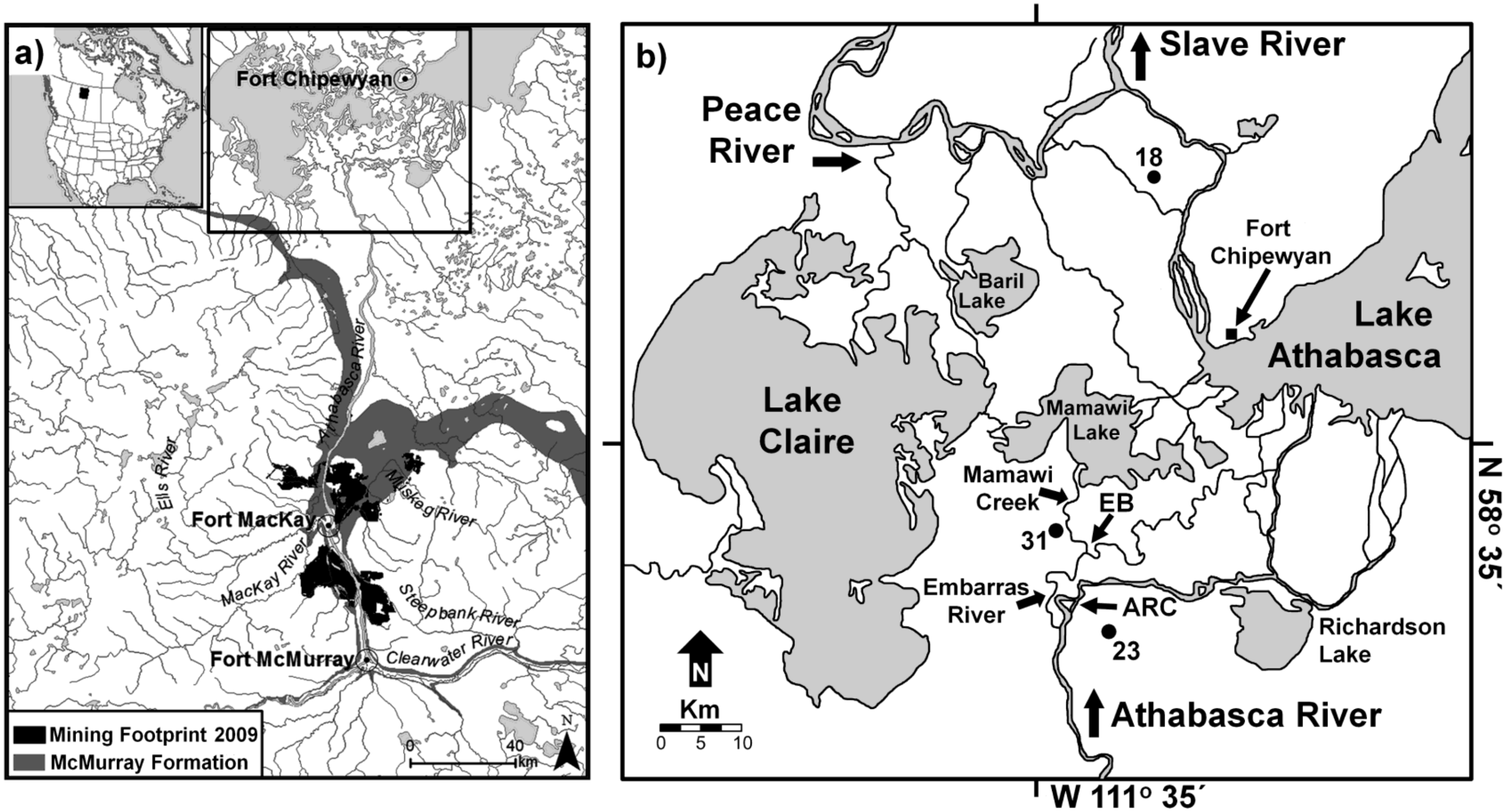

Figure 4.1 a) Map showing locations of near-surficial Athabasca oil sands exposures of the McMurray Formation (light grey), the 2009 mining footprint (dark grey) and the downstream Peace-Athabasca Delta (top center box) in northern Alberta, Canada (modified after Timoney and Lee, 2011). Top-center box in **a)** outlines area shown in panel **b)** identifying locations of the study lakes; PAD 18 (N 58° 53.7', W 111° 21.7'), PAD 23 (N 58° 23.5', W 111° 26.6') and PAD 31 (N 58° 29.6', W 111° 31.0') which are shown as solid circles. Also shown are locations of the Athabasca River Cutoff (ARC) and the Embarras Breakthrough (EB). The ARC, an engineered channel excavation in 1972, straightened and deepened the Athabasca River at the location of a large meander bend where ice-jam floods occurred, and reduced flood frequency at PAD 23. The EB, a natural avulsion that occurred in 1982, has increased flood frequency at PAD 31 because it directs substantial and increasing Athabasca River flow towards PAD 31 via Mamawi Creek. Further details on these geomorphic changes are provided by Wolfe *et al*. (2008b).

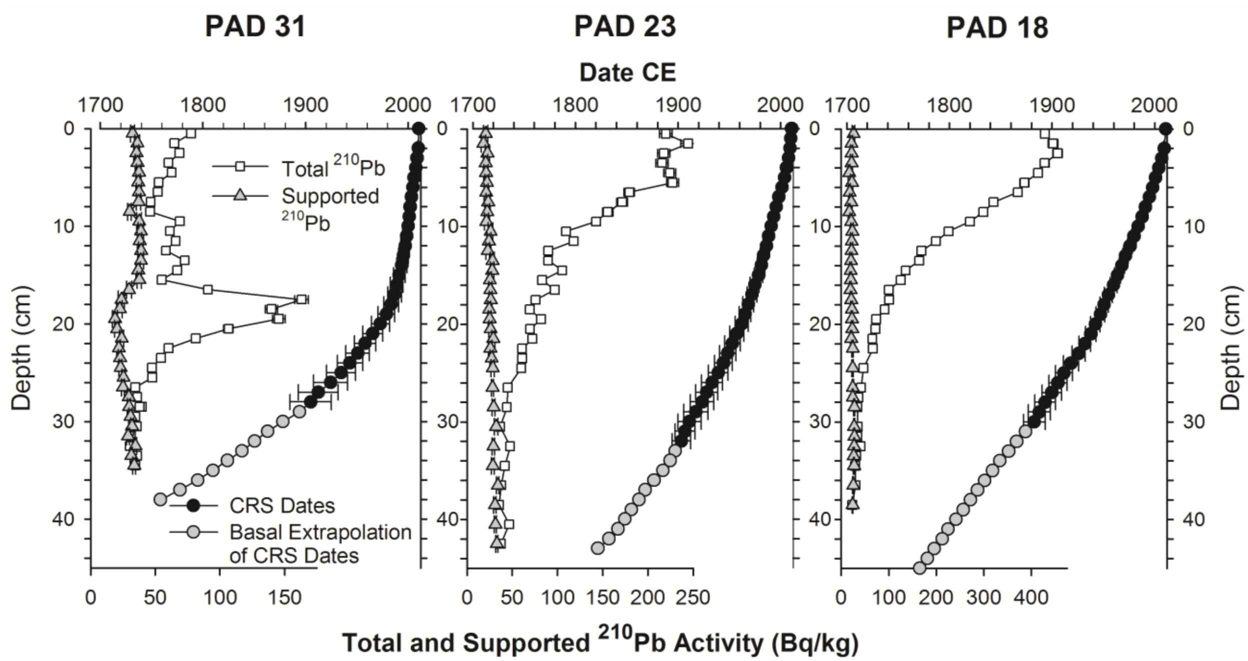

Figure 4.2 ^{210}Pb activity (supported and total (= supported + unsupported)) and depth-age profiles for sediment cores taken from the three study lakes (PAD 31, PAD 23, PAD18) in the Peace-Athabasca Delta, northern Alberta (error bars = ±2 SD). The irregular ^{210}Pb activity profile for PAD 31 is a result of an increase in sedimentation rate associated with increased flooding following the Embarras Breakthrough in 1982 (Wolfe *et al*., 2008).

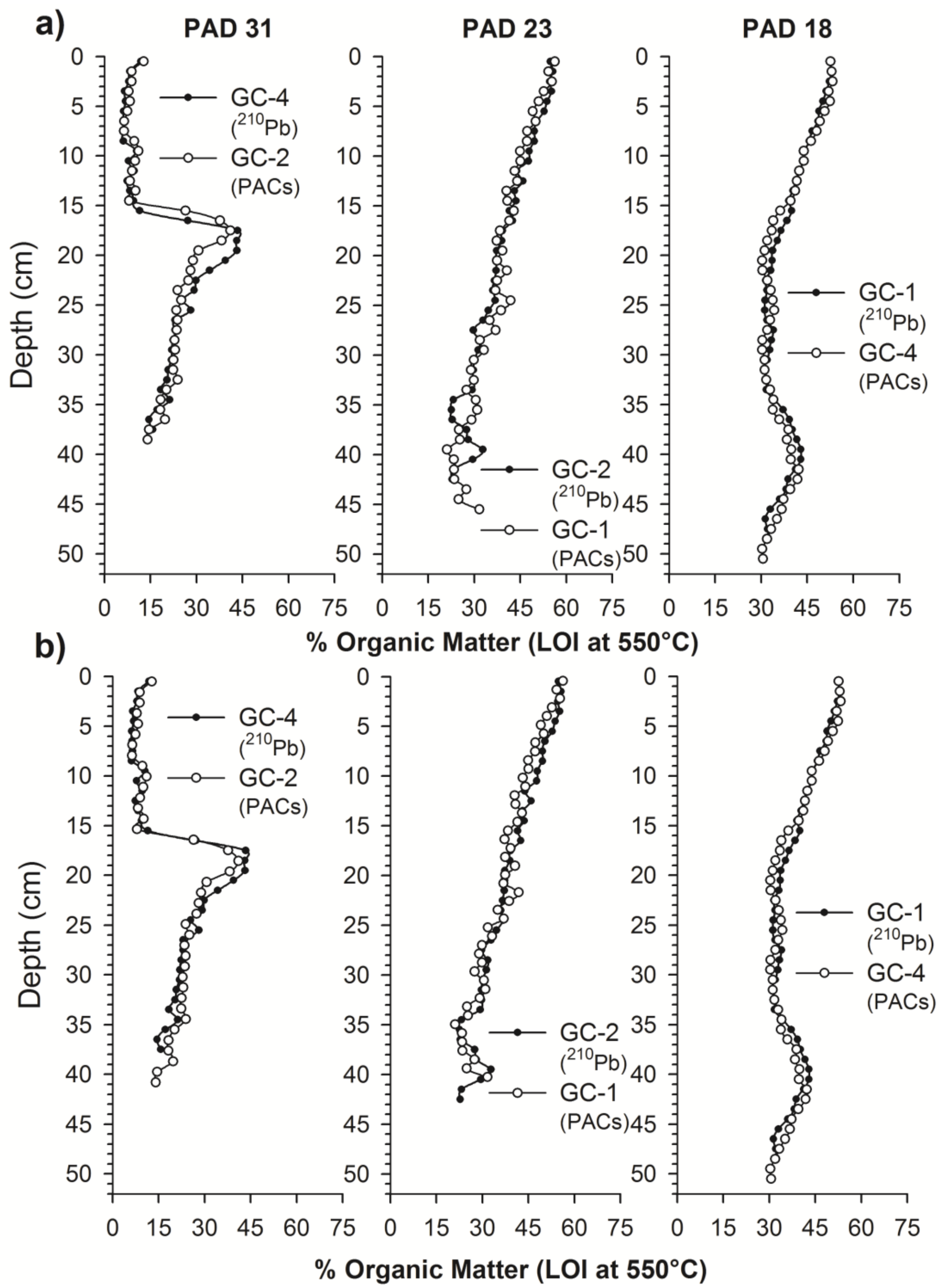

Figure 4.3 Graphs showing stratigraphic profiles of organic matter (OM) content in duplicate cores taken from each of the three study lakes in the Peace-Athabasca Delta, northern Alberta. One of the cores from each lake was analyzed for ^{210}Pb dating and the other provided material for analysis of PACs. Upper panel a) shows the raw data, whereas the lower panel b) shows the data after vertical adjustment of the OM content profile for the core that was not dated. ^{210}Pb-derived dates from the dated core were transferred to the corresponding undated cores used for PAC analyses (for details see 4.3.3 ^{210}Pb dating of sediment cores). Note that no depth adjustments were required for cores from PAD 18.

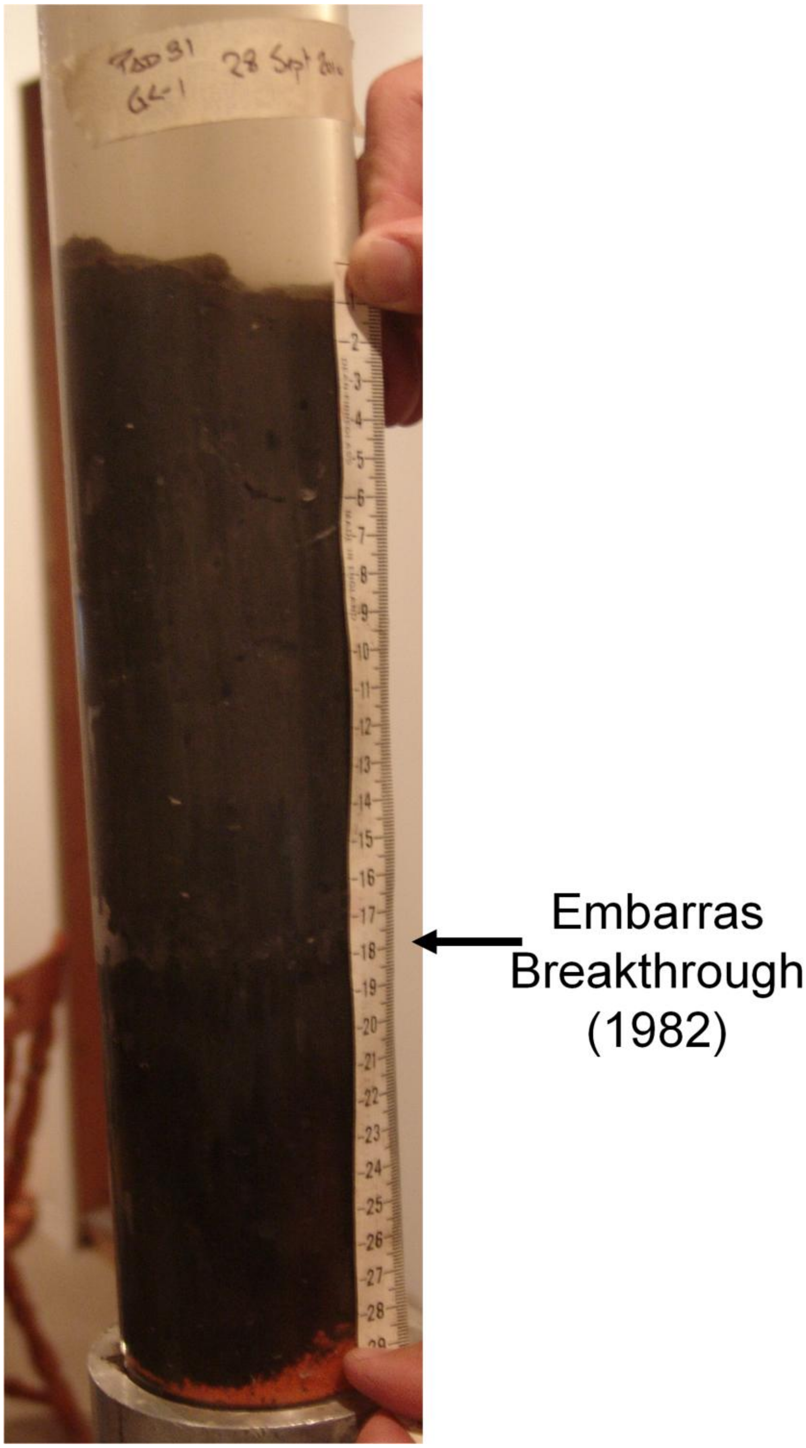

Figure 4.4 Photograph of a sediment core obtained from PAD 31 showing the stratigraphic contact at 18 cm depth marking the Embarras Breakthrough in 1982, which increased the lake's flood susceptibility. Post-1982 sediments are lighter coloured and contain more mineral matter than the darker, organic-rich sediments deposited pre-1982.

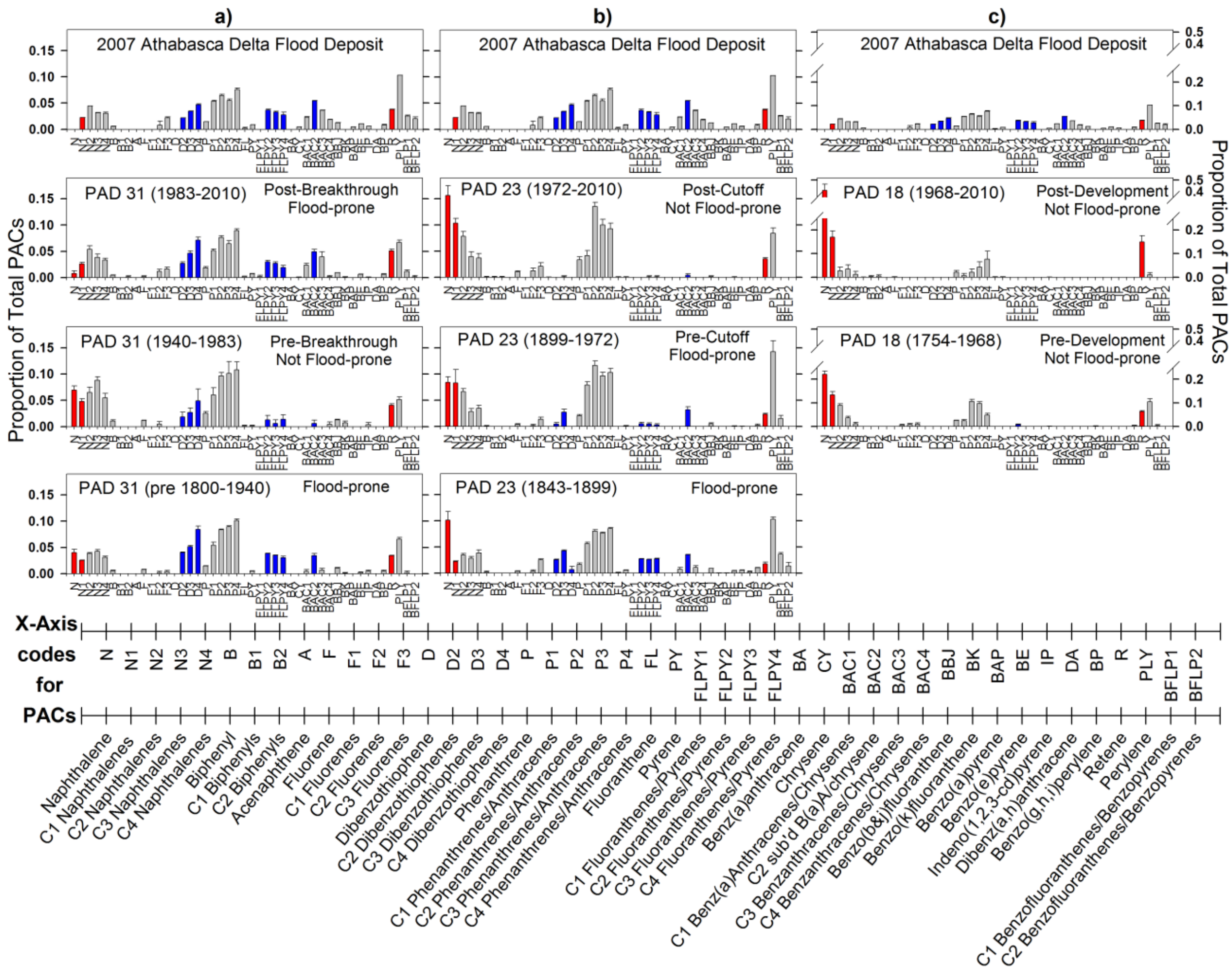

Figure 4.5 Bar graphs showing average composition of polycyclic aromatic compounds (PACs), expressed as relative concentration (proportion; error bars ±1 SEM) in **a)** the 2007 Athabasca Delta flood deposit and three intervals of differing flood regime at PAD 31, **b)** the 2007 Athabasca Delta flood deposit and three intervals of differing flood regime at PAD 23, and **c)** the 2007 Athabasca Delta flood deposit and two intervals that distinguish pre- and post-1967 onset of major commercial oil sands development at not flood-prone PAD 18 (note different scale of vertical axis). Names of the PAC compounds and the corresponding codes are presented along the lower expanded horizontal axis. Blue vertical bars are PACs identified by SIMPER analysis as river-transported indicator compounds common in sediments deposited during flood-prone intervals. Red vertical bars are PACs identified by SIMPER analysis as indicator compounds in sediments deposited during not flood-prone periods (see 4.35 Numerical analysis, Table 4.1).

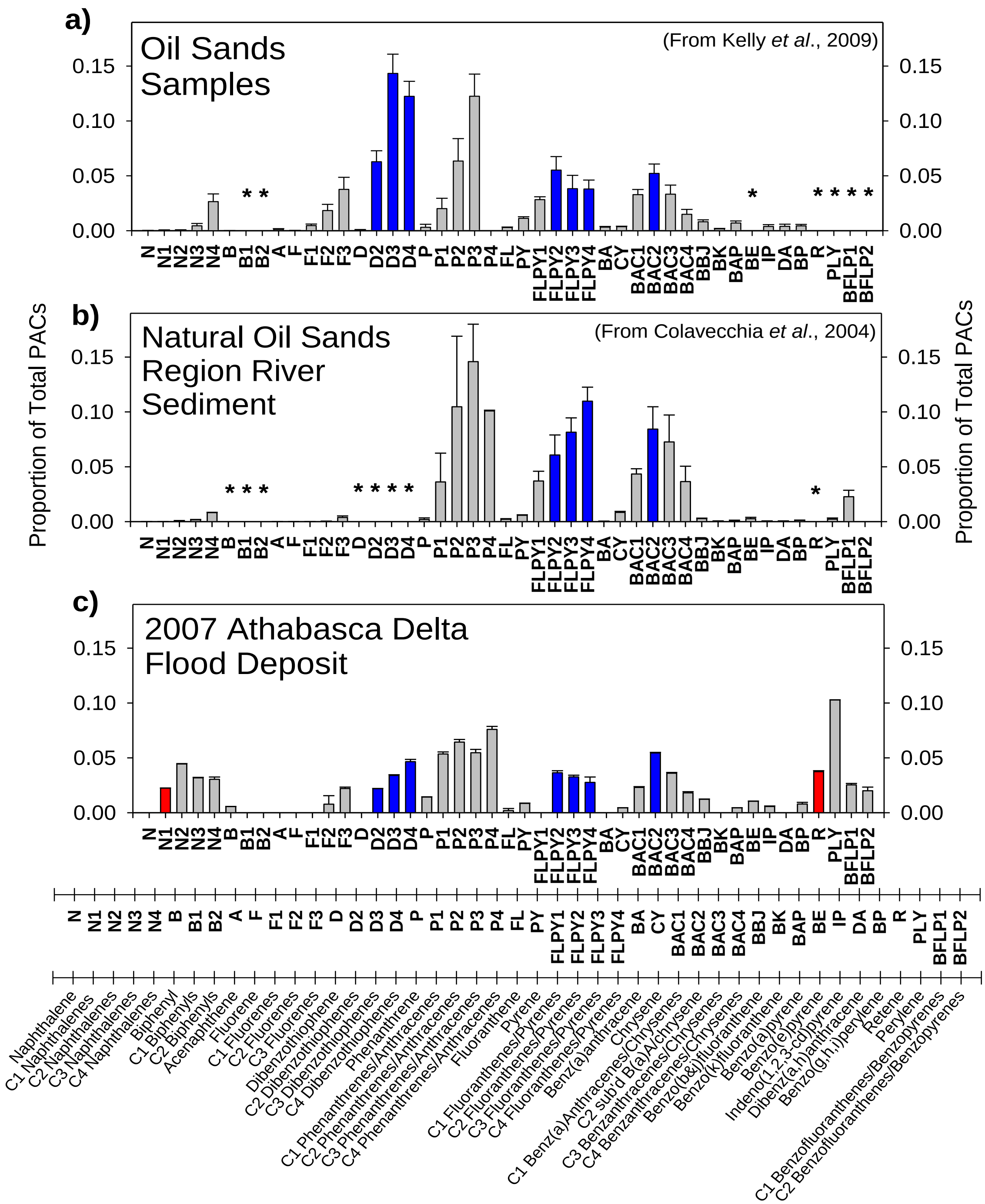

Figure 4.6 Bar graphs showing average composition of polycyclic aromatic compounds (PACs), expressed as relative concentration (proportion; error bars = ±1 SEM) in **a)** oil sands samples from Syncrude, Steepbank River mouth, and east and west banks of the Athabasca River (from Kelly *et al*. 2009), **b)** natural oil sands region river sediment (from Colavecchia *et al*. 2004) and **c)** the 2007 Athabasca Delta flood deposit. Names of the PAC compounds and the corresponding codes are presented along the lower expanded horizontal axis. Blue vertical bars are PACs identified by SIMPER analysis as rivertransported indicator PACs deposited during flood-prone intervals (Table S1). Red vertical bars are PACs identified by SIMPER analysis as common in sediments deposited during not flood-prone periods (Table 4.1). ***** identifies PACs that were not measured in one sample but were measured and reported in another sample presented in the figure.

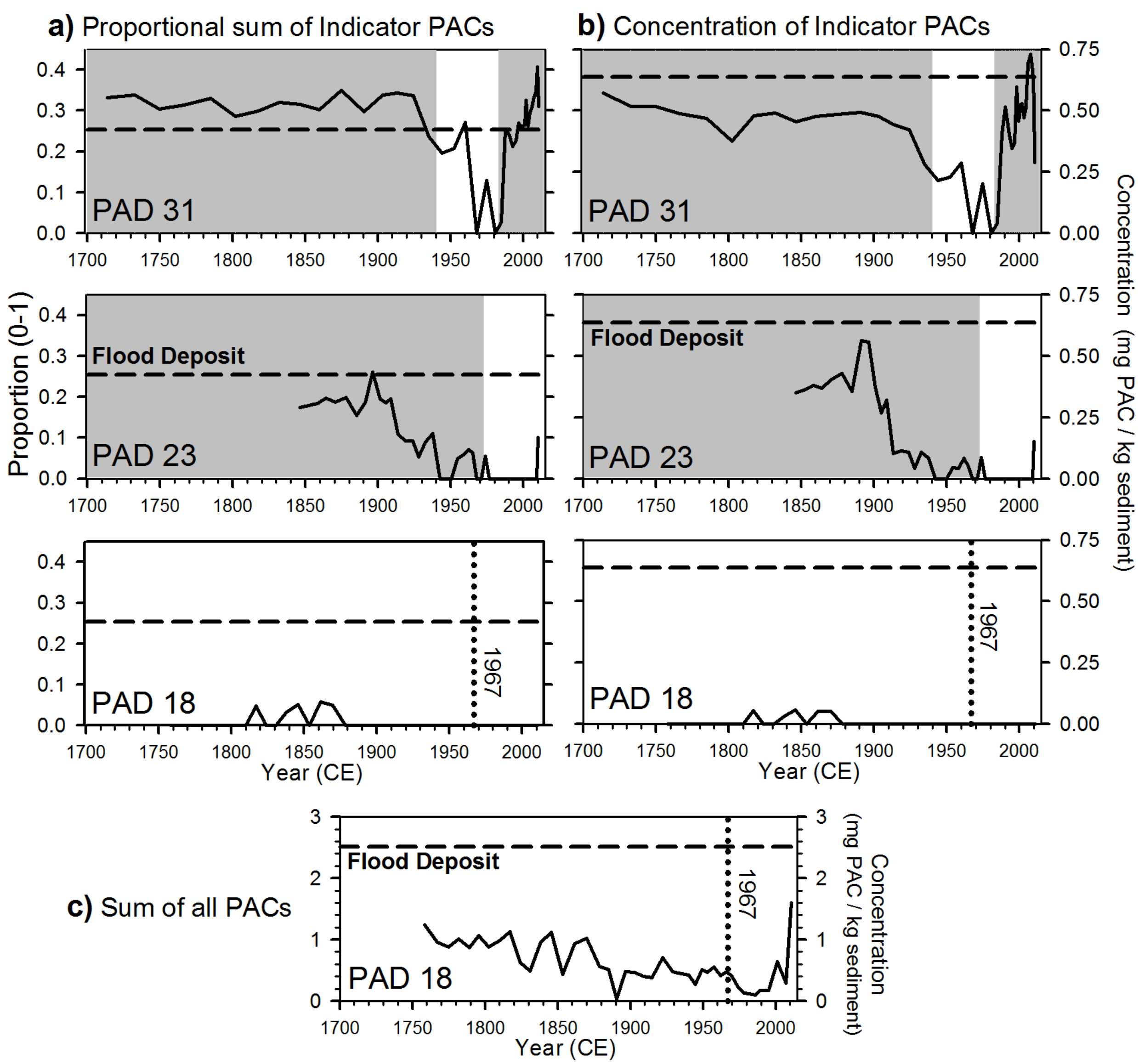

Figure 4.7 Stratigraphic records from sediment cores of the three study lakes (PAD 31, 23, 18) showing **a)** the sum of the proportions of the seven river-transported indicator PACs (C2-through C4-dibenzothiophenes, C2- through C4-fluoranthenes/pyrenes, C2-sub'd B(a)A/chrysene), and **b)** the sum of the concentration of the seven river-transported indicator PACs. Panel **c)** shows the total PAC concentration in the sediment core from PAD 18. Grey shading identifies periods when the lakes were flood-prone. Absence of shading identifies periods when the lakes were not flood-prone. The dotted vertical line in plots for PAD 18 identifies 1967, the year when major commercial operations began (Gosselin *et al*., 2010; Schindler, 2010). Dashed horizontal lines in panels **a)** and **b)** correspond to the average value for the sum of the seven river-transported indicator PACs in the 2007 Athabasca Delta flood deposit, where **a)** shows the proportion (= 0.254) and **b)** shows the concentration (= 0.638 mg/kg). Dashed horizontal line in **c)** shows the total PAC concentration in the 2007 Athabasca Delta flood deposit (2.518 mg/kg).

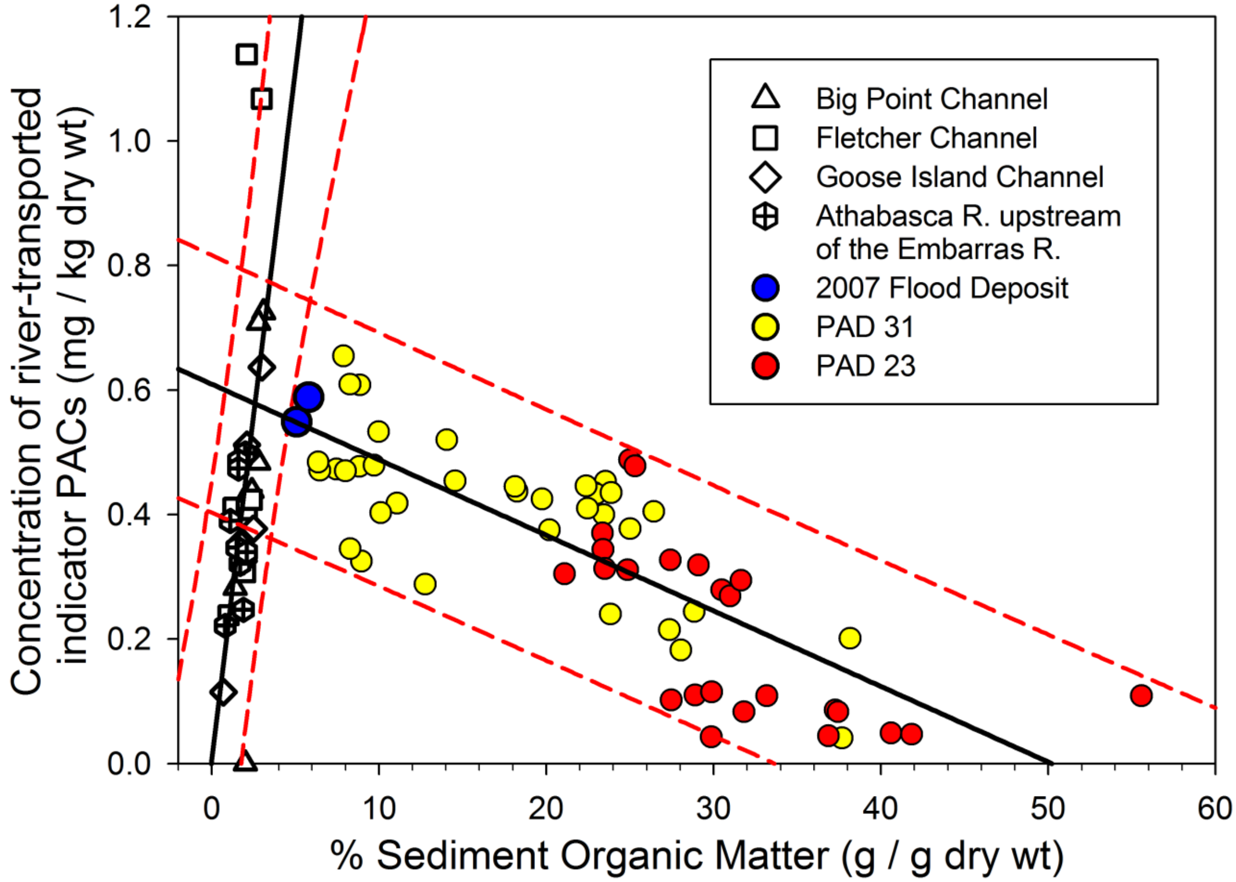

Figure 4.8 Scatterplot showing the relations between organic matter (as a percentage of dry sediment mass) and concentration of river-transported indicator PACs in sediments of lakes PAD 23 (solid red circles) and PAD 31 (solid yellow circles) in the Athabasca Delta (data from this study), in bottom sediments of the Athabasca River and its distributaries at four stations within the Athabasca Delta (open symbols; data from RAMP23), and in sediments deposited on land between Mamawi Creek and PAD 31 by an ice-jam flood in spring of 2007 (solid blue circles; data from this study). Data include the sum of the concentration of six of the seven river-transported indicator PACs that were common to both the lake sediment data set (this study) and the river bottom sediment (RAMP23; note: FLPY-4 was not reported by RAMP). The lines of best fit (solid black line) and 95% prediction intervals (dashed red lines) are presented for linear regressions of sediment organic matter content and river-transported indicator PAC concentrations for both the river bottom sediments and the lake sediments.

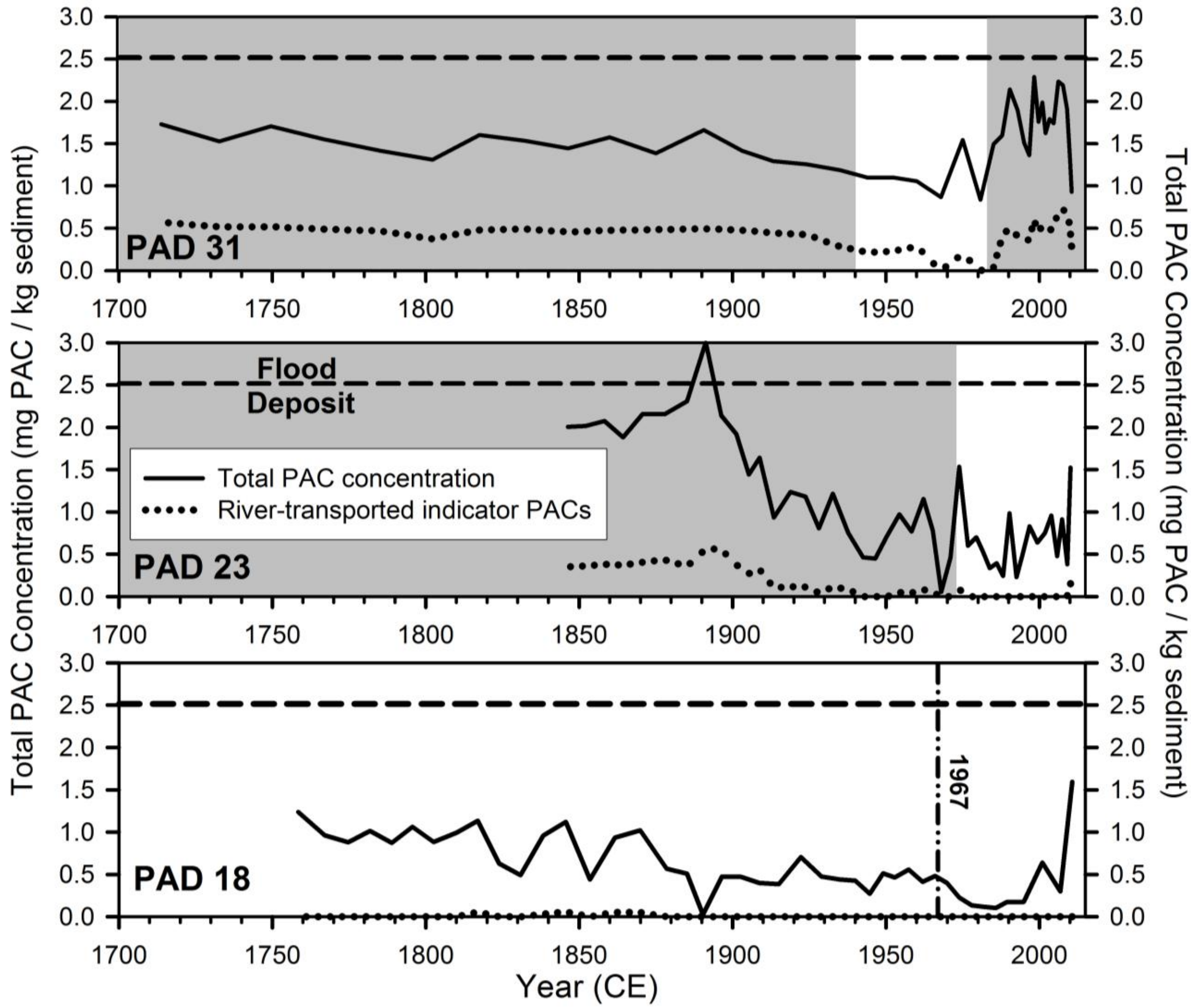

Figure 4.9 Stratigraphic records showing the total PAC concentration (solid line) and the concentration of the seven PACs indicative of a bitumen origin and transport by the Athabasca River (dotted line) in the sediment cores from lakes PAD 31, PAD 23 and PAD18 in the Peace-Athabasca Delta (PAD), northern Alberta, Canada. Grey shading identifies periods when the lakes were flood-prone. Absence of shading identifies periods when the lakes were not flood-prone. The dashed-dotted vertical line in the plot for PAD 18 identifies 1967, the year when major commercial oil sands operations began. The dashed horizontal line in all three panels corresponds to the average value for the total PAC concentration in the 2007 Athabasca Delta flood deposits (2.518 mg/kg).

4.8 Tables

Table 4.1 Results of similarity percentages (SIMPER) analysis of PAC composition in sediment core samples from the three study lakes of the Peace-Athabasca Delta, northern Alberta, with samples categorized as flood-prone or not-flood prone, to identify PACs most indicative of river transport versus other vectors and processes. Further details are presented in 4.3.5 Numerical analyses and 4.4.2 Identification of river-transported indicator PACs. The indicator PACs for flood-prone intervals are highlighted as blue vertical bars in Figure 4.5, 4.6 and presented as a sum in Figure 4.7a, b, 4.9. The indicator PACs for not flood-prone intervals are highlighted as red vertical bars in Figure 4.5, 4.6.

	Between-group Dissimilarity (flood-prone *vs* Not flood-prone)		Within-group Similarity (Flood-prone or Not Flood-prone)		Average Proportion of total PACs (0-1)	
	Average Dissimilarity %	Contri-bution %	Average Similarity %	Contri-bution %	Flood-prone	Not flood-prone
Indicator PACs for Flood-prone intervals						
C4 Dibenzothiophenes	2.24	4.41	2.1	2.99	0.04	0
C3 Dibenzothiophenes	2.01	3.96	3.19	4.55	0.04	0
C2 sub'd B(a)A/chrysene	1.86	3.68	2.83	4.04	0.04	0
C2 Fluoranthenes/Pyrenes	1.21	2.4	1.61	2.3	0.02	0
C2 Dibenzothiophenes	1.18	2.32	1.48	2.12	0.02	0
C3 Fluoranthenes/Pyrenes	1.11	2.19	1.47	2.1	0.02	0
C4 Fluoranthenes/Pyrenes	0.94	1.86	1.02	1.45	0.02	0
Indicator PACs for Not flood-prone intervals						
Napthalene	8.62	17.01	14.8	24.41	0.05	0.212
C1 Napthalenes	4.81	9.5	8.92	14.71	0.04	0.12
Retene	1.97	3.88	4.3	7.09	0.03	0.07

Chapter 5

Conclusions and Recommendations

The Peace-Athabasca Delta (PAD) in northern Alberta (Canada) is a wetland of international significance. It is the world's largest boreal delta, is supports one of the highest densities of waterfowl in Canada and serves as a key migratory node for four North American flyways of migratory waterfowl (MRBC, 1981; Prowse and Conly, 2000). The PAD is a vast (~6000 km^2; Peters *et al*. 2006) and hydrologically complex landscape located at the west end of Lake Athabasca. It receives water from two major rivers (the Peace and Athabasca rivers) and outflow of Lake Athabasca. These waters merge at the PAD to become the Slave River and flow northwards to Great Slave Lake, ultimately emptying into the Beaufort Sea via the Mackenzie River. Research in this thesis examined the role of hydrology as a factor controlling epiphytic diatom communities and limnological conditions, and delivery of upstream-sourced contaminants to lakes of the PAD. The individual research chapters make important contributions to our knowledge of the hydroecology (Chapter 3) and contaminant dispersal (Chapter 4). And, I demonstrate that novel artificial substrate samplers provide an effective bio-monitoring tool for tracking flood events from analysis of accrued epiphytic diatom communities (Chapter 2).

5.1 Chapter 2: epiphytic diatoms for bio-monitoring of flood events

Numerous studies have shown diatom communities to be useful indicators of water quality (Hall and Smol, 1992; Lavoie *et al*., 2006; Kelly *et al*., 2008; Simpson and Hall, 2009). Diatom communities have an advantage over discrete measurements of water conditions, in that diatom communities integrate water-quality conditions over time and provide information on the conditions and stressors experienced by the aquatic community (Lavoie *et al*., 2006). Importantly, a diatom-based bio-monitoring program has a key advantage over many other potential bio-indicator taxonomic groups. Diatoms preserve well in most lake sediment profiles and so can be used in paleolimnological studies to track past environmental changes and influential events. Knowledge of contemporary relations between diatom community composition and water quality and limnological conditions (Hall and Smol, 1992; Kelly *et al*., 2008; Simpson and Hall, 2009), and possibly contaminant relationships (De Jonge *et al*., 2008; Morin *et al*., 2008; Cattaneo *et al*., 2011), may be applied to paleo-diatom communities in the sedimentary record to allow hindcasting of past conditions (Reid *et al*., 1995). This feature could prove particularly useful in the PAD because long-term water quality and contaminant data are surprisingly scant for this ecologically-significant landscape (MRBC, 1981; Prowse and Conly, 2000).

Previous paleolimnological studies have shown that good stratigraphic preservation of sedimentary diatom assemblages can indeed be found in PAD lakes (Hall *et al*., 2004; Wolfe *et al*., 2005; Johnston *et al*., 2010), so that long-term reconstructions of hydrolimnological conditions are possible. Commonly, diatom-environment relations are determined via a training set of >30 lakes, where diatom assemblages in surficial sediments (top ~1 cm) of lakes are related to broad environmental gradients via the construction of transfer functions. These transfer functions are then applied to diatom assemblages in lake sediment cores to reconstruct past environmental conditions such as lake water pH, nutrient concentrations, and salinity, as well as air temperature (Hall and Smol, 1996; Lotter *et al*., 1997; Korhola *et al*., 2000; Battarbee *et al*., 2001). As the surficial sediments will typically contain the remains of diatom communities spanning a few years, there is an aspect of temporal disconnect between the measured lake conditions and the time period during which the diatom community existed. In a training set that utilizes lakes that maintain relatively stable environments, modest year-to-year variability does not present a significant problem. However, in highly dynamic systems such as lakes in the PAD, year-to-year variability can be large, thus requiring a tighter temporal connection between measured environmental conditions and the algal community, if accurate diatom-environment relations are to be obtained.

For the above reasons, utilizing epiphytic diatoms and artificial substrates (as a means of collection) as a bio-monitoring tool for the PAD was explored. Such an approach allows strict temporal control between the measured community and limnological conditions and also targets a diverse and highly productive component of the PAD flora with a strong bio-indicator capacity. Artificial substrates are advantageous over natural substrates, and have been employed by researchers for epiphytic algae sampling for >100 years. However, their use remains contentious as to whether they adequately mimic natural substrates (Amireault and Cattaneo, 1992; Lane *et al*., 2003).

The study design of Chapter 2 allowed the comparison of the epiphytic diatom community composition between flooded and non-flooded lakes, while also comparing the epiphytic diatom community composition accrued on artificial substrate samplers (consisting of polypropylene sheets) and two common macrophyte taxa. Flood events were shown to exert a strong and significant control on the epiphytic diatom community. Substrate effects, while statistically significant in a study of sufficient power such as ours, are minor compared to limnological effects (see Table 2.2). This study shows that the relative contribution to differences in epiphytic diatom communities by the three factors can be characterized as: *individual lake* *effect* > *lake flood class effect* >> *substrate effect*. One very important finding was that the difference in epiphytic diatom community composition attributable to using an artificial substrate was found to be equivalent to that attributable to sampling from different macrophyte taxa. Results in Chapter 2 justify the use of artificial substrates in the PAD as they show that the variation in diatom community composition imposed by the use of artificial substrates is no worse than the variation introduced when epiphytic samples are compared among different host macrophyte taxa. Artificial substrates allows for standardization by removing variation due to confounding effects such as substrate age, location within a lake and water depth (Amireault and Cattaneo, 1992).

Central to Chapter 2 was the capacity to compare the epiphytic diatom community composition between flooded and non-flooded lakes. Quantification of the relative contribution to the similarity and dissimilarity by individual diatom taxa to the epiphytic diatom community composition between flooded and non-flooded lakes via SIMPER analysis enabled the identification of indicator taxa for the presence and absence of flooding. Of particular interest were five diatom taxa which were identified to be “strong flood indicators”. These were consistent components of the contemporary epiphytic diatom community in the flooded lakes, but were rare or absent in the non-flooded lakes. Applying the knowledge gained from the contemporary field experiment, a diatom-inferred flood record was produced from a ~180-year sediment record of diatom community composition from PAD 5. The sediment intervals showing an increased abundance of these “strong flood indicators” were inferred to be time periods when the lake likely received ice-jam floodwaters. The diatom-inferred flood record for PAD 5 proved congruent with a magnetic susceptibility-derived flood record from a nearby lowland oxbow lake (Wolfe *et al*., 2006), as well as a flood record derived from historical documents (PADTS 1996).

These findings confirm that perturbations of limnological conditions due to flood events are sufficient to alter the epiphytic diatom community in demonstrable ways that can be detected in a sediment record. Comparison of epiphytic diatoms in flooded and non-flooded lakes in this study provides a promising approach to detect flood events in a paleolimnological context. This approach appears most applicable for use in the more elevated lake basins in the PAD for which magnetic susceptibility is generally unsuitable for detecting flood events.

While this study identified responses of epiphytic diatom communities to flood events, the implications may be broader for the field of paleolimnology. Specifically, it provides a methodological approach to detect short-lived, pulse-type disturbances. Previously, paleolimnology has successfully developed and applied the use of surface sediment “training sets” to detect and quantify limnological changes due to ramp and press disturbances (*sensu* Lake 2000). That flood-pulse disturbance events can be identified by our approach should be of interest not only to those interested in reconstructing records of flood events, but also to those interested in reconstructing records of other pulse-type disturbances such as hurricanes and pollutant spills in lentic systems.

5.2 Chapter 3: Role of flooding on limnological conditions of lakes in the PAD

Following construction of the WAC Bennett Dam on the Peace River, a series of reports and investigations of the potential hydrological and ecological impacts on the PAD were conducted (PPADS, 1971 and PADPG, 1973). These reports created the prevailing paradigm that declining water levels and river connectivity would reduce not only the supply of water to perched basin lakes, but also the concentration of nutrients. This, in turn, would negatively affect the productivity of perched basin lakes deprived of floodwaters (Fuller and LaRoi, 1971; Dirschl, 1972; Gill, 1973). The concept that flooding of PAD lakes is crucial for maintaining nutrients and aquatic productivity in perched basins remains pervasive in the peer-reviewed literature (Prowse *et al*., 2006; Anisimov *et al*., 2007), yet it was never rigorously tested.

Chapter 3 presents the results of a systematic study of limnological conditions throughout the ice-free season in several PAD lakes and rivers over three years (2003-05) to provide data that can be used to assess the veracity of the concepts described above. Contrary to the prevailing paradigm (Fuller and LaRoi, 1971; Dirschl, 1972), results of this study suggest that regular flooding is not required to maintain high nutrient concentrations in perched basin PAD lakes. Instead, the opposite appears to be the case based on evidence that concentrations of the main nutrients and ions TKN, TIN, DP and K are highest in closed-drainage lakes and lowest in rivers and open-drainage lakes (see Figure 3.4, 3.7, 3.8). During flood events, affected lakes receive TP contained within the minerogenic suspended sediment. TP rapidly (over days-weeks) settles out of the water column after floodwaters subside, such that by summer non-flooded lakes have TP concentrations comparable to flooded lakes. These general trends, which do not support the flooding-nutrient paradigm, have also been observed downstream in the Slave River Delta and the Mackenzie River Delta (Emmerton *et al*., 2008; Sokal *et al*., 2008; 2010).

This study identified that the responses of hydrolimnological conditions to flooding operate at two distinct timescales in lakes of the PAD. The responses are summarized in Figure 3.10 which is repeated as Figure 5.1 in this chapter as it effectively summarizes the timescales and properties of hydrolimnological change in the PAD. One timescale involves the short-term responses of lakes over a period of weeks to months after flooding. Floods exchange a substantial volume of water in the shallow floodplain lakes with isotopically-depleted river water that is higher in content of P-rich suspended sediment and DSi, calcium and SO_4, and lower in pH. The turbid river waters reduce water clarity of flooded lakes (increased Kd-par). In the weeks to months after a flood, lake water becomes isotopically-enriched because of evaporation. The river-supplied sediments settle out of the water column (increasing water clarity) and a progressive shift to limnological conditions that resemble those of non-flooded restricted-drainage lakes occurs (Figure 3.5b, 5.1). Thus, restricted-drainage lakes oscillate along the horizontal axis (Figure 5.1) in response to the rapid exchange with floodwaters. Restricted-drainage lakes move leftwards on this axis due to evaporation and sedimentation processes that lower TSS and TP concentrations, and also in response to increased pH and decreased DSi due to autotrophic production. Following a flood event, restricted-drainage lakes shift to the right on the horizontal axis, more closely resembling river water conditions.

In contrast to the relatively rapid, seasonal to intra-annual changes that follow a flood event, the limnological transition from restricted-drainage to closed-drainage hydrological conditions occurs over a much longer timescale. In the absence of flooding over multiple years to decades, within-basin processes dominate, leading to greater limnological heterogeneity among lakes (Junk and Wantzen, 2004; Thomaz *et al*., 2007; Wantzen *et al*., 2008). Closed-drainage lakes are characterized by high water clarity, high concentrations of DOC, TKN, bio-available nutrients and ions and low concentrations of suspended sediments and SO_4. In this region of semi-arid climate, concentrations of these variables increase because of evaporation, a finding that has previously been observed in lakes of central Alberta with long water residence times (Curtis *et al*., 1995).

Given expected trajectories of change in river discharge (Wolfe *et al*., 2008b), limnological conditions of the Athabasca Delta will become less dominated by short-term (intrato inter-annual) oscillations due to frequent river flooding of perched basins (see the horizontal axis of Figure 5.1). This transition to increasing hydrologic closure of PAD lakes, if it happens, will be accompanied by an increase in water transparency and bio-available forms of nutrients, which will promote primary production (see vertical axis in Figure 5.1). These findings are consistent with McGowan *et al*. (2011), who found sediments of closed-drainage lakes to be more abundant in algal and plant pigments relative to restricted- and open-drainage lakes. Results are also congruent with examinations of nutrient-hydrologic gradients in lakes of the Slave River Delta (Sokal *et al*., 2008, 2010) and Mackenzie River Delta (Emmerton *et al*., 2008) downstream of the PAD.

5.3 Chapter 4: Natural versus anthropogenic supply of organic contaminants to the PAD

The potential impacts of the Athabasca Oil sands development have come to dominate both public and scientific discourse over the health of the PAD (Timoney and Lee, 2009, 2011; Schindler, 2010; Wingrove, 2010). Industrial development of the Athabasca Oil Sands began in 1967, increased slowly until the 1980s, and increased steeply thereafter (Schindler, 2010; Gosselin *et al*., 2010). This growth is a main contributor to Canada becoming the world's 6th largest producer of oil as of 2009 (IAE 2010, see Table 11). Recent articles by Kelly *et al*. (2009; 2010) and Timoney and Lee (2009; 2011) have increased concerns over transport of oil sands pollutants to the lower Athabasca River and the PAD. Their findings have reignited concerns that the Regional Aquatic Monitoring Program (RAMP) is unable to alert society to sources of pollution and cannot track trends over time (Ayles *et al*., 2004; Burn *et al*., 2011). These studies stimulated public alarm that has led to the initiation of a new Integrated Oil Sands Environmental Monitoring Program by Environment Canada (Environmental Canada, 2011a-e). One of the recommendations made by the new program was to collect sediment cores from lakes of the PAD to reconstruct loadings of contaminants to the PAD. Lake sediment cores can record loading of PACs from pre-industrial to current times, using consistent and scientifically-rigorous methods. This would allow establishment of natural baseline loadings as well as evaluation of the significance of oil sands-development as an additional source of PACs to the PAD. Neither is known, yet both are of critical importance to assess if Athabasca oil sands development is increasing the emissions and transport of PACs to the PAD.

Chapter 4 of this thesis entitled "***Natural processes dominate the delivery of polycyclic aromatic compounds to the Athabasca Delta downstream of oil sands development***" examines continuous ~200-year records of PAC deposition at three lakes in the PAD for which past hydroecological conditions were well known from prior studies (Hall *et al*., 2004; Wolfe *et al*., 2007, 2008a,b). Two of the lakes are within the floodplain of the Athabasca Delta (PAD 23 and PAD 31) and have changed over time in their susceptibility to river flooding. One lake (PAD 18) is in the Peace Delta, perched above the influence of flood events, and records aerial deposition of PACs to the PAD region. The results provide important advances to our understanding of the deposition of PACs in the PAD and allow us to answer the important research questions, as stated below.

Is the Athabasca River a significant vector for the transport and deposition of bitumen-related PACs to the PAD?

Yes. Statistical analysis of PAC composition in 127 sediment intervals, classified as flood-prone or not-flood prone (based on previous knowledge) from the three lakes, identified seven PACs that were most strongly associated with river flooding. The seven river-transported indicator PACs were independently verified, as these same seven PACs are clearly elevated in the 2007 Athabasca River flood deposit (see Figure 4.5). Furthermore, these seven PACs comprise 51% of total PAC content measured in oil sands samples by Kelly *et al*. (2009). This confirms that the Athabasca River is the major vector of bitumen-related PACs to the PAD. Most strikingly, this has been the case for >200 years, indicating that natural erosion and transport of the McMurray oil sands material by the Athabasca River and tributaries has been a major process for the delivery of PACs to the PAD.

Is there evidence to indicate that industry has measurably altered the composition and concentration of PACs in sediments of lakes receiving floodwaters from the Athabasca River, from that provided during the pre-impact period due to riverbank erosion and subsequent downstream transport by the Athabasca River?

No. PAD 31 shows high and similar concentrations and proportions of the river-transported indicator PACs (which are bitumen-related) during the two time periods of high flood susceptibility (1983 to 2010 and ~1720 to 1940), both post- and pre- oil sands development (see Figure 4.3). The average concentration during 1983-2010 [0.476 mg/kg ± 0.165 (1 SD)] does not differ significantly from that of the pre-1940 interval (0.466 mg/kg ± 0.065). Similarly, the average proportion of the river-transported indicator PACs during 1983-2010 [31% ± 5 (1 SD)] does not differ significantly from that of the pre-1940 interval (32% ± 5 (1 SD)]. This shows that the vast majority of the bitumen-associated PACs deposited in the recent sediments of PAD 31 can be accounted for by natural processes. Furthermore, the greatest abundance of the river-transported indicator PACs in PAD 23 occurred prior to ~1900 (see Figure 4.3). Declining flood frequency since the Little Ice Age corresponds to declining PAC deposition in PAD 23. After the Athabasca River Cut-off (1972), PAD 23 became not-flood prone and river-transported

PACs declined to below detection limits in several sediment intervals. This highlights both the importance the Athabasca River as a vector for the transport of bitumen-related PACs to PAD lakes and hydro-geomorphic changes as a mechanism for temporal and spatial control of PAC deposition within the delta.

We carefully considered multiple ways to present these data, including in flux units (e.g., as mass of PACs per unit area per unit time) to directly assess if industrial activity is accelerating the rate of delivery of PACs to the delta. But, this was not possible based on the experimental design of this study, because at PAD 31 sedimentation rates increased (Figure 4.2) when the lake became more susceptible to flooding following the Embarras Breakthrough (Wolfe *et al*., 2008b). As a consequence, it is not possible to distinguish natural hydrological causes of changes in PAC *fluxes* from those potentially due to industrial activities because they are confounded in time. Rather, we contend that if industry has substantially enhanced PAC loads to the delta, then the likelihood of doing so with the same sedimentary *concentration* and *composition* of PACs that has occurred naturally due to erosion of the Athabasca River would seem highly unlikely, but remains to be tested at additional sites. However, we note that Timoney and Lee (2011) have concluded that oil sands industrial activity is related to increasing sedimentary PCA *concentration* in the Athabasca River.

Is there evidence to indicate that industrial emissions are increasing atmospheric deposition of PACs in the delta?

No. There is no evidence to indicate that industrial emissions from the Athabasca oil sands are increasing atmospheric deposition of PACs in the delta at this time. PAD 18 is a closed-drainage lake perched well above the deltaic plan. The lowest total PAC concentrations within the ~250-year PAD 18 record occurred during the 1980s and 90s. Given the rapid expansion of oil sand development during this time period (Schindler, 2010), and a lack of concurrent rise in PAC concentrations at PAD 18, it is apparent that PAC deposition at PAD 18 has not been elevated by aerial deposition from industrial oil sands production. Throughout the PAD 18 record, the PACs found are predominantly pyrogenic in origin. Their source most likely is from forest fires, which have been the dominant source of PACs to PAD 18 over the last ~250 years.

None of the seven river-transported indicator PACs (which comprise ~51% of total PACs in bitumen deposits) were detected in PAD 18, with exception of FLPY-2 in a few samples that were deposited during the 1800s. This may indicate that some floodwaters and bitumen-derived PACs reached PAD 18 during the 19th century. During the Little Ice Age, the difference between the surface of PAD 18 and the open-drainage network of the PAD was ~2.3 m less than it is today (Johnston *et al*., 2010). This likely made flooding of high-elevation basins such as PAD 18 during extreme ice-jam events much more likely than is presently the case.

If we consider that the 250-year record from PAD 18 is representative of natural atmospheric deposition (plus within basin sources), then we can approximate what the mean natural, long-term atmospheric deposition of PACs is to the PAD. The total inventory of PACs by mass in the PAD 18 sediment record is 0.123 mg. As this sediment core has an area of 45.6 cm^2, it follows that the long-term average aerial deposition (plus within basin sources) of PACs to PAD 18 is ~0.108 mg PACs / m^2 / year. If we exclude the five intervals during the 19th century that may have experienced some flooding (due to the presence of FLPY-2) and the post-development period (1967-2010), the mean annual total PAC deposition for the residual ~170 years of the pre-development record at PAD 18 is little different at ~0.106 mg PACs m^2 / year. In comparison, the long-range aerial deposition of combined particulate and dissolved PACs due to industrial oil sands emissions inferred using the equations provided by Kelly *et al*. (2009) anticipates that PAD 18 would receive ~0.4 pico g PACs / m^2 / year. Or, for the southernmost portion of the PAD, the PAC deposition rate is inferred to be as much as ~7.0 pico g PACs / m^2/year. These amounts are about 4-5 orders of magnitude less than the average long-term annual rate of natural deposition recorded at PAD 18 for the last 250 years. While the total annual aerial PAC deposition near the bitumen upgrader (AR-6) reported by Kelly *et al*. (2009) is considerable at 1.7 tonnes (within a 50 km radius of AR-6), only a much smaller fraction would deposit on, or be transported to the Athabasca River and the PAD. While aerial deposition of PACs due to oil sands operation might be a concern in the Fort McMurray area, the PAD is sufficiently remote that elevated aerial PAC deposition from oil sands activities appears highly unlikely. Thus, the ~250-year long record from PAD 18 identifies that atmospheric delivery of PACs is dominated by natural, mainly pyrogenic, sources of PACs, with no measurable additional contributions by oil sands development.

As an environmental issue, the oil sands have become highly political at national and international levels. Consequently, our findings presented in Chapter 4 are likely to be met with considerable scepticism by some. However, examination of other data and findings that were generated prior to our study provide considerable support for the major findings presented in Chapter 4 that: 1) natural erosion of the McMurray formation by Athabasca River and its tributaries provides a large source of PACs to the lower Athabasca River, and 2) industry has not measurably contributed additional loading of PACs to lakes in the Athabasca sector of the delta beyond natural supplies. The following examines how our findings fit within the context of evidence provided by previous studies.

Conly *et al*. (2002) evaluated channel stability of the Athabasca River and tributaries in the lower Athabasca River with the objective to determine bank erosion rates at locations of natural exposures of bitumen sands. The purpose of their study was to estimate what proportion of total river-transported sediment entering the PAD via the Athabasca River could be attributed to natural fluvial processes in the lower Athabasca River. Of the total 6.35 Mt of suspended sediment passing the Embarras gauging station annually, it was concluded that at most 3% and possibly less than 1% was likely derived from bitumen exposures along the Athabasca River and tributaries. Conly *et al*. (2002) concluded that the expectation of finding naturally-derived PACs in the lower reaches of the Athabasca River system would therefore be limited (Conly *et al*., 2002). However, even 1% of 6.35 Mt is more than a trivial amount. This is equivalent to 63,500 tonnes of natural oil sands sediment potentially delivered to the PAD annually. Approximately 12% of this oil sands derived sediment or ~7600 tonnes is likely to be actual bitumen (Babadagli *et al*., 2008; Gosselin *et al*., 2010). For comparison, by mass this is approximately equivalent to one fifth of the Exxon Valdez spill deposited every year (Peterson *et al*., 2003).

Given an estimate of 63,500 tonnes of oil sands derived sediment eroded annually, a rough expectation of the naturally derived PAC loadings can be derived. The PAC content of the bitumen sands examined by Kelly *et al*. (2009) was 0.0095% PAC by weight, while that reported by Colavecchia *et al*. (2004) was 0.0275 % PACs by weight. These estimates of PAC content yield a range of 6 - 17.5 tonnes of total PACs potentially entering the PAD annually from natural erosion and transport of bitumen sands material by the Athabasca River and tributaries. Assuming that natural erosion of McMurray Formation contributes 6 - 17.5 tonnes of PACs carried by the Athabasca River annually to the PAD, and that this source dominates total PAC delivery to the PAD, the average total PAC concentration in 6.35 Mt of Athabasca River suspended sediment reaching the PAD could roughly be expected to be 0.94 - 2.73 mg PACs /kg sediment. This encompasses the mean concentration of 1.368 mg PACs / kg sediment ± 0.564 (1 SD, range: 0.293-2.777 mg/ kg) measured in sediments from the Athabasca River and distributary channels in the PAD by RAMP (RAMP sites BPC-1, FLC-1, GIC-1 and ATR-ER sampled from 2000-2010; see RAMP 2010). Similarly, the mean total PAC concentration of lake sediment **deposited during flood-prone intervals** at PAD 23 and 31 was observed to be 1.506 mg PACs / kg sediment ± 0.556 (1 SD, range: 0.053-3.008 mg/ kg). Thus, the observed PAC concentrations in river and lake sediments of the Athabasca Delta are congruent with the quantity of oil sands material naturally eroded and transported by the Athabasca River as estimated by Conly *et al*. (2002).

The approach taken in the preceding paragraphs to estimate natural bitumen and PAC loadings to the Athabasca River deserves further refinement. Additional natural and anthropogenic loadings of PACs to the upper and lower Athabasca River exist, and these would also have to be taken into consideration to produce a more accurate accounting of PAC loadings to the PAD. However, it is clear that natural loading of bitumen-related PACs by the Athabasca River is expected to be a large and significant source of PACs deposited in the PAD.

The results of Chapter 4 indicate that oil sands development to date has not led to an elevation in PAC contamination over natural sources in PAD lakes. The concentration of PACs observed in PAD sediments are less than that commonly measured in soils from urban environments (Bradley *et al*., 1994; Mauro *et al*., 2006). While higher than one might expect from a pristine area, the observed sediment PAC concentrations are attributable to natural processes. Sediments of the Mackenzie Delta and adjacent Beaufort Sea have also been reported to naturally possess high PAC concentrations, similar to the PAD (Yunker *et al*., 1993; Yunker and MacDonald, 1995; Headley *et al*., 2003). Furthermore, a large component of the total PACs present in the Mackenzie Delta and Beaufort Sea can be associated with natural petrogenic sources (Yunker *et al*., 1993; Yunker and MacDonald, 1995; Headley *et al*., 2003). This petrogenic component, however, was sufficiently different in composition from that of the Athabasca oil sands to rule it out as the dominant source (Headley *et al*., 2003). Instead, a mixture of natural oil seeps and erosion of naturally-occurring coal and bitumen deposits along the Mackenzie River were deemed to be the dominant source(s) of PACs found in the Mackenzie Delta (Yunker *et al*., 1993; Yunker and MacDonald, 1995; Headley *et al*., 2003).

Naturally high PAC concentrations are observed in both the Peace-Athabasca Delta and the Mackenzie Delta. This is not entirely surprising given that sediments of terrestrial portions of the Mackenzie drainage basin are rich in fossil fuel deposits of bitumen/oil, natural gas and even coal. The high natural PAC burdens in these systems may give rise to the concern that lower additional anthropogenic PAC loadings would be required to induce toxic effects than would be the case in regions of lower natural PAC burdens.

5.4 Recommendations for future research

In the Peace-Athabasca Delta, natural processes continue to dominate over upstream anthropogenic influences. PAC concentrations in the sediments of PAD lakes have not been found to increase due to oil sands industry, and evidence suggests the concentration of PACs in the Athabasca River sediment load has not changed appreciably over the last ≥200 years. In contrast, water quantity and the timing of flows to the PAD have fluctuated dramatically over centennial and millennial timescales in response to climatic shifts that alter the volume and timing of water release from glaciers and alpine snowpacks in the Rocky Mountain headwaters region (Edwards *et al*., 2008; Wolfe *et al*., 2008a, 2011; Johnston *et al*., 2010). Consequently, anticipated declining river flows should be the focus of future concerns regarding alteration of the PAD ecosystem and water supplies supporting western Canadian and American society (Schindler and Donahue, 2006; DeBeer and Sharp, 2007, Edwards *et al*., 2008; Wolfe et al., 2008a, 2011; Johnston *et al*., 2010).

The PAD is an important hydroecological node in the Mackenzie Drainage Basin, and declines in headwater supply as well as potential impacts of pollutants and water quality issues, stemming from human development upstream, are likely to be expressed in the PAD before such impacts are detectable in other environments further downstream (i.e., in the Slave River Delta or Mackenzie River Delta). Therefore, it is prudent that the PAD and its major river inflows and outflows should be included in a long-term monitoring and environmental stewardship program. Long-term monitoring data are urgently needed to track changes in hydrological and limnological conditions of the PAD and assess oil-sands related pollution and other potential impacts. Recently Environment Canada announced their intent to develop a world-class monitoring program for the lower Athabasca River watershed inclusive of the PAD, at an estimated cost of $50 million per year.

A monitoring plan for PAD lakes should be based around a landscape-scale program representative of the hydrological gradient evident among lakes within the delta. The 63 lakes originally surveyed by Wolfe *et al*. (2007) would fulfill this requirement and provide a useful head start to any PAD lake monitoring program, as considerable data are already available for these lakes. This author would also recommend including a few more sites in the eastern region of the Athabasca Delta sector of the PAD, as this area is underrepresented in the selection of lakes by Wolfe *et al*. (2007). Additionally, multiple sampling sites should be considered for the large open-drainage lakes to capture within-lake heterogeneity of these larger and more complex basins. Fifty to eighty monitoring sites should be divided into two or three tiers of sampling frequency with a set of core lakes sampled intensively every year, while the higher tier lakes would receive more basic monitoring with a more detailed sampling conducted on a rotating basis every 3-5 years.

Given the variety of long-term concerns facing the PAD, a monitoring program should be designed to determine spatial and temporal trends in hydrology ($\delta^{18}O$, $\delta^{2}H$), limnology (water quality: nutrients, DOC, Kd-par, pH, Chl *a*, major ions, specific conductance and pollutants), and sediment pollutants and toxicity. While physical and chemical sampling of PAD water and sediments needs to be part of this program, a bio-monitoring component is also needed for detection of impact and impairment of ecosystem function integrated from a variety of potential stressors. Epiphytic diatoms are discussed for this role below.

5.4.1 Epiphytic diatoms and artificial substrates and bio-monitoring of the PAD

This author suggests that diatom communities, and in particular epiphytic diatom communities of PAD lakes, would be a very useful target group for a bio-monitoring program and that the artificial substrate samplers used in Chapter 2 would be well-suited for this role. The bio-monitoring of diatom communities would provide complementary information to the fish bio-monitoring program proposed by Environment Canada (2011d) and afford some distinct advantages over a fish-based bio-monitoring program.

Fish have been recommended as a bio-monitoring target group for the PAD and have an established capacity as integrators and indicators of environmental stress (Environment Canada, 2011d). Fish would indeed be a valuable component of a bio-monitoring program for the open-drainage portion of the PAD. However, fish are absent from the majority of PAD lakes due to prolonged winter hypoxia common in perched basin PAD lakes. In contrast, diatoms are common to all lakes of the PAD. Furthermore, unlike fish, diatom remains are abundant and preserve well in the lake sediment so that that the enumeration of the past diatom communities via sediment cores can be readily obtained. Diatom community composition has been repeatedly shown to be responsive to changes in water quality and aquatic conditions. This allows hind-casting of lake conditions for many decades to centuries in the past (Hall and Smol, 1992; Battarbee *et al*., 2001; Kelly *et al*., 2008; Simpson and Hall, 2012). This aspect is particularly useful for a dynamic system such as the PAD, where lake monitoring data are sparse to non-existent and long-term responses to varying climatic conditions are a major concern.

While landscape-scale sampling of diatom communities is typically done by sampling surficial lake sediments, artificial substrates targeting the epiphytic diatom community has some advantages. The main benefits of artificial substrates for studies of contemporary epiphytic diatom-environment relations from a large number of water bodies are numerous: 1) They include: standardization of not only substrate, but also colonization time and position within the water column. 2) Polypropylene sheets can easily be transferred to incubation chambers for a variety of measurements of productivity and physiological processes (i.e., chlorophyll fluorescence, photosynthetic efficiency, phyto-toxic response to PACs). 3) The large biomass that can be easily collected can simplify measurement of elemental and isotopic composition (of algal organic matter; $\delta^{18}O$, $\delta^{2}H$, $\delta^{13}C$, and diatomaceous opaline silica; $\delta^{18}O$ and $\delta^{30}Si$), as well as uptake of inorganic and organic pollutants. 4) Deployment and collection of artificial substrates can facilitate sampling the diatom community during the same time frame as limnological sampling. This would likely lead to more accurate species-environment relations for environments where year-to-year variability is high, such as the deltas of the Mackenzie River drainage system.

5.4.2 Hydrolimnology and ecology of the Peace-Athabasca Delta

Research on seasonal and inter-annual patterns of variation in limnological conditions of PAD lakes along a gradient of basin hydrology proved instructive in elucidating the role of flooding on the physical and chemical conditions of perched basin lakes. However, there are further uncertainties regarding the hydroecology of the PAD related to the biological communities of the perched and open-drainage basins that need further investigation.

Phytoplankton abundance is generally low in lakes of the PAD and considerably lower than expected based on water column nutrients in the perched basin lakes. It may be that phytoplankton standing crop in the perched basin PAD lakes are limited by a combination of high zooplankton grazing (exerting top-down control of phytoplankton standing crop) and high macrophyte standing crops which limit the availability of space and light needed for phytoplankton. Investigating these possibilities would involve assessment of zooplankton and phytoplankton abundance, measures of the productivity and biomass turn-over of both phytoplankton and zooplankton in PAD lakes. Additionally, measures of macrophyte competition for space and light should be performed on a series of lakes positioned along the hydrological gradient similar to our study design. This would allow testing of the hypothesis that top-down control of phytoplankton is greater than that of bottom-up control of phytoplankton abundance in PAD lakes, and likely other northern lentic systems, as hypothesized by Flanagan *et al*. (2010).

Primary productivity and its relative contribution from the various major groups of biota in PAD lakes with respect to the hydrologic gradient are still inadequately described. For a comprehensive study, *in-situ* measurements of the production and biomass of macrophytes, epiphyton, phytoplankton and heterotrophic bacteria should be performed. Additionally, measurements of macrophyte canopy optical thickness in relation to standing crop and occupied water volume and its affect on light availability to other primary producers (phytoplankton and epipelic algae) should be obtained. This study should be done on a number of PAD lakes through the open-water season so that a seasonal integration of the productivity of these four groups can be calculated and compared across the hydrological gradient. Such a project could be accompanied by a parallel project conducting a stable-isotope based food web analysis of the primary producers and consumer groups (zooplankton / other invertebrates and fish when present). This information will allow us to better understand the flow of energy and controls on primary production in PAD lakes and similar systems. This could provide Parks Canada with relevant information for resource management decisions aimed at providing or maintaining habitat for the park’s flora and fauna.

5.4.3 Transport and deposition of pollutants in the Peace-Athabasca Delta

The findings of Chapter 4 give a strong indication of the important role of natural fluvial processes of the Athabasca River in transporting bitumen related pollutants to the PAD. While our findings indicate that the concentration and composition of PACs in sediments of PAD lakes have not changed measurably since inset of industrial mining and processing, further research is warranted given the importance of this issue and the PAD. Although our results indicate that the PACs present are due to natural processes this does not preclude there being a negative impact on the biota of the PAD nor the people of Fort Chipewyan. Sediment toxicity to invertebrates and effects on higher consumers should be conducted from PAD sediments collected along gradients of hydrology and contaminant concentration to investigate this possibility.

The study undertaken in Chapter 4 should be expanded to include more lakes both in the Athabasca and Peace Delta sectors of the PAD and the Athabasca River floodplain south of the PAD. Further studies of the deposition of PACs in PAD lakes should aim for 1) more replication (i.e., more lakes = greater confidence in any trends or lack thereof), 2) wider geographic scope within the PAD, and 3) lakes should be chosen from a gradient of hydrology and flood frequency.

The scope of further paleo-contaminant studies should be broadened to include and assess what natural and anthropogenic pollutants may be associated with the Peace River catchment (i.e., Peace River bitumen deposits, pulp and paper mills etc.) as well as the Athabasca River catchment. An expanded range of bitumen and non-bitumen related contaminants (i.e., PACs, alkanes, heavy metals, chlorinated phenolics, dioxins and furans) as well as other long-range transported contaminants such as PCBs and other organic pollutants likely to be of concern should be examined (Gummer *et al*., 2000, 2006; Wrona *et al*., 2000, Environment Canada 2011a).

Further investigation of the temporal and spatial distribution of contaminants should include both a paleolimnological component similar to that taken in Chapter 4, but also a large scale (≥60 lakes) spatial sampling of surficial lake sediments from floodplain lakes of the PAD and from the upstream portions of both the Peace and Athabasca Rivers. A portion of these sediment collections could be used for invertebrate toxicity assays and longer-term microcosom studies. The more primary question to be asked is: how representative are the findings of Chapter 4? In particular, can we use the results from Chapter 4 to predict the sediment PAC concentration found in other PAD lakes based on the sediment organic matter content? The basis for this expectation is outlined below.

There exists a strong negative relationship between lake sediment PAC concentration and organic matter (see Figure 4.8, 5.2, 5.3, Table 5.1). This negative relationship likely reflects the dilution of river-sourced contaminants by within-lake organic matter production (see Figure 5.2). River sediment is principally mineral matter with a small amount of organic matter. When river sediment inputs are absent or rare for a PAD lake, flux of inorganic matter and PACs eroded from the McMurray formation can be expected to be low, while within-lake generated organic matter (which is independent of the supply of river transported organic matter and absorbed PACs) becomes a main component of the lake sediment budget. Examination of the relation between lake sediment organic matter and PAC concentrations (Figure 4.8, 5.2, 5.3 Table 5.1) suggest that the processes governing the supply of PACs and organic matter to PAD 23 and 31 sediments has not increased PAC delivery post-development. So, given the PAC-organic matter relation for PAD 23 and 31:

1) Can the relation in Table 5.1 predict the sediment PAC concentration from sediment cores and surficial sediments of other Athabasca Delta Lakes? Some candidate lakes for coring

are PAD 26, 27, 35, and 39, (see Hall *et al*., 2004; Wolfe *et al*., 2007 for locations) due to the range of lake sediment organic matter content represented by these lakes and that their water depths suggest that long-term persistence of lacustrine conditions is likely for these sites.

2) Or, if the general negative relation holds true, does the slope and intercept of the relation vary appreciably among lakes? Would lakes with increasing distance from the river exhibit higher y-intercept values (see Figure 5.2) reflecting greater winnowing of coarse-grained materials so that lakes more distant from the river receive flood–transported sediment that is finer-grained, higher in organic matter and as a consequence higher in PACs?

3) Do the lakes of the Peace River Delta exhibit different relations between sediment organic matter content and PAC concentration than lakes of Athabasca Delta?

Additional analysis (alkanes, heavy metals, chlorinated phenolics, dioxins and furans) conducted on sediment cores as well as delta-wide sampling of surface sediments from >60 lakes is also needed, as PACs are not the only contaminants for which there are concerns (Gummer *et al*., 2000, 2006; Timoney and Lee, 2009, 2011; Kelly *et al*., 2010). Such evidence-based science is needed (Schindler, 2010) to establish the relevant natural loads of contaminants and potential anthropogenic augmentation of contaminant transport to the PAD by the Athabasca and Peace rivers. This knowledge is urgently needed for sound policy implementation and could serve as a model approach to competently identify temporal trends, or the lack thereof, in contaminant delivery to the PAD and similar systems such as the Slave River or Mackenzie River Deltas.

5.5 Figures

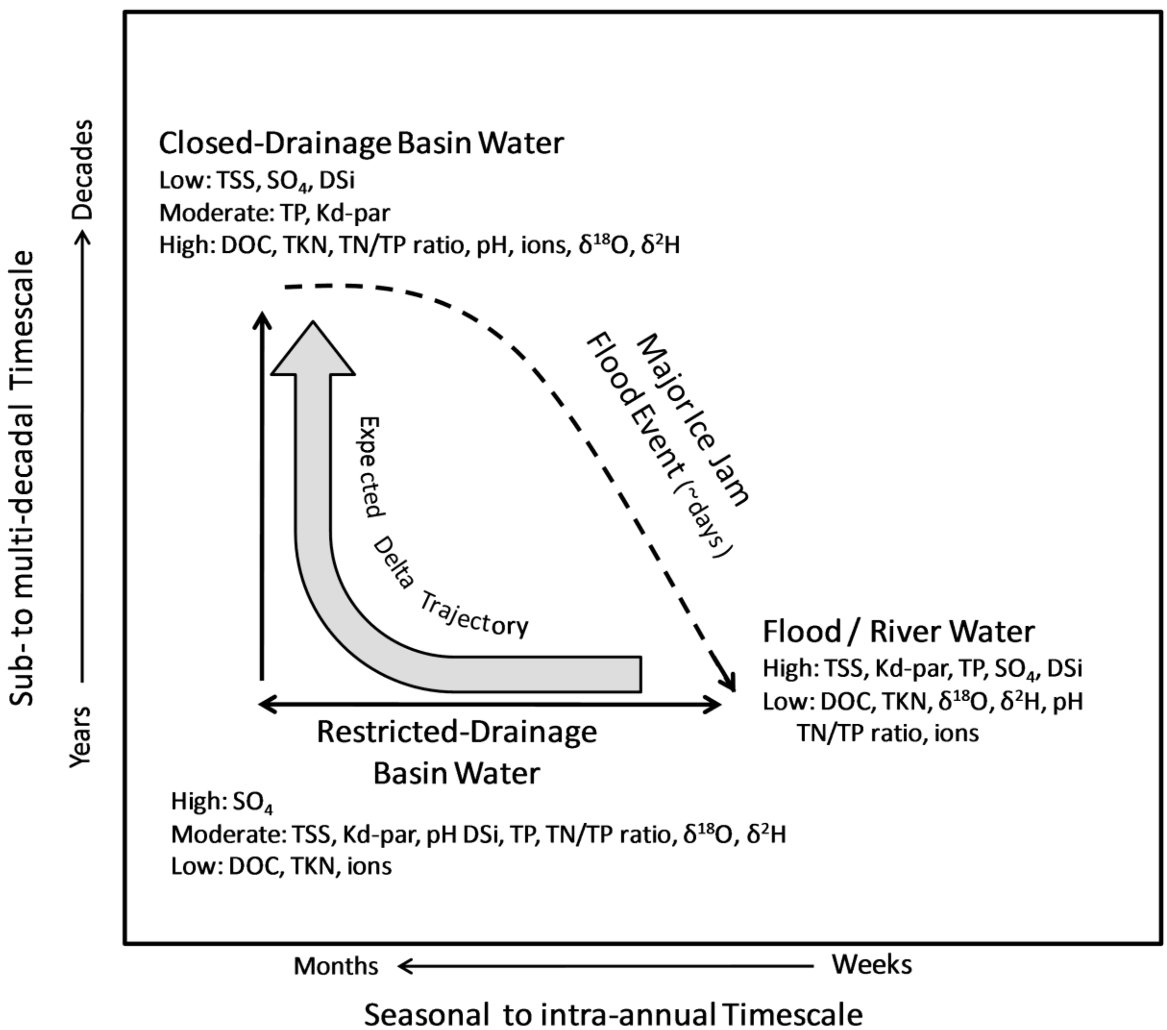

Fig 5.1 (Fig 3.10 from Chapter 3) Schematic diagram illustrating the two different timescales of limnological change in response to periodic, but variable, flooding of floodplain lakes in the Peace-Athabasca Delta (based on information provided by the Principal Components Analysis, Figures 3.4 and 3.5). The horizontal axis (modelled after PCA axis 1 in Figures 3.4 and 3.5) captures relatively short-term changes in limnological conditions because of influence of periodic flooding and processes that ensue after flooding ceases. The vertical axis (modelled after PCA axis 2 in Figures 3.4 and 3.5) captures longer term limnological changes when lakes do not flood for many years to decades. Flooding of either a closed-drainage or restricted-drainage lake resets the limnological properties of the lake to those of river water (lower right corner). The large curving arrow illustrates the expected delta trajectory in coming decades in response to continued decline in river discharge, ice-jam flood events and increasing human consumptive uses of river water that will ultimately lead to an increase in the proportion of PAD lakes that have closed-drainage hydrological and limnological conditions.

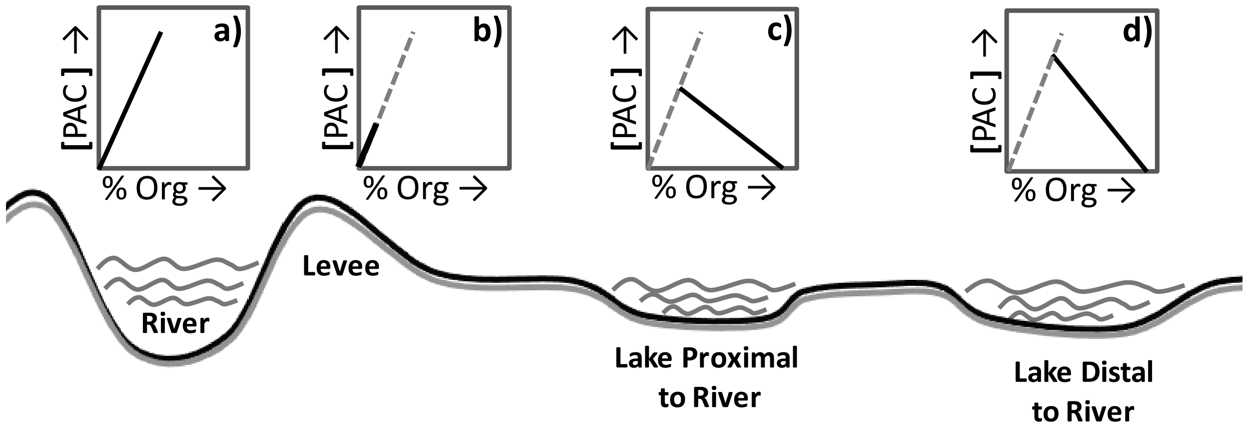

Figure 5.2 Schematic diagrams depicting the relations between sediment organic matter content (% of sediment dry mass) and PAC concentrations (solid black line in Panels **a-d**) in flood-deposited sediments across the Athabasca Delta landscape from rivers, to levees and to lakes of varying hydrological connectivity to the rivers. In river sediment (Panel **a)**), PAC concentrations co-vary positively with sediment organic content, with a y-intercept of ~ 0. Sediment organic matter is low (0-5%) in river sediment (bedload) and also positively co-varies with the abundance of fine grained material as well as with total PAC concentration (see Fig 1.2). During overbank flooding, river sediment is deposited on levees (Panel **b)**), which inherit the relationship between sediment organic matter and PAC concentrations seen in Panel **a)**. However, due to hydrological particle size sorting, flood deposits on levees possess a relatively high proportion of larger grained river sediment, and thus will be low in both organic matter (~0-1%) and PAC content compared to lakes. In other words, flood deposits on levees have the same slope and origin (0-0) for the PACs vs. % organic matter as seen in river sediment, but with values restricted to the lower range. This scenario applies to the actual flood deposit layers, not to the more organic rich layers of entombed humus material produced between flood events (see Fig. 3 in Hugenhotlz *et al*., 2009). As river flood waters progress away from the river, either via overland flow or via small distributary channels, particle size sorting affects will continue as water velocity declines. With increasing flow distance, the river sediment fraction transported inland becomes increasingly fine grained, higher in organic matter content, and, therefore, more elevated in bulk PAC concentration. Floodplain lakes (Panels **c)** and **d)**) receive this finer grained fraction and associated elevated PAC content during flood events. While these river sediment inputs consist of a finer, more organic rich fraction compared to average river sediment, the % organic matter remains low (~1-6%) compared to the sediment that will typically accumulate in a floodplain lake from autogenic production in the absence of flooding (typically 30-70% organic matter). Within lake production of organic matter (Panels **c)** and **d)**) enters lake sediments independent of the source of river-derived organic matter and associated PACs, and, therefore, acts as a diluent with respect to the original relation of river sediment organic matter content vs. PAC concentration. Consequently, in flood plain lakes (Panels **c)** and **d)**) there exists a strong negative co-variation between sediment organic matter content and PAC concentration. Furthermore, the Y-intercept for this relation in lakes (solid-black line in Panels **c)** and **d)**) and that seen in river sediment (depicted as the dashed-grey line in **c)** and **d)**) should represent the average composition of river sediment (with respect to organic matter content and PAC content) that enters the floodplain lake.

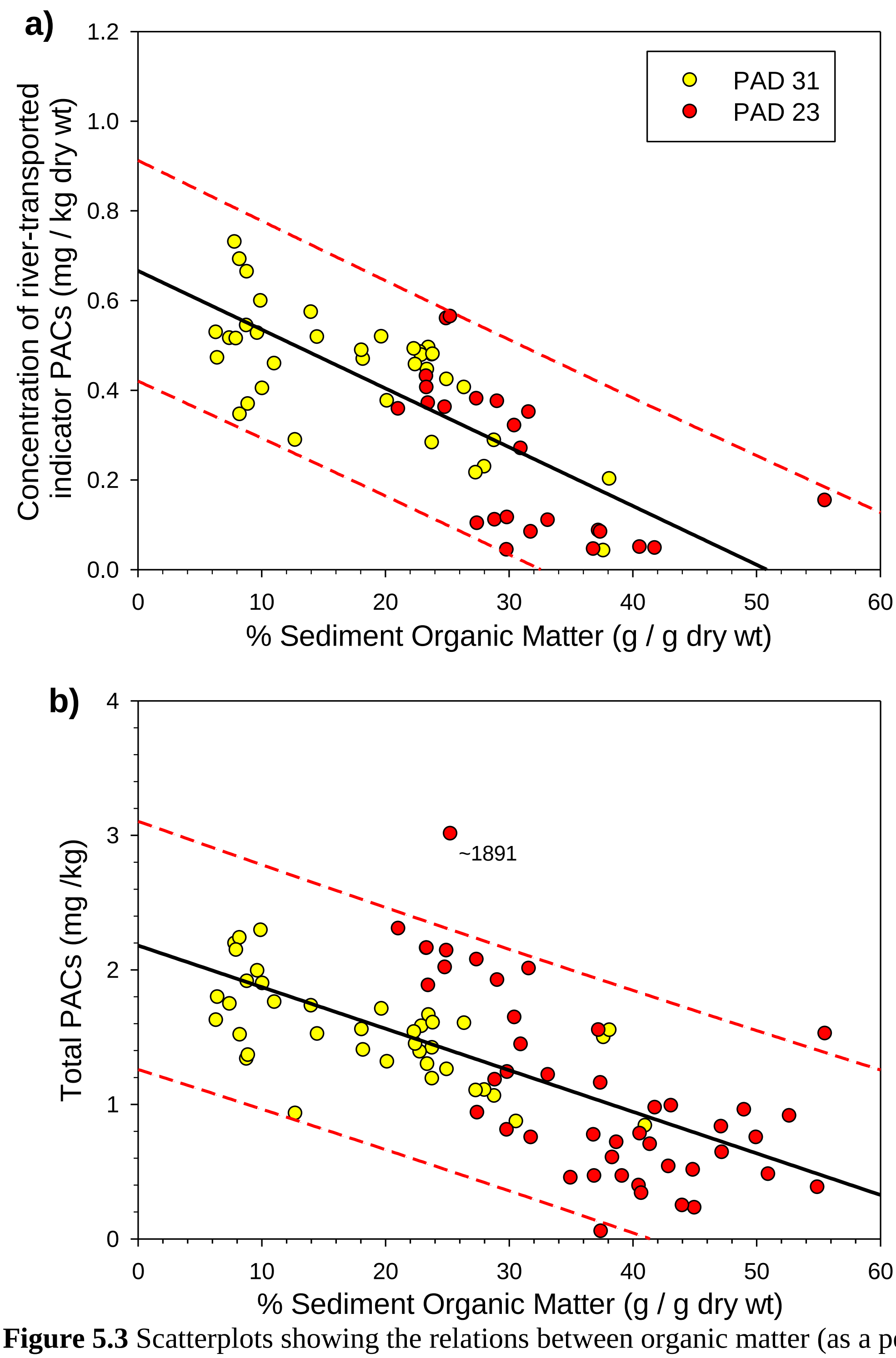

Figure 5.3 Scatterplots showing the relations between organic matter (as a percentage of dry sediment mass) and **a)** concentration of river-transported indicator PACs and **b)** total PACs in sediments of lakes PAD 23 (solid red circles) and PAD 31 The lines of best fit (solid black line) and 95% prediction intervals (dashed red lines) are presented for the linear regressions are derived from sediment organic matter content vs. total PAC concentrations and all non-zero river-transported indicator PAC concentrations (see Table 5.1 for details).

5.6 Tables

Table 5.1 Regression statistics of river-transported indicator PAC and total PAC concentrations versus % sediment organic matter for all non-zero PAD 23 and PAD 31 data, pre- and post-1967 sample data.

River-transported indicator PACs (sum of 7) vs. % organic matter

	Regression			Y intercept			Slope		
	N	R^2 (%)	P-value	intercept	std Dev	P-value	Slope	std Dev	P-value
All Data	61	58.05	<0.0001	0.6664	0.2445	<0.0001	-0.0131	0.0008	<0.0001
pre-1967*	41	66.32	<0.0001	0.9234	0.1684	<0.0001	-0.0224	0.0008	<0.0001
post-1967**	20	62.18	<0.0001	0.6023	0.1503	<0.0001	-0.0107	0.0008	<0.0001

Total PACs vs. % organic matter

	Regression			Y intercept			Slope		
	N	R^2 (%)	P-value	intercept	std Dev	P-value	Slope	std Dev	P-value
All Data	84	45.21	<0.0001	2.1809	1.0815	<0.0001	-0.0309	0.0056	<0.0001
pre-1967	44	28.93	<0.0001	2.6003	0.7827	0.0002	-0.0433	0.0061	<0.0001
post-1967	40	57.98	<0.0001	2.0003	0.7400	<0.0001	-0.0280	0.0052	<0.0001

Only non-zero concentration data was used which excluded * 3 and **20 samples.

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Chapter 1

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Appendices

Appendix A

The following is the limnological data used in **Chapter 2** for Principle Components Analysis (PCA, see Figure 2.2)

Table A.1 Chemical and physical characteristics of water in the study ponds from the Peace-Athabasca Delta (2005 data).

	Unit	PAD 1 Spring	PAD 1 Sum	PAD 1 Fall	PAD 5 Spring	PAD 5 Sum	PAD 5 Fall	PAD 8 Spring	PAD 8 Sum	PAD 8 Fall	PAD 54 Spring	PAD 54 Sum	PAD 54 Fall	Peace River Spring	Peace River Sum	Peace River Fall
pH		7.97	9.73	7.27	7.92	10.59	9.73	7.34	8.50	8.73	7.97	9.04	8.11	8.03	8.41	8.21
SP Cond	µS/cm	322	293	294	252	230	230	169	210	199	246	195	182	246	228	234
Alkalinity	mg/L	141.0	149.0	138.0	118.0	109.0	117.0	63.8	92.1	88.9	100.0	76.9	75.0	101.0	97.9	100.0
Ca^{2+}	mg/L	32.8	26.0	25.7	27.1	16.9	18.7	21.3	26.2	23.2	32.4	20.2	17.3	36.4	33.7	32.4
Cl^-	mg/L	11.20	9.55	8.79	5.54	3.13	3.11	4.14	5.10	4.94	2.70	2.21	2.16	1.45	1.04	1.31
K^+	mg/L	15.10	18.70	16.60	10.20	12.60	12.20	4.91	7.25	6.92	7.87	8.57	8.00	8.10	7.80	7.39
Mg^{2+}	mg/L	8.84	7.64	6.07	8.86	8.03	6.89	3.71	2.79	2.36	2.89	2.65	2.39	3.08	0.66	0.62
Na^+	mg/L	13.40	16.90	13.90	9.26	10.60	10.10	4.67	7.46	6.64	5.85	6.20	5.82	5.49	3.81	3.78
DSi	mg/L	1.04	0.63	1.68	0.83	0.47	0.23	3.56	5.87	2.29	3.08	1.09	0.24	4.15	3.63	3.46
SO_4^{2-}	mg/L	7.64	2.19	2.56	4.13	1.44	2.86	11.90	7.85	5.77	21.90	19.40	15.35	23.80	22.30	22.50
DOC	mg/L	43.0	51.0	47.0	25.4	30.1	28.2	14.7	15.6	15.3	7.9	7.3	6.8	11.6	10.4	5.3
DIC	mg/L	32.4	27.4	30.9	28.2	16.3	23.9	15.9	21.6	20.1	24.4	16.6	16.8	23.1	23.2	22.3
DP	µg/L	24.2	16.5	37.2	22.8	29.7	24.2	15	25.4	45.1	10.7	6.6	8.8	104	129	52
TP	µg/L	39.2	23.1	41.7	50.7	38.4	66.7	25.0	55.4	66.5	32.8	16.1	14.7	7930	780	150
TN	µg/L	1,980	2,360	2,560	1,480	2,130	2000	635	857	1,040	331	507	437	890	404	199
NO_3^-	µg/L	20	63	231	53	235	264	139	174	285	37	9	80	117	41	37
NH_4^+	µg/L	59	23	6	155	8	5	19	5	5	26	70	< 5*	15	7	< 5*
TSS	mg/L	1.5	2.6	4.2	4.6	1.6	0.0	4.8	2.1	1.6	11.8	0.9	1.2	902.1	48.4	23.1
ISS	mg/L	0.1	1.0	2.4	1.7	0.8	0.0	2.3	1.1	0.0	9.8	0.5	0.7	816.8	43.0	20.4
OSS	mg/L	1.4	1.6	1.8	2.9	0.9	0.0	2.5	1.1	1.6	2.0	0.4	0.4	85.3	5.3	2.7
Chl *a*	µg/L	3.1	1.6	3.5	9.0	1.2	4.7	3.5	6.9	1.2	1.8	1.7	1.1	1.5	1.9	2.2
K_dPar	m^{-1}	1.66	2.27	3.57	1.93	2.22	2.88	1.90	1.72	1.45	2.11	0.82	0.63	64.48	4.74	3.47

Sum = Summer, * Below detection limit of 5 µg/L

Appendix B

Supplementary figures and tables for Chapter 3.

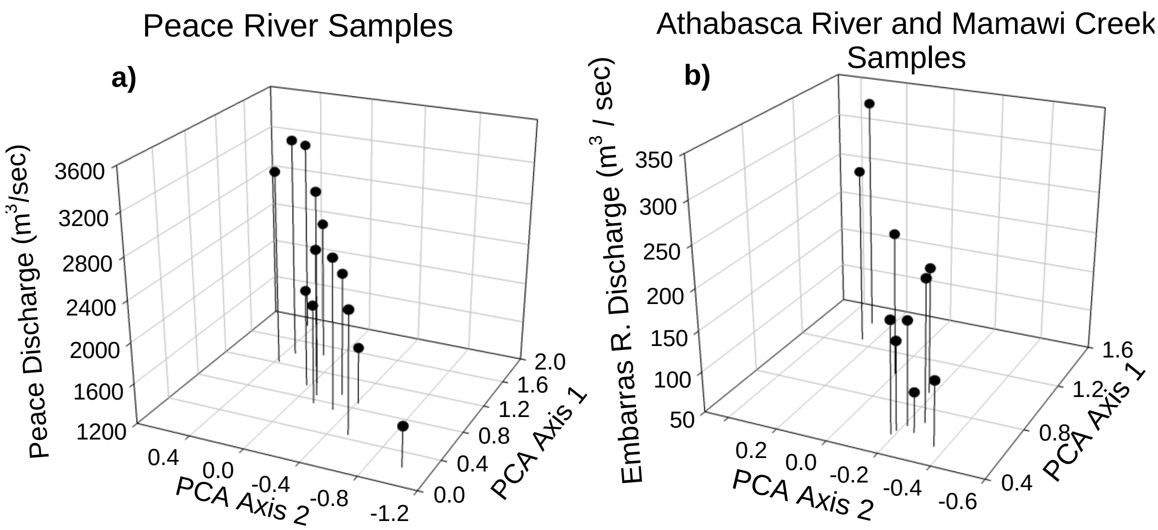

Figure B.1 PCA scores from **Fig 3.4** for **a**) the Peace River samples collected at Rockey Point versus Peace River Discharge measured at Peace Point (Station 07KC001, Hydrat 2005; Environment Canada) and **b**) Athabasca River and Mamawi Creek samples versus Embarras River discharge (Station 07DD003, Hydrat 2005; Environment Canada). Mamawi Creek carries Athabasca River water received via the Embarras River.

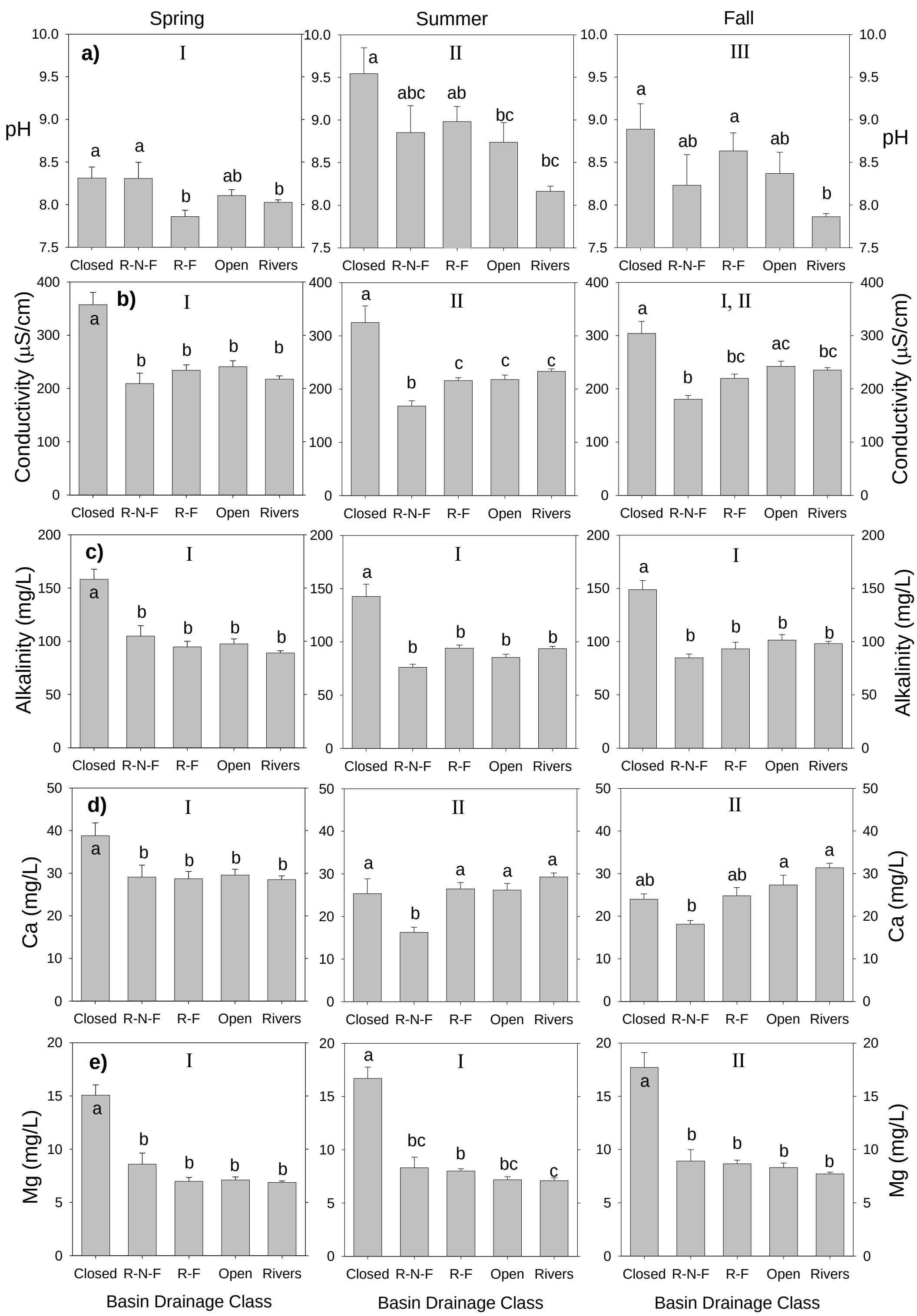

Figure B.2 Mean (**a**) pH, (**b**)specific conductivity, (**c**) mean alkalinity, (**d**) calcium, (**e**) magnesium in the rivers and hydrological lake categories of the Peace–Athabasca Delta during spring (mid-May to mid-June), summer (late June to early August), early fall (late August to September) of 2003, 2004 and 2005. Error bars = 1 S.E.

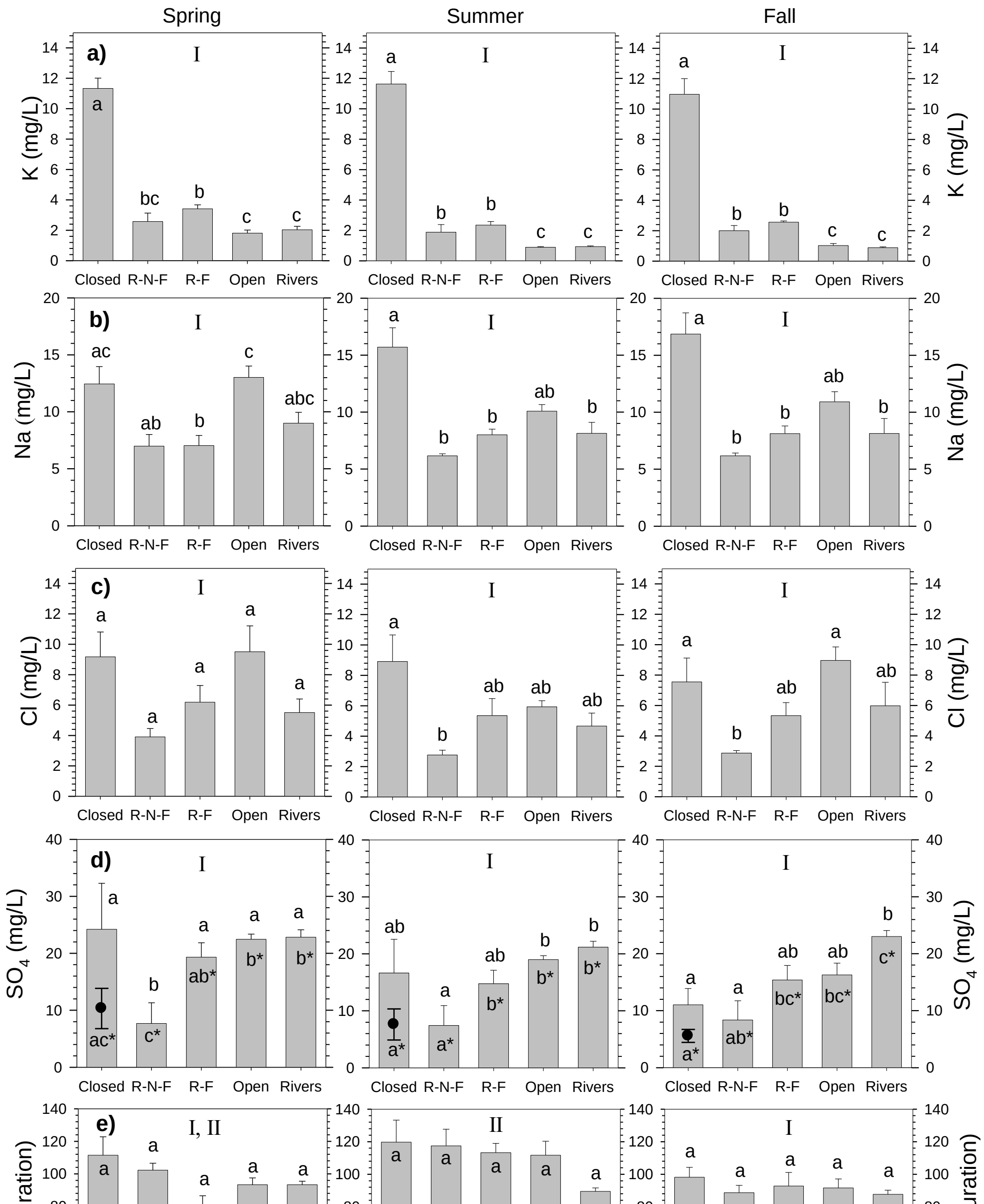

Figure B.3 Mean (**a**) potassium, (**b**) sodium, (**c**) chloride, (**d**) sulphate, (**e**), dissolved oxygen saturation in the rivers and hydrological lake categories of the Peace–Athabasca Delta during spring (mid-May to mid-June), summer (late June to early August), early fall (late August to September) of 2003, 2004 and 2005. Error bars = 1 S.E. **Note** that in (**d**), the closed-drainage mean excluding PAD 9 for sulphate is shown by the closed circles +/- 1 standard error. PAD 9 was found to have unusually high sulphate concentration, this is most apparent during spring and was well above what is typically seen in rivers of the PAD excluding them as a source. The high sulphate concentration in PAD 9 may be related to the water observed seeping out of fractures in the bedrock on the east side of PAD 9 in June of 2003.

Table B.1 Chemical and physical characteristics of water in the study lakes and rivers from the Peace-Athabasca Delta (2003-05 data). D-Class refers to water body drainage class; c= closed-, r=restricted-, o=open-drainage, Rv=river and s= shield lake.

Lake	date	season	D-Class	Alk	Ca	Cl	TKN	Mg	DOC	DP-mg	TP-mg	K	Si	Na	SO_4
PAD 1	8-Jun-03	spring	c	199	47.9	18.9	3.5	16.5	68.6	0.051	0.102	14.4	4.79	19.4	27
PAD 1	30-Jun-03	summer	c	191	44.2	18.3	1.5	19.3	72.8	0.05	0.083	13.1	3.23	21.7	23
PAD 1	18-Jul-03	summer	c	212	40.8	19.2	3.8	20.5	74.7	0.044	0.084	13.7	2.91	22.6	19
PAD 1	20-Aug-03	fall	c	166	27.6	7.9	2.8	20	73.9	0.092	0.099	12.2	0.85	24.8	5
PAD 1	6-Jun-04	spring	c	192	39.7	15	2.1	19.7	72.9	0.02	0.04	10.9	2.8	18.8	12
PAD 1	1-Aug-04	summer	c	137	17.4	14.7	2.7	20.1	66.5	0.03	0.05	10.3	0.48	23.6	8.2
PAD 1	21-Aug-04	fall	c	160	22	17.8	1	24.2	49.4	<0.05	0.07	12.1	0.183	26.4	6
PAD 1	13-Sep-04	fall	c	182	20.7	17.4	1	22.7	49.7	<0.05	0.06	11.3	0.153	24.6	6
PAD 1	16-May-05	spring	c	141	32.8	11.2	1.98	15.1	43	0.0242	0.0392	8.84	1.04	13.4	7.64
PAD 1	1-Aug-05	summer	c	149	26	9.55	2.37	18.7	51	0.0193	0.0311	7.64	0.15	16.9	2.19
PAD 1	14-Sep-05	fall	c	138	25.7	8.79	2.56	16.6	47	0.0372	0.0417	6.07	1.68	13.9	2.56
PAD 5	27-Jun-03	summer	c	189	31.6	7.9	3.2	16.4	53.5	0.021	0.054	12.1	4.67	16.4	7
PAD 5	22-Jul-03	summer	c	167	29.8	8.1	4.2	12.8	45.7	0.02	0.038	13.2	6.04	16.1	11
PAD 5	25-Aug-03	fall	c	146	23.1	2	2.6	12.7	50.3	0.018	0.031	11.9	3.26	18.7	10
PAD 5	2-Jun-04	spring	c	154	31.2	6	1.7	13.5	51.6	0.02	0.03	9.53	0.361	12.4	4.1
PAD 5	17-Jul-04	summer	c	110	13.7	6.5	2.4	13.6	50.6	0.02	0.04	11.2	9.04	15.8	3.8
PAD 5	23-Sep-04	fall	c	116	20.4	4.6	0.54	14.7	36.3	0.06	0.1	8.9	1.85	16.6	7
PAD 5	15-May-05	spring	c	118	27.1	5.54	1.48	10.2	25.4	0.0228	0.0507	8.86	0.83	9.26	4.13
PAD 5	19-Jul-05	summer	c	109	16.9	3.13	2.13	12.6	30.1	0.0297	0.0384	8.03	0.47	10.6	1.44
PAD 5	14-Sep-05	fall	c	117	18.7	3.11	2	12.2	28.2	0.0242	0.0667	6.89	0.23	10.1	2.86
PAD 8	22-May-03	spring	r	74.4	21.1	7.9	0.97	5.66	13.6	0.024	0.09	3.84	3.69	7.54	22
PAD 8	1-Jun-03	spring	r	86.1	27.7	8.3	0.74	6.28	11.6	0.026	0.06	3.8	4.61	8.02	24
PAD 8	13-Jun-03	spring	r	93.5	29.5	8.6	0.72	6.47	11.9	0.019	0.027	3.63	5.07	7.75	22
PAD 8	12-Jul-03	summer	r	92.0	27.5	7.63	0.88	6.97	12.93	0.015	0.0297	2.31	0.15	10.14	18.33
PAD 8	9-Aug-03	fall	r	95.3	29.7	8.1	0.76	8.03	13.2	0.021	0.04	2.89	0.41	8.86	13
PAD 8	31-May-04	spring	r	75.5	23.1	4.0	0.81	5.0	20.5	0.01	0.05	2.5	1.16	4.9	8.4
PAD 8	22-Jul-04	summer	r	94.4	26.15	6.05	0.765	7.7	25.55	0.01	0.04	2.565	2.395	8.25	6
PAD 8	16-Sep-04	fall	r	112	33.0	6.2	1.00	8.0	13.1	<0.05	0.06	2.3	2.47	8.4	11

PAD 8	18-May-05	spring	r	63.8	21.3	4.14	0.635	4.91	14.7	0.015	0.025	3.71	3.56	4.67	11.9
PAD 8	15-Jun-05	spring	r	81.5	26.3	4.41	0.804	5.98	15.1	0.014	0.0332	3.55	5.65	5.83	11.4
PAD 8	24-Jul-05	summer	r	92.1	26.2	5.1	0.857	7.25	15.6	0.0254	0.0554	2.79	5.87	7.46	7.85
PAD 8	14-Sep-05	fall	r	88.9	23.2	4.94	1.04	6.92	15.3	0.0451	0.0665	2.36	2.29	6.64	5.77
PAD 9	22-May-03	spring	c	138	43.6	7.4	1.8	17.4	29.3	0.042	0.064	13.9	3.91	10.2	91
PAD 9	27-May-03	spring	c	149	52.8	7.3	1.6	18.6	36.3	0.087	0.112	12.5	2.28	10.2	73
PAD 9	26-Jun-03	summer	c	92.5	27.6	6.6	2.2	12.3	33.4	0.067	0.088	11	2.15	12.6	55
PAD 9	21-Jul-03	summer	c	167	42.2	9.8	3	19.8	49.8	0.053	0.102	14.5	5.99	15.1	58
PAD 9	26-Aug-03	fall	c	186	30.6	10.3	2.8	22.1	64.9	0.086	0.125	14.2	0.8	17.7	24
PAD 9	1-Jun-04	spring	c	163	44.7	5.1	1.5	14.9	49.8	0.04	0.09	11.1	0.985	8.3	32
PAD 9	17-Jul-04	summer	c	108	17.4	5.8	1.2	15.9	47.1	0.04	0.05	13.1	0.31	12.5	20
PAD 9	22-Sep-04	fall	c	156	25.4	9.3	1.80	22.3	26.6	0.05	0.09	15.1	0.407	16.7	23
PAD 9	16-May-05	spring	c	125	43.3	5.12	1.11	12.9	17.6	0.0382	0.0577	13.5	1.41	5.97	51
PAD 9	20-Jul-05	summer	c	124	23.9	3.45	1.51	16.3	20.4	0.0393	0.0539	13	1.86	8.08	26
PAD 9	14-Sep-05	fall	c	132	23.6	4.58	1.59	16.1	19.5	0.0371	0.0586	12.2	0.47	8.57	18.9
PAD 15N	22-May-03	spring	r	97.8	24.8	4.2	0.78	7.09	7.5	0.04	0.455	5.33	3.89	5.84	29
PAD 15N	2-Jun-03	spring	r	104	42.9	3.7	1.1	9.6	8.4	0.023	0.21	3.98	4.63	5.93	26
PAD 15N	9-Jul-03	summer	r	93.2	26.8	2.5	0.69	9.67	9	0.009	0.031	3.08	0.23	6.89	28
PAD 15N	7-Aug-03	fall	r	65.8	16.9	1.9	0.75	9.38	10.3	0.021	0.054	2.48	1.05	6.24	26
PAD 15N	2-May-04	spring	r	102	26.9	2.5	0.29	9.5	22.3	0.01	0.10	2.82	1.687	5.8	6.3
PAD 15N	14-Jun-04	spring	r	132	34.4	3.1	0.52	11.4	37.6	0.01	0.02	3.40	0.444	6.6	14
PAD 15N	29-Jul-04	summer	r	70.8	10.7	5.2	0.70	9.7	18.4	0.01	0.02	2.66	2.90	6.54	8.0
PAD 15N	20-Sep-04	fall	r	83.0	15.1	2.4	0.58	11.2	9.5	0.05	0.07	2.3	1.67	6.8	8
PAD 15S	2-Jun-03	spring	r	98.2	27.9	4.2	0.79	7.64	8.3	0.023	0.221	4.56	4.71	5.96	26
PAD 15S	9-Jul-03	summer	r	104	33.5	2.6	0.75	8.87	9.7	0.009	0.024	3.25	1.09	6.45	27
PAD 15S	7-Aug-03	fall	r	86.4	24.7	2.7	0.52	10.1	8.4	0.024	0.032	3.13	0.51	6.19	27
PAD 15S	14-Jun-04	spring	r	134	34.2	3.0	0.46	11.4	30.2	0.01	0.01	3.31	0.707	6.6	13
PAD 15S	29-Jul-04	summer	r	89.2	17.0	2.2	0.58	11.2	20.7	0.01	0.02	2.54	0.81	6.46	10.4
PAD 15S	20-Sep-04	fall	r	102	20.4	2.7	0.55	12.0	8.7	0.05	0.06	2.6	1.09	6.8	11
PAD 18	22-May-03	spring	s	109	21.3	2	0.54	8.85	14.7	0.007	0.019	4.63	0.24	7	3
PAD 18	28-May-03	spring	s	109	25.2	2.2	0.8	8.73	14.3	0.013	0.017	4.15	0.36	6.62	3
PAD 18	25-Jun-03	summer	s	109	24.5	1.9	2.2	8.5	16.3	0.004	0.009	3.69	0.17	7.2	3

PAD 18	24-Jul-03	summer	s	109	25.4	2	0.62	8.61	14.8	0.004	0.007	4.21	0.17	6.56	4
PAD 18	15-Aug-03	fall	s	110	24.5	4.3	1.1025	9.4767	15.57	0.0083	0.01	3.96	0.18	6.40	4
PAD 18	4-Jun-04	spring	s	105	22.4	2.0	0.60	9.2	35.6	0.01	0.01	3.93	0.428	6.6	1.1
PAD 18	18-Jul-04	summer	s	107	23.9	1.8	0.38	9.8	28.9	0.01	0.01	4.06	0.16	6.88	1.0
PAD 18	21-Sep-04	fall	s	111	24.0	2.1	0.48	10.0	12.8	0.05	0.05	4.1	0.204	7.0	1
PAD 23	22-May-03	spring	r	68.9	30.6	3.9	0.99	4.48	11.2	0.025	0.069	3.28	2.19	5.39	3
PAD 23	29-May-03	spring	r	73.1	15.1	4.1	1	4.66	11.4	0.022	0.056	3.24	1.02	5.55	3
PAD 23	28-Jun-03	summer	r	75.1	17.3	3.2	0.88	4.97	13	0.017	0.035	2.1	0.38	6.18	3
PAD 23	23-Jul-03	summer	r	72.7	17.5	2.6	1.1	4.9	12.7	0.011	0.027	1	1.18	5.71	3
PAD 23	2-May-04	spring	r	89.7	24.6	4.0	0.86	6.8	19.3	0.01	0.07	3.26	3.273	6.7	0.6
PAD 23	5-Jun-04	spring	r	77.3	18.7	3.5	0.77	5.2	20.2	0.02	0.05	2.75	0.130	5.7	0.6
PAD 23	19-Jul-04	summer	r	71.9	16.2	2.4	0.67	5.8	21.3	0.01	0.03	1.02	1.13	6.03	1.0
PAD 23	24-Sep-04	fall	r	83.2	19.8	3.1	1.10	6.0	11.8	0.05	0.09	1.5	1.07	5.8	1
PAD 31	22-May-03	spring	r	117	22.0	8.3	1.10	7.49	15.5	0.019	0.089	3.79	3.84	11.1	18
PAD 31	6-Jun-03	spring	r	136	34.4	9.3	0.75	8.27	14.1	0.023	0.043	3.44	5.14	11.9	15
PAD 31	18-Jun-03	spring	r	107	26.7	9.3	0.91	8.29	15.1	0.011	0.034	2.70	0.73	12.2	13
PAD 31	6-Jul-03	summer	r	92.0	26.5	6.0	0.70	7.58	13.3	0.017	0.038	1.34	3.83	9.60	20
PAD 31	17-Jul-03	summer	r	82.7	20.7	6.5	0.79	7.27	13.2	0.025	0.038	2.20	1.74	9.80	17
PAD 31	30-Jul-03	summer	r	77.1	17.6	19.6	1.6	8.11	14.4	0.032	0.058	1.61	1.09	10.1	14
PAD 31	21-Aug-03	fall	r	89.3	19.1	9.4	1.6	8.72	17	0.029	0.124	2.62	4.59	10.5	12
PAD 31	2-May-04	spring	r	29.6	10.3	1.6	0.89	2.2	2.6	0.01	0.05	1.21	0.746	2.5	4.0
PAD 31	13-Jun-04	spring	r	93.4	17.9	6.0	0.7	9.5	24.5	0.01	0.02	0.4	0.369	11.0	2.4
PAD 31	23-Jul-04	summer	r	103	31.1	4.1	0.55	8.0	26.7	0.02	0.05	1.37	7.04	8.43	14.4
PAD 31	12-Sep-04	fall	r	122	32.6	5.5	1.50	10.9	12.4	0.05	0.13	2.4	9.64	10.3	16
PAD 31	5/16/2005	spring	r	102	31.8	7.02	0.561	6.77	14.9	0.0201	0.0496	2.27	2.54	10.7	16.3
PAD 31	15-Jun-05	spring	r	102	32.2	4.91	0.654	7.17	15.6	0.0157	0.0306	1.31	6.01	9.83	13.5
PAD 31	7/18/2005	summer	r	109	33.4	4.52	0.762	7.9	14	0.0177	0.0742	1.22	7.01	8.44	17.2
PAD 31	9/14/2005	fall	r	134	34.5	6.78	0.797	10	14.8	0.0192	0.0319	2.43	0.3	10.6	11.4
PAD 45	22-May-03	spring	o	93.3	27.3	11.8	0.37	6.5	13.3	0.022	0.395	3.01	5.15	12.8	26
PAD 45	26-May-03	spring	o	94.2	28.7	9.8	0.89	6.49	15.1	0.038	0.356	2.25	5.63	12	23
PAD 45	10-Jun-03	spring	o	109	30.3	11.4	0.63	7.18	13.5	0.013	0.094	2.15	5.07	13.1	25
PAD 45	24-Jun-03	summer	o	89.7	29.5	6.7	0.66	6.51	10.3	0.012	0.155	1.24	3.95	10.2	24

PAD 45	11-Jul-03	summer	o	82.9	27.4	5.3	0.6	6.16	12.9	0.014	0.077	0.94	4.03	9.97	22
PAD 45	12-Aug-03	fall	o	97.1	30.7	12.4	0.46	7.76	8.9	0.016	0.027	0.92	3.9	11.3	24
PAD 45	2-May-04	spring	o	78.2	24.7	11	0.56	6.7	20.6	0.01	0.08	1.77	5.434	14.1	18
PAD 45	9-Jun-04	spring	o	83.1	25.4	4.8	1.3	6.5	26.0	0.02	0.369	1.31	5.56	10.5	20
PAD 45	14-Jul-04	summer	o	93.5	29.4	5.5	0.43	8.0	18.2	0.01	0.04	0.78	3.86	8.77	20.2
PAD 45	13-Sep-04	fall	o	93.3	27.4	5.4	0.50	7.1	11.8	0.05	0.11	0.9	6.56	8.1	17
PAD 45	14-Sep-05	fall	o	105	30.3	9.83	0.439	8.29	10.2	0.0145	0.0404	0.87	4.87	11.3	20
PAD 45T1	11-Jul-03	summer	o	90.4	27.2	5.6	0.58	6.61	14.6	0.011	0.021	1.07	2.53	10.3	19
PAD 45T1	12-Aug-03	fall	o	98.9	24.4	10.3	0.88	8.43	15.4	0.019	0.039	1.02	0.17	9.8	17
PAD 45T1	2-May-04	spring	o	79.0	24.2	12	0.46	7.2	20.3	0.02	0.05	3.70	3.078	13.9	19
PAD 45T1	9-Jun-04	spring	o	121	36.1	12	0.69	8.7	32.1	0.01	0.06	1.81	2.85	15.9	24
PAD 45T1	13-Jul-04	summer	o	68.1	15.7	8.4	0.72	8.2	20.5	0.01	0.02	1.08	2.01	13.5	17.1
PAD 45T1	13-Sep-04	fall	o	86.1	13.4	10.6	0.73	10.8	14.6	0.05	0.07	0.7	0.223	16.1	7
PAD 45T1	22-May-05	spring	o	103	33.9	15.3	0.471	7.7	13.1	0.0125	0.048	2.12	4.48	15.8	24.8
PAD 45T1	1-Aug-05	summer	o	92.1	28	6.44	0.868	7.89	13.3	0.012	0.035	0.75	0.67	11	19.9
PAD 45T1	14-Sep-05	fall	o	134	35.1	8.32	0.592	8.84	13.1	0.0268	0.0521	1.95	0.41	11.2	8.25
PAD 45T2	11-Jul-03	summer	o	80.8	26.7	5.3	0.73	6.25	13.2	0.015	0.084	0.8	4.33	9.72	20
PAD 45T2	9-Jun-04	spring	o	81.5	25.0	4.7	0.98	6.5	25.2	0.02	0.29	1.28	5.44	10.3	20
PAD 45T2	13-Jul-04	summer	o	90.7	28.3	6.2	0.48	7.4	18.1	0.01	0.13	0.85	4.99	8.54	18.0
PAD 45T2	13-Sep-04	fall	o	92.0	27.5	5.3	0.58	7.0	11.5	0.05	0.15	0.9	6.72	8.1	17
PAD 45T2	22-May-05	spring	o	95	29.7	9.68	0.454	7.35	12.4	0.0187	0.211	1.7	5.13	13.2	21.4
PAD 45T2	1-Aug-05	summer	o	84.8	27	4.67	0.615	7.01	15.5	0.0165	0.0653	0.87	5.31	8.87	16.1
PAD 45T2	14-Sep-05	fall	o	105	29.9	9.61	0.411	8.26	10.3	0.0141	0.0332	0.89	4.76	11.4	19.9
PAD 54N	22-May-03	spring	r	86.6	28.6	4.9	0.86	7.3	9	0.029	0.731	7.22	4	6.31	33
PAD 54N	4-Jun-03	spring	r	93.9	30	3.7	0.66	7.07	8.3	0.014	0.142	3.81	4.01	5.69	31
PAD 54N	16-Jun-03	spring	r	98.6	31.5	3.6	0.82	7.19	7.9	0.006	0.063	3.82	3.89	5.73	30
PAD 54N	3-Jul-03	summer	r	103	34.5	3	0.52	7.69	8.6	0.008	0.026	3.4	2.35	6.27	29
PAD 54N	15-Jul-03	summer	r	99.7	31.3	2.9	0.21	7.56	7.9	0.006	0.012	3.19	1.58	6.51	29
PAD 54N	20-May-05	spring	r	100	32.4	2.7	0.331	7.87	7.9	0.0107	0.0328	2.89	3.08	5.85	21.9
PAD 54N	28-Jul-05	summer	r	82.6	22.4	2.24	0.45	8.67	7.2	0.0067	0.0161	2.71	1.08	6.22	20.2
PAD 54N	14-Sep-05	fall	r	79.2	18.6	2.2	0.44	8.19	6.6	0.0087	0.0136	2.41	0.32	5.87	15.7
PAD 54N	2-May-04	spring	r	108	34.0	2.9	0.24	9.6	22.6	0.01	0.02	3.20	1.336	6.5	20

PAD 54N	11-Jun-04	spring	r	115	34.3	3.2	0.27	9.2	24.4	0.01	0.01	3.12	0.522	6.3	19
PAD 54N	28-Jul-04	summer	r	80.2	19.3	2.2	0.34	9.0	17.6	0.01	0.01	2.82	0.79	6.28	16.7
PAD 54N	17-Sep-04	fall	r	83.5	19.3	3.2	0.41	9.7	6.6	0.05	0.05	2.8	0.391	6.6	17
PAD 54S	4-Jun-03	spring	r	94	30.1	4.1	0.73	6.94	7.9	0.02	0.126	4.17	4.2	5.48	29
PAD 54S	16-Jun-03	spring	r	99.7	30.3	3.5	0.55	7.31	7.5	0.012	0.065	3.58	3.85	5.59	30
PAD 54S	3-Jul-03	summer	r	103	33.9	2.9	0.5	7.72	8.5	0.007	0.021	3.28	2	6.7	28
PAD 54S	15-Jul-03	summer	r	95.2	29.4	3	0.56	7.7	7.3	0.007	0.013	3.07	1.43	6.39	28
PAD 54S	28-Jul-05	summer	r	71.1	17.9	2.17	0.564	8.47	7.3	0.0065	0.016	2.58	1.09	6.17	18.6
PAD 54S	14-Sep-05	fall	r	70.7	15.9	2.12	0.433	7.81	6.9	0.0089	0.0158	2.37	0.15	5.77	15
PAD 54S	11-Jun-04	spring	r	114	33.5	3.0	0.39	9.0	31.8	0.01	0.01	3.08	0.341	6.2	19
PAD 54S	28-Jul-04	summer	r	71.7	16.8	2.5	0.65	9.3	15.8	0.01	0.01	2.97	0.89	6.53	16.3
PAD 54S	17-Sep-04	fall	r	76.5	16.2	3.2	0.35	8.9	7.0	0.05	0.06	2.6	0.391	6.1	17
L.Athabasca	26-May-03	spring	o	85.5	28.2	8.6	1.2	6.21	14.2	0.033	0.133	2	5.48	10.7	20
L.Athabasca	10-Jun-03	spring	o	84.9	23.8	9.6	0.59	5.67	11.7	0.018	0.125	1.84	4.66	9.54	19
L.Athabasca	24-Jun-03	spring	o	64.7	20.6	6.5	0.6	4.64	7.3	0.01	0.19	1.3	3.33	7.67	18
L.Athabasca	11-Jul-03	summer	o	80.3	23.8	5.3	0.61	5.64	13.7	0.011	0.094	0.99	5.13	9.22	18
L.Athabasca	8-Aug-03	fall	o	90.2	28	9.1	0.55	7.26	10	0.023	0.044	0.91	4.77	9.5	23
PAD R1	22-May-03	spring	Rv	70.7	22	7.6	0.6	5.33	10	0.028	0.447	3.75	4.81	9.04	26
PAD R1	2-Jun-03	spring	Rv	69.2	17.7	7.6	0.7	4.74	11.1	0.044	0.17	2.16	4.27	9.27	20
PAD R1	16-Jun-03	spring	Rv	64.1	19.3	6.4	0.59	4.41	7.9	0.013	0.104	1.69	3.83	6.91	16
PAD R1	3-Jul-03	summer	Rv	78.5	26.9	5.8	0.5	5.91	10	0.011	0.273	1.4	4.37	8.65	21
PAD R1	15-Jul-03	summer	Rv	51.6	14.9	5.2	0.49	3.7	6.3	0.079	0.133	1.35	3.7	5.4	14
PAD R1	6-Aug-03	fall	Rv	78.2	27.8	7	0.38	6.34	10.1	0.055	0.079	0.94	4.62	6	18
PAD R2	22-May-03	spring	Rv	85.3	30.8	3.1	0.79	6.84	14.7	0.02	0.682	3.27	4.71	6.53	33
PAD R2	4-Jun-03	spring	Rv	95.9	31.6	2.2	0.68	6.72	7.8	0.006	0.403	2.72	5.02	4.34	24
PAD R2	16-Jun-03	spring	Rv	92.4	30	2	0.46	6.54	7.1	0.006	0.25	1.33	3.68	3.67	22
PAD R2	3-Jul-03	summer	Rv	95.7	32.7	1.5	0.72	7.02	6.3	0.005	0.289	1.11	3.85	4.39	24
PAD R2	15-Jul-03	summer	Rv	87.8	29.5	5.7	1.8	6.18	10.6	0.015	2.52	0.9	4.93	3.77	28
PAD R2	6-Aug-03	fall	Rv	95.5	37	1.6	0.5	7.18	7.8	0.016	0.181	0.72	4.35	3.47	26
PAD R2	2-May-04	spring	Rv	81.7	29.6	2.1	0.47	6.9	16.3	0.01	0.38	1.18	4.235	5.1	22
PAD R2	11-Jun-04	spring	Rv	94.4	31.7	1.0	0.46	7.6	19.9	0.01	0.25	0.8	3.772	4.3	23
PAD R2	28-Jul-04	summer	Rv	99.9	33.2	1.0	0.60	7.8	22.8	0.01	0.40	0.90	5.57	4.04	23

PAD R2	17-Sep-04	fall	Rv	101	33.9	1.2	1.30	8.1	13.2	0.05	0.63	1.0	5.62	5.0	24
PAD R2	20-May-05	spring	Rv	101	36.4	1.45	0.773	8.1	11.6	0.0104	0.793	3.08	4.15	5.49	23.8
PAD R2	28-Jul-05	summer	Rv	97.9	33.7	1.04	0.404	7.8	10.4	0.0129	0.078	0.66	3.63	3.81	22.3
PAD R2	14-Sep-05	fall	Rv	100	32.4	1.31	0.199	7.39	5.3	0.0052	0.015	0.62	3.46	3.78	22.5
PAD R3	22-May-03	spring	Rv	82.2	24.7	14.9	0.93	6.13	11.8	0.022	0.455	2.91	4.36	14.3	27
PAD R3	4-Jun-03	spring	Rv	93.7	39.3	59.8	0.35	8.73	12.7	0.007	0.076	2.31	1.93	38.1	56
PAD R3	3-Jul-03	summer	Rv	87.7	28.6	7.5	0.35	6.53	10.6	0.011	0.164	1.22	4.12	9.6	23
PAD R3	15-Jul-03	summer	Rv	88.8	26.7	13.7	0.58	6.49	12.5	0.009	0.081	1.26	3.94	12.5	26
PAD R3	17-Aug-03	fall	Rv	92.9	34.6	25.2	0.58	8.17	11.6	0.015	0.147	1.43	3.29	20.5	30
PAD R4	22-May-03	spring	Rv	89.4	24.8	9.7	0.95	6.53	14.5	0.023	0.257	2.35	5.87	12.2	24
PAD R4	28-Jun-03	summer	Rv	85.1	28.6	6	1	6.49	11.4	0.014	0.591	1.28	4.48	10.2	24
PAD R4	11-Jul-03	summer	Rv	78.5	24.8	5.2	0.4	6.01	13.2	0.014	0.164	0.81	4.6	8.99	20
PAD R4	5-Jun-04	spring	Rv	76.9	24.1	5.4	1.5	6.2	24.0	0.02	0.79	1.26	5.351	10.4	19
PAD R4	16-May-05	spring	Rv	95.8	28.8	7.64	0.372	7.31	11	0.0136	0.0388	1.46	4.63	11.9	18.7
PAD R4	24-Jul-05	summer	Rv	99.4	31.4	7.31	0.546	8.07	10.6	0.0132	0.0663	0.87	5.37	10.2	18.6
PAD R4	14-Sep-05	fall	Rv	104	29.7	9.49	0.454	8.2	9.7	0.0139	0.0629	0.91	4.95	11.5	19.8
PAD R5	22-May-03	spring	Rv	91.3	26.3	9.4	0.62	6.62	14.5	0.025	0.256	2.17	5.84	12	24
PAD R6	22-May-03	spring	Rv	88.6	26.7	9.3	0.8	6.37	14.1	0.021	0.239	2.24	6.04	12.4	22
PAD R7	22-May-03	spring	Rv	92.1	27.1	9.5	0.76	6.65	14.5	0.022	0.222	2.53	5.87	12.4	23
PAD R7	6-Jun-03	spring	Rv	96.5	32.5	8.5	0.42	6.8	8	0.019	0.353	1.73	5.03	9.17	24
PAD R7	18-Jun-03	spring	Rv	86.2	26.4	6.7	0.39	6.44	8.6	0.01	0.174	1.28	3.99	8.14	22
PAD R7	5-Jul-03	summer	Rv	82.1	27.5	5.7	0.72	6.02	13.9	0.013	0.257	1.04	5.09	10.3	21
PAD R7	30-Jul-03	summer	Rv	89.9	28	1.5	0.5	7.26	10.7	0.018	0.082	1.13	4.71	10.4	22
PAD R7	21-Aug-03	fall	Rv	89.4	30.2	7	0.36	7.52	11.1	0.017	0.081	1.09	4.44	8.34	24
PAD R7	2-May-04	spring	Rv	79.5	24.7	10	0.7	6.7	21.6	0.02	0.1	1.77	5.787	14.2	17
PAD R7	10-Jun-04	spring	Rv	82.2	25	5	1.1	6.5	24.4	0.02	0.36	1.24	5.76	10.3	19
PAD R7	23-Jul-04	summer	Rv	94.8	30.3	3.5	1	7.1	24.5	0.01	0.51	1.12	7.01	8.38	15.3
PAD R7	12-Sep-04	summer	Rv	94.5	29.3	5.4	0.89	7.6	11.6	0.05	0.05	0.9	6.62	8.6	18
PAD R7	20-Sep-05	fall	Rv	107	30.7	9.06	0.395	8.42	8.4	0.0119	0.0801	0.93	4.44	11.4	22.9
PAD R11	22-May-03	spring	Rv	71.9	22.7	7.7	0.85	5.74	8.3	0.034	0.403	4.33	4.68	9.07	28
PAD R11	30-Jun-03	summer	Rv	67.9	22.2	6.1	0.64	5.02	8.3	0.01	0.213	1.4	3.8	8.11	19
PAD R11	18-Jul-03	summer	Rv	63.9	17.3	6	0.56	4.41	8.5	0.014	0.146	1.04	3.98	6.95	18

PAD R11	9-Aug-03	fall	Rv	67.4	21.8	6.6	0.44	5.5	8.1	0.019	0.065	0.99	4.36	6.84	15
PAD R11	31-May-04	spring	Rv	80.8	23.6	11	0.76	6.3	18.8	0.02	0.23	1.29	4.63	13	16
PAD R11	22-Jul-04	summer	Rv	80.1	24.8	5.1	0.67	6.1	18.6	0.01	0.2	0.89	5.73	7.07	13.7
PAD R11	15-Sep-04	fall	Rv	66.7	19.1	5.8	0.22	5.1	4.6	0.07	0.11	0.8	4.4	6.2	12
PAD R27	22-May-03	spring	Rv	68.2	23.5	7.1	0.82	5.6	8.7	0.074	0.193	3.94	4.39	7.17	29
PAD R27	8-Jun-03	spring	Rv	76.4	25.3	8.5	0.65	5.34	9.8	0.022	0.046	2.43	4.66	8.47	23
PAD R27	30-Jun-03	summer	Rv	79.1	23.8	6.7	0.61	5.58	9.2	0.01	0.046	1.7	4.17	8.8	21
PAD R27	18-Jul-03	summer	Rv	86.9	26.3	6.4	0.61	5.69	10.1	0.01	0.031	1.62	4.63	8.43	18
PAD R27	9-Aug-03	fall	Rv	89.9	28.1	6.5	0.6	6.63	10.6	0.031	0.049	1.49	4.39	7.65	16
PAD R27	31-May-04	spring	Rv	64.9	19.6	5.4	0.48	5	12.9	0.01	0.03	1.92	1.748	6.2	10

Table B.2 Chemical and physical characteristics of water in the study lakes and rivers from the Peace-Athabasca Delta (2003-05 data). D-Class refers to water body drainage class; c= closed-, r=restricted-, o=open-drainage, Rv=river and s= shield lake.

Lake	date	season	D-Class	pH	Temp	Cond	DO%	DOmg	Zmax (m)	Zmean (m)	Kd-par	Chl *a* (ug/ L)	TSS (mg/L)	ISS (mg/L)	OSS (mg/L)
PAD 1	8-Jun-03	spring	c	7.80	14.8	459	68.3	6.72	80	56	3.02	0.47	4.0	3.0	2.0
PAD 1	30-Jun-03	summer	c	8.99	19.7	416	106.9	9.31	90	62	2.37	3.09	2.0	0.9	1.1
PAD 1	18-Jul-03	summer	c	8.63	19.6	489	72.1	6.51	80	59	2.44	2.52	5.0	3.0	2.0
PAD 1	20-Aug-03	fall	c	9.92	18.3	371	117.3	10.66	70	54	2.30	1.08	2.0	1.0	1.0
PAD 1	6-Jun-04	spring	c	8.43	15.4	394	89.5	8.43	90	66	1.79	1.22	8.0	1.0	6.0
PAD 1	1-Aug-04	summer	c	9.98	14.5	307	70.8	6.85	75	53	1.63	1.58	7.0	4.0	3.0
PAD 1	21-Aug-04	fall	c	8.71	12.9	338			70	49	1.79	1.60	1.0	0.0	1.0
PAD 1	13-Sep-04	fall	c	8.75	11.1	378	98.4	10.85	70	46	1.72	1.58	2.7	0.8	1.9
PAD 1	16-May-05	spring	c	7.97		322				94	1.66	3.08	2.0	1.0	1.0
PAD 1	1-Aug-05	summer	c	9.73	19.7	297	188.2	17.11	115	90	2.27	1.63	2.0	0.0	1.0
PAD 1	14-Sep-05	fall	c	7.27	10.2	273	80.3	9.02	135	112	3.57	4.68	2.0	1.0	1.0
PAD 5	27-Jun-03	summer	c	7.48	20.7	368	30.0	2.61	90	54	1.84	2.45	4.0	2.0	2.0
PAD 5	22-Jul-03	summer	c	8.74	23.8	324	125.4	10.42	85	54	1.48	1.03			
PAD 5	25-Aug-03	fall	c	8.55	14.2	297	83.5	8.42	70	42	1.42	3.05			
PAD 5	2-Jun-04	spring	c	8.45	17.9	297	110.6	10.05	90	57	1.31	2.37			
PAD 5	17-Jul-04	summer	c	9.91	26.3	248	134.6	10.29	75	40	1.46	5.33	1.6	0.5	1.1
PAD 5	23-Sep-04	fall	c	10.07	7.6	226	113.3	13.54	75	42	3.05	1.53	3.0	1.0	2.0
PAD 5	15-May-05	spring	c	7.92		252				70	1.93	8.96	5.0	2.0	3.0
PAD 5	19-Jul-05	summer	c	10.59	19.1	230	135.1	12.52	95	63	2.22	1.19	6.0	3.0	3.0
PAD 5	14-Sep-05	fall	c	9.73	9.5	230	95.6	10.70	100	71	2.54	4.68	5.0	2.0	3.0
PAD 8	22-May-03	spring	r	7.86		198					2.10	6.83	2.0	1.0	1.0
PAD 8	1-Jun-03	spring	r	7.60	19.5	224	86.7	7.71	160	99	1.85	1.24	0.0	0.0	0.0
PAD 8	13-Jun-03	spring	r	7.74	14.5	234	91.4	9.15	170	117	1.59	1.45	7.5	5.0	2.5
PAD 8	12-Jul-03	summer	r	9.14	21.4	220	135.3	11.63	180	125	1.40	1.65	3.0	1.3	1.7
PAD 8	9-Aug-03	fall	r	7.86	20.7	241	78.2	6.90	180	122	1.18	1.95			
PAD 8	31-May-04	spring	r	7.81	12.4	162	79.6	8.08	150	71	1.94	10.56			
PAD 8	22-Jul-04	summer	r	7.97	20.6	206	89.0	7.75	160	83	1.79	7.50	2.3	1.3	1.0
PAD 8	16-Sep-04	fall	r	8.19	10.4	230	101.0	11.33	140	73	1.51	22.34	5.7	3.6	2.1

PAD 8	18-May-05	spring	r	7.34		166				95	1.90	3.54			
PAD 8	15-Jun-05	spring	r	7.60		200				133	2.07	4.90	10.3	6.9	3.5
PAD 8	24-Jul-05	summer	r	8.50	17.1	208	105.2	10.13	190	135	1.72	6.89	3.9	1.8	2.1
PAD 8	14-Sep-05	fall	r	8.73	10.0	199			185	116	1.45	1.25	4.4	1.8	2.6
PAD 9	22-May-03	spring	c	9.00		452					1.60	4.39	4.0	0.8	3.2
PAD 9	27-May-03	spring	c	8.94	18.8	435	136.3	12.58	80	39	1.54	0.90	4.7	3.4	1.2
PAD 9	26-Jun-03	summer	c	10.38	22.4	292	167.8	14.15	75	37	1.29	3.34	2.1	1.1	1.1
PAD 9	21-Jul-03	summer	c	7.87	22.7	475	85.2	7.12	65	31	3.69	3.51	1.6	0.0	1.6
PAD 9	26-Aug-03	fall	c	9.35	15.5	387	119.6	11.81	55	27	1.99	2.08	2.5	0.5	2.0
PAD 9	1-Jun-04	spring	c	8.40	15.6	355	129.2	12.24	65	33	2.29	9.12	0.9	0.1	0.7
PAD 9	17-Jul-04	summer	c	10.38	23.0	280	162.6	13.15	50	18	1.98	1.39	0.8	0.0	0.8
PAD 9	22-Sep-04	fall	c	9.13	10.5	349	107.9	12.01		15	1.50	5.52	5.3	2.6	2.7
PAD 9	16-May-05	spring	c	8.12		339					1.58	2.33			
PAD 9	20-Jul-05	summer	c	9.86	19.3	275	103.8	9.40	90	49	2.67	1.19	1.9	0.0	1.9
PAD 9	14-Sep-05	fall	c	8.12	8.3	265	68.2		85	41	2.62	5.36	3.9	2.2	1.7
PAD 15N	22-May-03	spring	r	8.01		246					12.06	19.75	2.9	0.8	2.1
PAD 15N	2-Jun-03	spring	r	7.92	19.6	250	31.6	2.77	50	40	7.65	23.26	2.4	1.0	1.4
PAD 15N	9-Jul-03	summer	r	9.33	20.9	226	136.0	12.02	80	61	0.94	2.96	3.3	2.2	1.1
PAD 15N	7-Aug-03	fall	r	10.42	21.4	213	141.2	12.29	95	51	1.60	4.84	4.5	2.4	2.1
PAD 15N	2-May-04	spring	r	7.37		212					2.60	7.39	153.5	138.5	15.0
PAD 15N	14-Jun-04	spring	r	8.38	17.6	268	111.0	10.04	110	71	0.90	1.42	51.8	46.3	5.5
PAD 15N	29-Jul-04	summer	r	10.16	22.4	180	160.2	13.38	110	76	1.07	1.43	4.9	3.4	1.6
PAD 15N	20-Sep-04	fall	r	9.80	7.1	161	97.3	11.81		68	1.44	5.99	5.0	3.6	1.4
PAD 15S	2-Jun-03	spring	r	7.34	16.2	240	35.7	3.44	160	80	7.98	10.92	13.3	10.7	2.7
PAD 15S	9-Jul-03	summer	r	8.78	19.4	248	106.6	9.55	170	104	1.05	5.93	6.2	5.0	1.2
PAD 15S	7-Aug-03	fall	r	8.92	20.4	228	85.0	8.52	140	74	1.08	2.44	2.2	0.4	1.8
PAD 15S	14-Jun-04	spring	r	8.15	16.6	267	95.5	8.82	145	74	0.84	0.72	6.3	4.1	2.2
PAD 15S	29-Jul-04	summer	r	9.15	22.5	198	135.6	11.06	195	92	0.79	2.67	43.7	37.3	6.3
PAD 15S	20-Sep-04	fall	r	8.46	8.2	203	85.4	10.07		85	1.44	1.60	3.2	2.1	1.1
PAD 18	22-May-03	spring	s	8.13		208			750	5	0.51	1.57	1.3	0.6	0.6
PAD 18	28-May-03	spring	s	8.30	14.4	209	107.0	10.69	750	5	0.62	1.07	3.5	2.6	0.8
PAD 18	25-Jun-03	summer	s	8.63	17.3	195	96.6	9.04	750	5	0.38	0.81	2.2	1.2	1.0

PAD 18	24-Jul-03	summer	s	8.36	21.2	222	100.5	8.66	805	5	0.44	0.74	4.1	2.8	1.3
PAD 18	15-Aug-03	fall	s	8.33	21.4	223	105.5	9.17	820	5	0.43	1.05	3.3	1.0	2.3
PAD 18	4-Jun-04	spring	s	8.21	14.8	195	99.5	9.72	830	511	0.46	0.24	0.4	0.0	0.4
PAD 18	18-Jul-04	summer	s	8.51	23.7	208	99.8	8.07	800	505	0.37	0.80	0.9	0.0	0.9
PAD 18	21-Sep-04	fall	s	7.98	10.3	203	78.2	8.43	800	498	0.59	1.65			
PAD 23	22-May-03	spring	r	7.90		140					1.88	8.01	2.1	1.2	0.9
PAD 23	29-May-03	spring	r	8.01	16.7	148	98.0	9.21	180	121	0.75	6.02	1.3	1.0	0.3
PAD 23	28-Jun-03	summer	r	8.10	21.2	153	132.1	11.63	190	120	0.82	3.08	0.9	0.2	0.7
PAD 23	23-Jul-03	summer	r	7.85	19.0	146	101.1	9.10	180	120	0.54	3.13	1.2	0.2	1.0
PAD 23	2-May-04	spring	r	8.11		184					1.29	8.74	2.0	0.0	2.0
PAD 23	5-Jun-04	spring	r	8.25	20.9	151	118.0	9.99	180	114	1.07	6.70	1.3	0.2	1.2
PAD 23	19-Jul-04	summer	r	7.99	22.4	139	97.4	7.97	170	107	1.42	13.76			
PAD 23	24-Sep-04	fall	r	7.29	8.6	155	73.9	8.61			1.63	12.93			
PAD 31	22-May-03	spring	r	8.17		268					2.43	16.49			
PAD 31	6-Jun-03	spring	r	8.34	16.6	299	110.7	10.65	140	90	1.68	1.70	13.2	5.8	7.4
PAD 31	18-Jun-03	spring	r	9.54	21.1	242	133.2	11.65	115	89	1.23	6.77	6.4	3.8	2.6
PAD 31	6-Jul-03	summer	r	9.39	19.6	211	140.7	12.59	120	98	1.56	3.78	0.9	0.2	0.7
PAD 31	17-Jul-03	summer	r	9.70	20.8	210	129.3	11.21	115	98	1.85	1.39	2.1	0.6	1.6
PAD 31	30-Jul-03	summer	r	9.78	22.7	204	142.7	12.22	120	91	1.73	2.59	13.5	7.5	6.0
PAD 31	21-Aug-03	fall	r	9.32	19.3	198	120.2	10.85	100	78	2.31	36.68	1.6	0.8	0.8
PAD 31	2-May-04	spring	r	7.33		72					1.14	0.81	4.8	3.1	1.7
PAD 31	13-Jun-04	spring	r	9.53	14.0	181	112.0	10.97	125	90	1.38	0.84			
PAD 31	23-Jul-04	summer	r	7.86	22.9	237	93.9	7.62	135	106	2.63	2.79			
PAD 31	12-Sep-04	fall	r	8.41	8.0	252	60.8	7.23	110	85	2.96	14.79			
PAD 31	5/16/2005	spring	r	8.29		249					1.73	4.79	8.5	3.2	5.3
PAD 31	15-Jun-05	spring	r	7.88		246					1.95	5.90	4.9	1.8	3.2
PAD 31	7/18/2005	summer	r	7.91		249					2.50	11.89	8.0	5.4	2.6
PAD 31	9/14/2005	fall	r	7.46	12.2	283	71.0		130	97	2.10	2.12	3.3	1.8	1.5
PAD 45	22-May-03	spring	o	8.16		249					8.89	12.18	20.8	16.5	4.3
PAD 45	26-May-03	spring	o	8.25	15.1	240	89.8	8.83		120	11.65	8.65	4.7	3.3	1.4
PAD 45	10-Jun-03	spring	o	7.61	17.6	211	89.3	8.65		130	4.92	3.32	9.2	6.2	3.0
PAD 45	24-Jun-03	summer	o	8.51	13.3	227	91.9	9.41		140	5.89	1.72	12.0	5.2	6.8

PAD 45	11-Jul-03	summer	o	8.53	22.3	201	101.4	8.64		150	3.85	2.49			
PAD 45	12-Aug-03	fall	o	8.41	18.9	272	115.2	10.50		135	1.71	1.72	7.6	4.4	3.2
PAD 45	2-May-04	spring	o	7.98		200					4.72	14.90	3.4	1.8	1.5
PAD 45	9-Jun-04	spring	o	8.02	13.8	199	85.7	8.43		115	16.37	4.67	4.9	3.0	1.9
PAD 45	14-Jul-04	summer	o	8.40	21.9	233	97.5	8.11		115	2.01	6.67	3.8	2.3	1.5
PAD 45	13-Sep-04	fall	o	7.84	11.2	216	91.1	9.98		95	8.40	1.56	135.0	117.0	18.0
PAD 45	14-Sep-05	fall	o	7.73		266					3.12	3.51	154.0	140.8	13.2
PAD 45T1	11-Jul-03	summer	o	9.43	23.6	205	129.1	11.04	95	83	1.67	1.38	40.3	35.1	5.1
PAD 45T1	12-Aug-03	fall	o	9.05	18.2	231	107.0	10.32	90	73	1.54	1.50	181.0	136.0	45.0
PAD 45T1	2-May-04	spring	o	8.27		276					2.26	8.34	37.1	28.8	8.4
PAD 45T1	9-Jun-04	spring	o	8.14	15.3	186	91.8	8.70	65	50	3.47	1.46	21.9	15.5	6.4
PAD 45T1	13-Jul-04	summer	o	9.92	24.9	198	145.7	11.57	70	53	1.30	1.56	37.6	32.8	4.8
PAD 45T1	13-Sep-04	fall	o	9.99	11.3	194	98.5	10.84			1.09	2.19	195.4	176.7	18.7
PAD 45T1	22-May-05	spring	o	7.96		293				99	2.26	4.34	16.6	13.7	2.9
PAD 45T1	1-Aug-05	summer	o	9.57	20.8	230	145.2	13.01	110	103	3.11	0.92	68.5	61.0	7.5
PAD 45T1	14-Sep-05	fall	o	8.03	11.5	263	83.9		110	98	2.27	1.32	28.9	24.7	4.3
PAD 45T2	11-Jul-03	summer	o	8.11	19.4	196	92.5	8.34	130	88	4.64	5.64	3.3	2.7	0.6
PAD 45T2	9-Jun-04	spring	o	7.93	15.7	200	85.5	8.09	100	57	13.05	3.49	1.2	0.5	0.7
PAD 45T2	13-Jul-04	summer	o	8.08	21.8	226	89.1	7.43	100	56	4.44	4.28	3.7	2.3	1.3
PAD 45T2	13-Sep-04	fall	o	7.95	10.1	212	92.8	10.42			9.83	2.14	16.5	13.2	3.3
PAD 45T2	22-May-05	spring	o	8.01		255				99	9.66	4.41	5.1	3.6	1.5
PAD 45T2	1-Aug-05	summer	o	8.24	17.9	213	93.2	8.80	140	103	6.05	2.64	1.0	0.0	1.0
PAD 45T2	14-Sep-05	fall	o	8.07	11.0	253	75.1		140	97	2.27	6.12	24.3	19.7	4.6
PAD 54N	22-May-03	spring	r	7.94		235					16.24	3.11	4.3	2.6	1.7
PAD 54N	4-Jun-03	spring	r	8.21	17.7	242	77.0	7.18	380	150	6.46	24.87	3.3	2.1	1.3
PAD 54N	16-Jun-03	spring	r	8.24	17.3	248	94.4	8.87	360	143	3.28	13.80	135.0	107.7	27.3
PAD 54N	3-Jul-03	summer	r	8.27	18.8	251	98.1	8.96	360	154	1.29	2.79	235.4	213.3	22.1
PAD 54N	15-Jul-03	summer	r	8.40	20.3	245	100.5	9.02	350	171	0.87	1.50	54.2	48.6	5.6
PAD 54N	20-May-05	spring	r	7.97	13.0	244				195	2.11	1.77	92.5	82.3	10.2
PAD 54N	28-Jul-05	summer	r	8.72	19.5	206			340	185	0.86	1.39	145.0	129.0	16.0
PAD 54N	14-Sep-05	fall	r	8.09	12.7	190	93.9		415	191	0.63	1.21	48.5	43.5	5.0
PAD 54N	2-May-04	spring	r	7.51		228					1.97	2.80	11.3	8.7	2.6

PAD 54N	11-Jun-04	spring	r	8.20	17.3	254	87.5	8.11	355	153	1.06	0.51	249.0	225.5	23.5
PAD 54N	28-Jul-04	summer	r	8.35	22.3	196	108.6	9.98	350	149	0.69	2.09	53.3	47.3	6.0
PAD 54N	17-Sep-04	fall	r	8.48	9.9	190	88.5	10.01	345	143	0.69	0.84	19.8	16.7	3.2
PAD 54S	4-Jun-03	spring	r	8.00	18.1	239	87.8	8.18	470	143	9.80	13.81	1.9	0.8	1.1
PAD 54S	16-Jun-03	spring	r	7.87	16.0	250	86.0	8.42	440	153	3.31	7.62			
PAD 54S	3-Jul-03	summer	r	8.41	18.4	250	89.6	8.24	450	175	1.18	1.32	11.4	9.3	2.1
PAD 54S	15-Jul-03	summer	r	8.60	19.6	235	108.9	9.86	400	173	0.71	1.66	1.8	0.9	0.8
PAD 54S	28-Jul-05	summer	r	9.36	19.5	183			400	197	0.94	1.97	1.8	1.5	0.4
PAD 54S	14-Sep-05	fall	r	8.13	11.8	174	83.9		455	204	0.63	0.95	7.0	5.4	1.6
PAD 54S	11-Jun-04	spring	r	8.36	17.7	251	93.8	8.56	420	201	0.64	1.46	4.1	2.8	1.3
PAD 54S	28-Jul-04	summer	r	8.96	21.7	179	101.7	8.47	415	195	0.73	2.62	0.5	0.0	0.5
PAD 54S	17-Sep-04	fall	r	8.88	10.2	178	98.4	11.04	410	190	0.81	2.03	2.1	1.0	1.2
L.Athabasca	26-May-03	spring	o	8.25	13.1	216	91.9	9.57		250	4.60	5.33	30.3	26.8	3.5
L.Athabasca	10-Jun-03	spring	o	8.02	15.4	215	90.1	8.85		250	5.32	4.45	12.4	10.1	2.3
L.Athabasca	24-Jun-03	spring	o	8.38	13.4	169	89.3	9.20		300	7.68	4.77			
L.Athabasca	11-Jul-03	summer	o	8.24	18.6	182	91.9	8.43		270	4.51	4.97			
L.Athabasca	8-Aug-03	fall	o	8.01	19.7	242	98.1			295	1.92	3.31			
PAD R1	22-May-03	spring	Rv	8.05		199					13.72	3.75	2.5	0.9	1.5
PAD R1	2-Jun-03	spring	Rv	8.10	11.2	184	96.5	10.35			8.13	2.88	0.5	0.0	0.5
PAD R1	16-Jun-03	spring	Rv	8.37	12.3	164	91.3	9.66			6.24	3.65	3.5	2.6	0.8
PAD R1	3-Jul-03	summer	Rv	8.14	15.8	189	84.7	8.23			10.50	2.75	7.6	0.8	6.8
PAD R1	15-Jul-03	summer	Rv	7.82	17.7	126	89.1	8.30			5.73	3.36	3.3	2.5	0.8
PAD R1	6-Aug-03	fall	Rv	7.95	18.8	207	84.4	7.69			3.69	5.61	45.7	41.0	4.7
PAD R2	22-May-03	spring	Rv	8.06		229					28.81	1.12	87.3	75.0	12.3
PAD R2	4-Jun-03	spring	Rv	8.06	16.3	167	99.2	9.46			14.23	1.28			
PAD R2	16-Jun-03	spring	Rv	8.33	15.1	167	101.0	9.94			7.91	0.82	49.3	39.4	9.9
PAD R2	3-Jul-03	summer	Rv	8.13	16.3	215	90.8	8.69			12.08	1.63	11.1	9.6	1.5
PAD R2	15-Jul-03	summer	Rv	7.89	17.5	260	90.0	8.42			103.40	1.06	172.5	156.5	16.0
PAD R2	6-Aug-03	fall	Rv	7.86	19.8	241	82.3	7.35			6.94	2.49	57.7	51.3	6.3
PAD R2	2-May-04	spring	Rv	7.82		195					5.16	1.67	209.3	158.3	51.0
PAD R2	11-Jun-04	spring	Rv	8.27		222					10.80	1.46	239.7	194.3	45.3
PAD R2	28-Jul-04	summer	Rv	8.01	21.7	229	90.2	7.46			17.63	0.66			
PAD R2	17-Sep-04	fall	Rv	7.79	9.0	230	89.8	10.18			57.58	1.93	32.3	26.3	6.0

PAD R2	20-May-05	spring	Rv	8.03		246					64.48	1.53	387.5	351.5	36.0
PAD R2	28-Jul-05	summer	Rv	8.15		232					4.74	1.88	290.0	267.0	23.0
PAD R2	14-Sep-05	fall	Rv	7.47	11.8	228	96.3				3.47	2.23	190.7	162.4	28.3
PAD R3	22-May-03	spring	Rv	7.92		239					14.35	9.83			
PAD R3	4-Jun-03	spring	Rv	8.06	17.8	423	86.9	8.10			3.97	4.02			
PAD R3	3-Jul-03	summer	Rv	8.20	16.7	222	99.4	9.50			7.07	4.32	142.0	115.6	26.4
PAD R3	15-Jul-03	summer	Rv	8.01	19.4	239	88.6	8.03			4.14	2.80	50.8	46.0	4.7
PAD R3	17-Aug-03	fall	Rv	8.16	21.2	318	108.0	9.43			5.19	3.08	133.1	120.2	12.8
PAD R4	22-May-03	spring	Rv	8.03		233					11.24	5.11	194.5	176.0	18.5
PAD R4	28-Jun-03	summer	Rv	8.13		217					46.29	4.08	654.0	598.0	56.0
PAD R4	11-Jul-03	summer	Rv	8.00		195					8.24	7.06	902.1	816.8	85.3
PAD R4	5-Jun-04	spring	Rv	8.06		186					25.22	3.06	48.4	43.0	5.3
PAD R4	16-May-05	spring	Rv	8.00		240					5.85	5.00	23.1	20.4	2.7
PAD R4	24-Jul-05	summer	Rv	8.09		250					6.52	5.51	182.0	165.0	17.0
PAD R4	14-Sep-05	fall	Rv	8.17		261					5.35	5.72	29.7	25.9	3.8
PAD R5	22-May-03	spring	Rv	8.06		236					10.64	4.23	77.5	67.5	10.0
PAD R6	22-May-03	spring	Rv	8.07		227					11.69	5.18	135.5	104.5	31.0
PAD R7	22-May-03	spring	Rv	8.10		236					11.19	4.12	46.2	37.0	9.2
PAD R7	6-Jun-03	spring	Rv	8.01	16.5	243	89.4	8.60			16.17	3.02	29.7	25.9	3.8
PAD R7	18-Jun-03	spring	Rv	8.18	18.9	216	99.3	9.05			10.40	10.95	137.6	124.8	12.9
PAD R7	5-Jul-03	summer	Rv	8.01	19.2	197	89.8	7.92			9.08	5.65	768.7	667.3	101.3
PAD R7	30-Jul-03	summer	Rv	8.14	24.2	245	94.1	7.73			3.62	4.51	173.5	139.5	34.0
PAD R7	21-Aug-03	fall	Rv	7.89	19.2	238	78.4	7.06			3.38	4.58			
PAD R7	2-May-04	spring	Rv	8.04		206					6.12	11.05			
PAD R7	10-Jun-04	spring	Rv	8.01	16.5	198	93.9	8.82			12.11	5.93	82.6	72.0	10.6
PAD R7	23-Jul-04	summer	Rv	7.82	21.9	219	83.8	6.99			20.50	4.13	331.7	301.9	29.7
PAD R7	12-Sep-04	summer	Rv	7.91	9.5	215					13.64	4.03	65.1	58.0	7.1
PAD R7	20-Sep-05	fall	Rv	8.28	11.7	274	89.6		1515		3.53	4.89	72.6	65.2	7.3
PAD R11	22-May-03	spring	Rv	7.94		205					12.00	5.76	52.7	47.9	4.8
PAD R11	30-Jun-03	summer	Rv	8.40	16.6	167	98.2	9.46			9.17	4.58	124.7	114.0	10.7
PAD R11	18-Jul-03	summer	Rv	7.86	18.8	164	91.9	8.38			8.45	3.13			
PAD R11	9-Aug-03	fall	Rv	7.99	20.0	182	81.1	7.23			2.70	4.06	134.3	123.9	10.4

PAD R11	31-May-04	spring	Rv	8.18	8.3	204	90.6	10.15			7.56	4.66	132.2	120.9	11.3
PAD R11	22-Jul-04	summer	Rv	8.02	19.7	166					8.99	3.40	267.0	245.0	22.0
PAD R11	15-Sep-04	fall	Rv	8.00	9.8	161					3.40	2.24	138.8	118.8	20.0
PAD R27	22-May-03	spring	Rv	8.00		199					7.87	12.60			
PAD R27	8-Jun-03	spring	Rv	7.90	15.8	205	95.0	9.06			2.73	2.89			
PAD R27	30-Jun-03	summer	Rv	8.52	18.8	203	102.5	9.29			2.09	3.92			
PAD R27	18-Jul-03	summer	Rv	8.43	20.4	226	93.1	8.15			1.64	8.77	44.6	33.9	10.7
PAD R27	9-Aug-03	fall	Rv	8.37	21.5	225	89.0	7.80			1.30	6.80	80.0	69.0	11.0
PAD R27	31-May-04	spring	Rv	8.07	12.5	156	88.4	8.94		205	1.63	3.10	259.0	234.0	25.0

Table B3 Location of sampling locations (Lat/Long hddd° mm.mmm') for lakes and rivers from the Peace-Athabasca Delta listed in Table B1, B2. Drainage Class refers to water body drainage class; c= closed-, r=restricted-, o=open-drainage, Rv=river and s= shield lake.

Lake or River #	Name	Drainage Class	Latitude N (WGS84)	Longitude W
Lakes				
PAD 1	Devils Gate	c	58 48.351'	111 14.820'
PAD 5	Spruce Island	c	58 50.788'	111 28.781'
PAD 8	Chillowey's Lake	r	58 48.688'	111 21.385'
PAD 9		c	58 46.491'	111 19.641'
PAD 15N	Pete's Creek north arm	r	58 57.018'	111 29.917'
PAD 15S	Pete's Creek south arm	r	58 56.570'	111 30.161'
PAD 18	Green Star	s	58°53.808'	111°21.385'
PAD 23		c	58 23.458'	111 26.705'
PAD 31	Johnny Cabin Pond	r	58 29.863'	111 31.105'
PAD 45	Lake Mamawi	o	58 36.373'	111 27.137'
PAD 45 T1	Lake Mamawi Embayment	o	58 34.578'	111 28.930'
PAD 45 T2	Lake Mamawi Creek Delta	o	58 35.625'	111 28.210'
PAD 54N	Horseshoe Slough north arm	r	58 52.120'	111 33.958'
PAD 54S	Horseshoe Slough south arm	r	58 51.873'	111 34.813'
Lake Athabasca	Fort Chip Bay	o	58 42.315'	111 05.860'
Rivers				
PAD R1	Revillon Coupé	Rv	58°54.838'	111°25.496'
PAD R2	Peace River (Rocky Pt.)	Rv	58 54.526'	111 34.999'
PAD R3	Chenal des Quatre Fourches	Rv	58°48.966'	111°33.869'
PAD R4	Athabasca River	Rv	58 21.157'	111 32.438'
PAD R5	Embarras River	Rv	58°29.548'	111°26.330'
PAD R6	Fletcher Channel	Rv	58 28.496'	111 04.562'
PAD R7	Mamawi Creek	Rv	58 33.811'	111 30.491'
PAD R11	Rivière des Roches	Rv	58 49.510'	111 16.837'
PAD R27	Chillowey's Creek	Rv	58 49.379'	111 20.272'