An Investigation into the Past and Present Ecological Status of Lake Diefenbaker using Paleolimnological and Whole Sediment Toxicity Techniques

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ABSTRACT

Recent anecdotal evidence has suggested that Lake Diefenbaker, a large reservoir in southern Saskatchewan, Canada, has been experiencing an increased frequency and severity of algal blooms, suggesting significant alterations in water quality. Due to limited historical water quality monitoring, a paleolimnological investigation of Lake Diefenbaker sediments was conducted in order to interpret spatial and temporal trends in the physicochemistry of sediment cores collected from mid-channel locations along a spatial gradient. Total phosphorus and three sediment species of phosphorus (apatite inorganic phosphorus, non-apatite inorganic phosphorus (NAIP) and organic phosphorus (OP) were measured along the vertical profile of the cores to interpret nutrient loading trends. Trends in historical primary productivity were inferred based on total organic carbon, total nitrogen, $\delta^{15}N$ values and the organic carbon to nitrogen (C:N) ratios. In addition, sub-fossil biological remains of diatoms and chironomid larvae were isolated from selected subsections of the sediment cores and identified to assess shifts in community compositions and to infer historical changes in reservoir water quality conditions.

Up-reservoir sampling locations showed consistent concentrations of total phosphorus and the three species of phosphorus, organic carbon, nitrogen, $\delta^{15}N$ values and C:N ratios in the vertical profile of collected sediment cores. This suggested relatively consistent nutrient loading and primary production in the up-reservoir regions for the period represented by the core profiles. Down-reservoir sediment cores showed an increasing trend in total phosphorus concentration, mainly in the more biologically available NAIP and OP fractions, and enrichment in organic carbon, nitrogen and ^{15}N in more recently deposited sediments. This combined with a decreasing C:N ratio in more recent sediments suggests increased nutrient loading to the sediments and increasing primary productivity at down-reservoir sites. Strong correlations between sediment total organic carbon content and the more biologically available sediment phosphorus fractions (NAIP and OP) suggest that phosphorus deposition patterns are strongly influenced by primary productivity within the reservoir.

The compositions of diatom and chironomid communities were consistent over time at up-reservoir locations, with *Stephanodiscus parvus* dominating the diatom communities and *Procladius sp.* dominating the chironomid communities. This suggests relatively stable and

consistent trophic status and primary productivity in this region. Conversely, major shifts occurred in the diatom and benthic chironomid communities at down-reservoir locations. These shifts were consistent with typical reservoir ontogeny. A shift in dominance from *Stephanodiscus parvus* to *Asterionella formosa*, *Tabellaria flocculosa* and *Stephanodiscus medius* followed by a shift to *Aulacosiera ambigua* suggests an initial period of eutrophy, followed by a period of mesotrophy, and finally a transition into a more productive system in recent years. The increase in relative abundance of the chironomid tribe Tanytarsini suggests rising levels of organic matter sedimentation, likely due to increased autochthonous primary productivity. Low chironomid head capsule counts were observed at all locations within Lake Diefenbaker. Despite the low head capsule counts, a 10-day whole-sediment toxicity test using *Chironomus dilutus*, revealed that Lake Diefenbaker sediments, in proximity to two potential point sources of contamination (aquaculture and municipal discharge), as well as two reference locations, were not of toxicological concern. Despite the lack of toxicity associated with Lake Diefenbaker sediments, it was concluded that Lake Diefenbaker sediments are likely poor habitat for chironomids.

This study suggests that primary productivity and nutrient status has remained relatively constant at up-reservoir locations for the period represented by the collected cores. This is likely due to up-reservoir locations being more riverine than down-reservoir regions, which results in increased turbidity causing phytoplankton populations to be light limited. Primary productivity appears to increase spatially with increased distance down reservoir, likely due to a gradual transition to more lacustrine environments, resulting in less turbidity and less light limitation. Temporally, down-reservoir locations appear to be showing increases in primary productivity and nutrient entrainment in sediments. This is likely a result of increased nutrient availability over time and entrainment of these nutrients in sediments at down-reservoir locations by primary producers.

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LIST OF ABBREVIATIONS

ANOVA	Analysis of variance
AP	Apatitie inorganic phosphorus
C:N	Carbon to nitrogen
ICP-MS	Inductively coupled plasma mass spectrometry
NAIP	Non-apatite inorganic phosphorus
OP	Organic phosphorus
S.D.	Standard deviation
S.E.M	Standard error of mean
TN	Total nitrogen
TOC	Total organic carbon
TP	Total phosphorus
$\delta^{13}C$	A measure of the stable isotope ratio of ^{13}C to ^{12}C in per mil (‰), which represents parts per thousand difference from a standard.
$\delta^{15}N$	A measure of the stable isotope ratio of ^{15}N to ^{14}N in per mil (‰), which represents parts per thousand difference from a standard.
$\delta^{34}S$	A measure of the stable isotope ratio of ^{34}S to ^{32}S in per mil (‰), which represents parts per thousand difference from a standard.

PREFACE

Chapter 1 is a general introduction and Chapter 4 contains a general discussion and conclusion related to the thesis research. Chapters 2 and 3 of the thesis are organized as manuscripts for publication in scientific journals. As a result, there is some repetition of introductions and methods throughout each data chapter. Chapters 2 and 3 have been submitted to the Journal of Great Lakes Research.

CHAPTER 1:
General introduction

1.1 Problem formulation

Lake Diefenbaker is a man-made reservoir created through the flooding of a portion of the South Saskatchewan River valley in November of 1967 after the construction of the Gardiner and Qu'Appelle dams (Environment Canada, 1988). Lake Diefenbaker is a major body of water on the Canadian prairies and according to the Saskatchewan Watershed Authority supplies 65% of Saskatchewan's drinking water. This reservoir now covers 500 km^2 of previously treeless prairie grassland (Hall et al., 1999). It has a maximum storage capacity of 9.4×10^9 m^3 of water and reaches a maximum depth of 62 m (Hall et al., 1999). Although Lake Diefenbaker currently supplies high quality water for both urban and agricultural use, anecdotal evidence suggests that algal blooms are occurring in Lake Diefenbaker with increasing frequency and severity. Algal blooms have been known to produce foul smelling and tasting water, decrease water clarity, and produce periods of anoxia that can lead to fish kills. Under certain conditions (i.e., nitrogen limitation) cyanobacterial blooms can become a concern. Cyanobacteria have the potential to release biotoxins to the surrounding freshwater environment and under extreme conditions these biotoxins can have negative effects on both human and environmental health.

Lake Diefenbaker has a variety of potential nutrient and contaminant sources including inflow from the South Saskatchewan River, municipal discharges (e.g., Swift Current, Elbow), runoff from farming (mostly wheat, barley and canola), wastes from cattle ranching operations, aquaculture (Wild West Steelhead), and a significant number of migratory birds. Annual water fluctuations, averaging approximately 6.3 m (1968-1994), influence shoreline erosion and may also act as another major source of nutrients (Hall et al., 1999). With current plans to increase construction of residential communities around the lake and a proposed expansion of the Wild West Steelhead aquaculture operation, an investigation into the water quality of the reservoir seemed prudent. Due to limited availability of historical data, it was difficult to assess whether some or all of Lake Diefenbaker was experiencing deteriorating water quality (which can result from increased nutrient input). Therefore, it was important to establish the historical trends in ecological status and nutrient loading in Lake Diefenbaker.

1.2 Paleolimnology

The lack of historical data regarding limnological conditions in Lake Diefenbaker, posed a problem for establishing baseline conditions of the reservoir and for determining the magnitude of any changes in environmental conditions (i.e. water quality) that may have occurred over time. Paleolimnology is a reliable approach to reconstructing past ecological conditions through the analysis of a combination of both biological (sub-fossil remains) and chemical signatures preserved within sediments. Eutrophication was believed to be the main concern in Lake Diefenbaker and thus the primary goal of this research was to reconstruct the nutrient status of this reservoir over time. Paleolimnological methods have been shown to reliably reconstruct water quality variables, including trophic status in lakes (Marsicano et al., 1995; Fritz, 1989; Christie & Smol, 1993; Brenner et al., 1993). Paleolimnological techniques were therefore used on subsections of sediment core samples to quantify both biological and chemical variables throughout the various layers of sediment. These layers represent different temporal periods. The biological and chemical data from each subsection were compared to other subsections within the sediment core profile to infer changes in the nutrient status of Lake Diefenbaker over time.

1.2.1 Biological remains

The sub-fossil remains of both diatoms (siliceous frustules) and chironomids (head capsules), in combination with physicochemical data, can be used to reconstruct spatial and past ecological conditions of the reservoir. This can be accomplished based on ecological preferences and tolerances of species identified in specific layers of the sediment profile.

1.2.1.1 Diatom communities as proxies for past ecological conditions

Diatom community compositions are commonly used as paleoindicators of water quality due to their sensitivity to nutrient concentrations, their general abundance and preservation in sediments of freshwater lakes, and the relative ease with which they can be identified to species level or lower (Karst & Smol, 2000; Dixit et al., 1992). Diatoms tend to be well preserved in sediment due to their siliceous cell walls, leading to the preservation of their frustules (Battarbee et al., 2001). Diatom identification can be based on the physical characteristics of the two valves of the theca. Changes in the diatom community assemblages over time can then be assessed based on diatom community composition within different sections of the sediment profile (Battarbee et al., 2001). Diatom community assemblages have been shown to be related to total phosphorus levels within reservoirs. Transfer functions have been developed to infer past total phosphorus levels based on subfossil remains of specific diatom community assemblages within the sediment (Rippey & Anderson, 1996). Therefore, diatom sub-fossil analyses of subsections of sediment cores can be used to provide information regarding nutrient status and trends over time.

Diatom siliceous microfossils can be isolated, identified, and quantified using the methods outlined by Hall & Smol (1992). The quantification of diatom remains (percent relative abundance) in the various sediment samples can be used in combination with other proxies (physicochemical and biological) that served as supporting data. Different diatom species have preferred environmental optima. By understanding the preferences of the different species and quantifying their relative abundances, we hope to be able to reconstruct the past nutrient status of Lake Diefenbaker. In a study conducted by Kling (1997) on sediment core samples collected from Lake Winnipeg, Manitoba, some common planktonic diatom species remains identified included *Auclacoseira islandica, Stephanodiscus binderanus* and *S. niagarae.* These observations are somewhat similar with previous work done on the Qu'Appelle arm of Lake Diefenbaker by Hall et al., (1999) who showed that since its creation in 1967 (and up to 1995), Lake Diefenbaker has undergone at least three major changes in diatom community assemblage. Lake Diefenbaker was initially (1969) dominated by *Stephanodiscus niagarae* and *Stephanodiscus parvus*, with subsequent increases (between 1968 and 1975) in *Cyclotella bodanica* v. *lemanica* and *Cyclotella michiganiana.* This was followed (between 1975 and 1986) by a decline in *Stephanodiscus* and *Cycotella* abundances and an increase in *Tabellaria flocculosa*, *Fragilaria crotonensis*, and *Aulacoseira ambigua.* Finally, between 1986 and 1995 (the year of core collection) *Aulacoseira ambigua* became the dominant diatom species. This study suggested that environmental conditions in Lake Diefenbaker shifted substantially during the first 30 years following reservoir formation. With growing residential communities, intensified uses for both municipal and recreational purposes, as well as increasing development upstream, there is a need to investigate any changes that may have occurred since 1995. In addition, a more rigorous sampling of Lake Diefenbaker in a spatial context, with emphasis placed on possible point sources of contamination (e.g., Swift Current Creek and the Wild West Steelhead operation), seemed prudent.

1.2.1.2 Chironomid communities as proxies for past ecological conditions

In addition to analysing diatom remains in the sediment, it is often useful to use a second ecological proxy to reconstruct past lake conditions. To that end, chironomid head capsules, which are usually well preserved in sediments, can be used to reconstruct historical chironomid communities. Chironomids tend to be sensitive to changes in organic sedimentation, oxygen concentration, and temperature (Merilainen et al., 2000; Hofmann, 1971a; Hofmann, 1978; Warwick, 1980; Wiederholm, 1980; Kansanen, 1985; Olander et al., 1997; Itkonen et al., 1999). Therefore, it was expected that assemblages of chironomid species would change as a result of eutrophication, as lower nutrient species assemblages would be replaced by species that are better adapted to deposition of higher levels of organic material (Devai & Moldovan, 1983) and reduced oxygen conditions at the sediment-water interface (Little et al., 2000). Certain chironomid taxa tolerate low oxygen concentrations through the use of haemoglobin (e.g., *Chironomus*), while others use behavioural adaptations (Little et al., 2000).

1.2.2 Physicochemical sediment properties

The physicochemical properties of sediment strata can be analyzed to reconstruct historical deposition of nutrients, trace metals and organic matter. These analyses provide supporting information for interpretation of sub-fossil data. Stable isotope ratios can be used to infer present and past nutrient source contributors to a reservoir.

1.2.2.1 Sedimentary phosphorus fractionation

In addition to anthropogenic nutrient sources, prairie lakes such as Lake Diefenbaker tend to be contained within catchment areas that are naturally rich in phosphorus (Schindler et al., 2008; Prepas & Trew, 1983). This phosphorus tends to be deposited into aquatic ecosystems in its pentavalent form, either dissolved in solution or bound to particulate matter (Correll, 1998).

Once in the water column, phosphorus may be released from particulate matter and, following the formation of orthophosphate through hydrolysis reactions, becomes available to algae, bacteria and plants (Correll, 1998). Once released into aquatic systems, phosphorus tends to be retained within the system through a combination of biological uptake of orthophosphates and through sedimentation of particulates and biological remains. As such, the combination of phosphorus conservation in aquatic systems, and phosphorus loading as the result of natural and anthropogenic processes, can cause serious changes to aquatic ecosystems.

The proliferation of cyanobacterial blooms (commonly referred to as blue-green algal blooms) as a result of increased nutrient inputs is a major concern for Lake Diefenbaker. Cyanobacteria are nitrogen-fixing bacteria and, according to the resource competition theory (Tilman et al., 1982), these organisms should out-compete other algal species under nitrogen limiting conditions. Therefore, if a lake experiences low nitrogen to phosphorous (N:P) ratios, cyanobacterial species should outcompete other non-nitrogen fixing bacteria (Tilman et al., 1982) resulting in cyanobacterial blooms. Under eutrophic conditions the high productivity of the cyanobacterial community is capable of producing periodic anoxic conditions at the sediment-water interface. These anoxic conditions cause a reduction and subsequent solubilisation of iron compounds from sediment, leading to the release of iron-bound phosphorus into the water column (Lukkari et al., 2007). This can cause a self-perpetuating cycle of decreasing water quality. An investigation into the phosphorous geochemical fractionation of the sediment of Lake Diefenbaker was intended to improve our understanding of phosphorous loading and phosphorus sources into and within this reservoir.

Phosphorus geochemical fractionation is useful in reconstructing past trends of nutrient inputs into Lake Diefenbaker. Three different sedimentary forms of phosphorous can be analyzed using the procedures outlined by Williams et al. (1976b): non-apatite inorganic phosphorous, apatite inorganic phosphorous and organic phosphorous. Non-apatite inorganic phosphorus represents the sedimentary phosphorus that is mostly bound to iron oxide, aluminum oxide, or hydroxide groups (Ruban and Demare, 1998). Under certain redox conditions, this phosphorus fraction may become mobile and thus available for biological uptake. The apatite inorganic phosphorus fraction consists of orthophosphates that are bound to calcium and are involved in the structure of apatite (Ruban and Demare, 1998). This fraction of phosphorus is redox insensitive and relatively immobile in sediments. It is therefore unavailable for biological uptake. Finally, organic phosphorus is phosphorus that is bound to organic matter and, under certain conditions (i.e., microbial degradation), can be released and made available for biological uptake (Ruban and Demare, 1998).

Changes to total concentrations of sedimentary phosphorous and phosphorus speciation in the different sediment layers can help to better understand the past nutrient status of Lake Diefenbaker. It should also help improve our understanding of the potential release of soluble forms of phosphorous into the water column, under certain environmental conditions (e.g., potential future reducing conditions).

Huptfer et al. (1995) describe how increases in phosphorus concentrations of surficial sediments, relative to deeper sediment profiles, have been interpreted in three ways. The first interpretation is that increased temporal sedimentation of phosphorus can occur due to increased eutrophication in some lakes (e.g., Jorgensen et al., 1975; Kamp-Nielsen, 1974). In other lakes this increasing trend can be explained by upward migration of dissolved phosphorus from deeper sediment horizons, with subsequent precipitation within surficial sediment layers (e.g., Kemp et al., 1974; Carignan and Flett, 1981). Finally, in other lakes this increase can be explained through diagenic loss of phosphorus from deeper sediment layers as a result of sediment aging and biogeochemical processes (e.g., changing redox potentials, microbial processes) (Tessenow, 1975). Therefore, the use of sediment phosphorus profiles as a tool for inferring temporal lake conditions should be used cautiously. Total phosphorus concentrations within the vertical profile of sediments represent the net result of dynamic historical processes, such as biological transformation, adsorption, desorption, release, diffusion, precipitation, and mineralization (Huptfer et al., 1995). Since lake sediments vary substantially in burial rates, chemical compositions, deposition rates, and biogeochemistry, interpretation of sediment profiles should be evaluated on a case by case basis. Under certain conditions, phosphorus profiles have been used successfully to interpret temporal trends in primary productivity within water bodies (e.g., Williams et al., 1967a; Mayer et al., 2006; Hiriart-Baer et al., 2011). Using sediment phosphorus profiles as a paleolimnological tool for interpreting temporal lake conditions should be evaluated based on a weight of evidence approach with other sediment measurements to ensure inferences derived are supported.

1.2.2.2 Stable isotope ratios

The phenomenon of isotopic variation is a mass-dependent phenomenon where chemical elements occur in the environment with a different number of neutrons in their nucleus (Peterson & Fry, 1987). Isotopes of the same element behave similarly in the environment since they have similar chemical properties. The addition of neutrons adds neutral mass to the atom, and does not affect the elements reactivity (Peterson & Fry, 1987). The atomic mass difference does, however, affect accumulation rates into organisms. Typically, the lighter isotope of an element can diffuse across the cell membrane of biological organisms at a greater rate than the heavier isotope of the same element (Peterson & Fry, 1987). In addition, many enzyme systems are able to distinguish isotopes, leading to enrichment of the preferred isotope. This can result in changes in isotopic ratios in the sediment profile that can be quantified using mass spectrometry techniques. Carbon and nitrogen stable isotopic ratios, as well as the C/N ratio within sediment, can indicate natural organic matter sources and thus discriminate natural from anthropogenic organic matter inputs in a system (Ruiz-Fernandez et al., 2002). The C/N ratio, carbon stable isotope ratios and the nitrogen stable isotope ratio have also proven to be reliable tracers that can discriminate between phytoplankton and terrestrial plant organic matter origins (Ruiz-Fernandez et al., 2002). Nitrogen stable isotope ratios have also been shown to be reliable tracers of organic matter deposits derived from human wastes, commercial fertilizers, soil organic nitrogen nitrate, and animal waste nitrate (Ruiz-Fernandez et al., 2002; Aravena et al., 1993). The goal was to determine the major historical organic matter source contributors in Lake Diefenbaker through the utilization of the stable isotope ratios of carbon, nitrogen and sulphur.

1.2.2.3 Stable isotope ratio for carbon

Organic matter content (measured as total organic carbon or TOC) represents an important physicochemical property of the sediment profile due to its function in the sorption of non-polar and non-ionic organic solutes and many trace metals from the overlying surface water (Kile et al., 1999; Chiou et al., 1983). The carbon isotopic ratio $^{13}C/^{12}C$ is influenced by a variety of factors in aquatic systems. One factor is the isotopic ratio in the dissolved inorganic carbon, which is influenced by the preferential uptake of the lighter ^{12}C isotope by photosynthetic organisms (Bernascon et al., 1997). Another factor is how temperature fluctuations affect the isotopic ratios between dissolved carbon dioxide and bicarbonate ions (Bernasconi et al., 1997; Mook et al., 1974). The bicarbonate ion is typically more enriched in ^{13}C than carbon dioxide at temperatures ranging from 5 to 25^{o}C (Bernasconi et al., 1997; Mook et al., 1974). Finally, phytoplankton communities can influence carbon isotopic ratios due to their preferential uptake of ^{12}C. In order to properly interpret trends in the ratio of $^{13}C/^{12}C$ ($\delta^{13}C$) the measured values must be normalized to account for the Suess Effect, which is a historical depletion of $\delta^{13}C$ as a result of anthropogenic fossil fuel burning. This normalization requires sediment horizons to be properly dated. As radiometric dating (^{210}Pb and ^{137}Cs) techniques are not applicable to Lake Diefenbaker due to its relatively recent formation in 1967, a correction for the Suess Effect was not possible. Therefore, $\delta^{13}C$ values are presented in Appendix B, but are not interpreted in the body of this thesis.

1.2.2.4 Stable isotope ratio for nitrogen

The nitrogen isotopic ratio in the sediment profile is determined as the ratio between ^{15}N (heavier and less abundant) and ^{14}N and can be used to differentiate between autochthonous and allochthonous sources of sedimentary materials. The nitrogen isotope ratio can also be used to identify the ammonium and nitrate originating from industrial and residential areas. Phytoplankton also tend to favour accumulation of the lighter ^{14}N isotope during their growth. As a result, their organic nitrogen profile tends to contain less ^{15}N than the nitrate in the surrounding surface water (Bernasconi et al., 1997; Altabet & Francois, 1994). Nitrogen stable isotope ratios have also been shown by Schwarcz (1991) to be reliable sediment tracers. Similar to carbon isotope ratios, nitrogen isotope ratios are consistently different in organic matter produced by terrestrial organisms in comparison to organic matter produced by aquatic organisms.

1.2.2.5 Stable isotope ratio for sulphur

Total sedimentary sulphur in sediment core samples can be analyzed as sulphur has important physicochemical properties that can influence the biological availability of phosphorous, as well as metals within the sediment. Sulphur has a strong ability to bind to iron in the sediment and can therefore isomorphically substitute for phosphorous at iron binding locations. Therefore, sulphur can displace phosphorus complexes in sediment and make phosphorus readily available for biological uptake.

Sulphur stable isotopes ratios have been used to differentiate between benthic and pelagic contributors of sedimentary sulphur, rooted-marsh plants versus phytoplankton-based sedimentary sulphur contributors, and evaluate point-source signatures of sulphur loading (Hobson, 1999; Peterson & Fry, 1987; Krouse, 1988; Krouse & Grinenko, 1991). Phytoplankton populations have only a small effect (1-2%) on sulphur isotope ratios (Peterson & Fry, 1987). Sulphur isotope ratios have, however, been known to fractionate at effects as great as 70% in some marine sediments due to dissimilatory sulphate reduction (Peterson & Fry, 1987). It was hypothesized that organic matter contributions from aquaculture could be traced using sulphur stable isotopes. Aquaculture (Wild West Steelhead Fish Farm) on Lake Diefenbaker sustains their rainbow trout on marine fish food. Therefore, it was hypothesized that the organic matter produced from the aquaculture operation would carry a distinct sulphur signature (e.g., increasing $\delta^{34}S$ over time). Following sediment core analysis of sulphur stable isotopes for five selected locations within Lake Diefenbaker, a characteristic signature was not observed. Due to the high cost of this analysis, the sediment core sulphur stable isotope analysis was limited to these five sites. The results of this analysis are shown in Appendix A.

1.2.2.6 Total metals

Trace metals were not expected to be found at toxic concentrations in sediment within Lake Diefenbaker. Never-the-less, there was a need to quantify trace metal concentrations to evaluate long-term metals trends. Reservoirs such as Lake Diefenbaker tend to be more susceptible to metal contamination due to common release of municipal wastewater into these systems (Balogh et al., 2009). Using sediment core samples it is possible to trace historical trends in anthropogenic loading to the reservoir due to settling particulate matter acting as a sink for trace metals (Balogh et al., 2009). Trace metals can also influence phosphorus availability. By evaluating the trace metals trends within sediment samples, inferences regarding the form and availability of phosphorus can be made. For example, iron can bind to phosphorus under certain conditions and decrease phosphorus bioavailability. Trends in trace metals can thus influence whether sediments act as a net source or net sink of phosphorus in Lake Diefenbaker.

1.3 Whole-sediment toxicity testing using Chironomus dilutus

Based on proximity to two potential sources of contaminants and nutrients, two field sites were identified as having the greatest potential for sediment toxicity (sediments near the Wild West Steelhead fish farm and Swift Current Creek outflow). According to Vermuelen (1995), anthropogenic activities often produce complex mixtures of pollutants that consist of metals, pesticides, and organic xenobiotics. Sediments can become contaminated through the deposition of such organic and inorganic contaminants (Rosiu et al., 1989). In reservoirs, the degree of contamination of the sediment is determined based on partition coefficients (i.e., availability) of the contaminants, particulate deposition rates and transport dynamics, and the specific characteristics (i.e., redox potentials, water and sediment chemistry) of the reservoir (Rosiu et al., 1989).

Whole-sediment toxicity tests were conducted on the upper layer of the cores to determine if the sediments were of toxicological concern. For the purposes of this study, analysis of the specific contaminants contained within the sediment profile (beyond trace metals and ammonia) were not conducted, unless some cores proved to be highly toxic, as extensive analysis would be time consuming and expensive (Vermeulen, 1995; Giesy & Hoke, 1989). Furthermore, environmental degradation and transformation processes can create new chemicals with different toxic mechanisms that would further complicate an identification process (Vermeulen, 1995). Thus, whole-sediment toxicity tests were used to provide an inexpensive and time efficient method of collecting ecologically relevant toxicity data.

1.4 Study objectives and hypothesis

The overall goal of this study was to reconstruct and interpret water quality trends (particularly in regard to nutrients), and hence environmental quality trends, in Lake Diefenbaker. As such, the objective of this investigation was to answer the following questions (null hypothesis listed in parenthesis):

1) Has the nutrient status (especially phosphorus) of Lake Diefenbaker changed over time since the creation of the reservoir? (H_0: Phosphorus concentrations in Lake Diefenbaker sediments have not changed significantly over time).
2) Have the diatom or chironomid communities in Lake Diefenbaker changed over time? If so, do changes correlate with water quality changes inferred from past and present sediment physicochemistry within Lake Diefenbaker? (H_0: The diatom and chironomid communities have not changed significantly over time).
3) Are sediments in Lake Diefenbaker, in proximity to point sources of contamination, toxic to *Chironomus dilutus*? Although the majority of sediments in Lake Diefenbaker are not anticipated to pose a toxicological threat to the associated benthic biota, sediments in proximity to key point sources of contamination (e.g., Swift Current Creek outflow and in proximity to the Wild West Steelhead aquaculture operation) have never been evaluated for toxicity. (H_0: Sediments in Lake Diefenbaker in close proximity to point sources of

contamination will show no significant toxic effects on survival or growth of *Chironomus dilutus*.)

CHAPTER 2:
Reconstructing temporal trends in reservoir productivity and nutrient availability within Lake Diefenbaker, a Great Plains reservoir, using depositional sediments[1]

2.1 Abstract

Recent anecdotal evidence has suggested that Lake Diefenbaker, a large reservoir in southern Saskatchewan, Canada, has been experiencing an increased frequency and severity of algal blooms, suggesting decreasing water quality. Due to limited historic water quality monitoring, a paleolimnological investigation of Lake Diefenbaker sediments was conducted in order to interpret spatial and temporal trends in the physicochemistry of eight collected sediment cores. Total phosphorus and three sediment species of phosphorus (apatite inorganic phosphorus, non-apatite inorganic phosphorus (NAIP) and organic phosphorus (OP)) were measured to interpret nutrient loading trends. Historical primary productivity was inferred based on total organic carbon, total nitrogen, $\delta^{15}N$ values and the organic carbon to nitrogen (C:N) ratio of collected sediment cores. Up-reservoir sampling locations showed consistent sediment concentrations of total phosphorus and the three species of phosphorus, organic carbon, nitrogen, $\delta^{15}N$ values and in the C:N ratio in the vertical profile. This suggested relatively consistent nutrient loading and primary production in the up-reservoir regions. Down-reservoir sediment cores showed an increasing trend in total phosphorus concentration, mainly in the more biologically available NAIP and OP fractions, and enrichment in organic carbon, nitrogen and $\delta^{15}N$ in more recently deposited sediments. This coupled with a decreasing C:N ratio trend in more recent sediments suggested increased nutrient loading to the sediments and increasing primary productivity at down-reservoir sites. Strong correlations ($p < 0.05$) between sediment

[1] Lucas B.T., Liber K., L.E. Doig. Reconstructing temporal trends in reservoir productivity and nutrient availability within Lake Diefenbaker, a Great Plains reservoir, using depositional sediments. Journal of Great Lakes Research. (In preparation).

total organic carbon content and the more biologically available sediment phosphorus fractions (NAIP and OP) suggest that phosphorus deposition patterns are strongly influenced by primary productivity within the reservoir.

2.2 Introduction

Lake Diefenbaker is a man-made reservoir created through the flooding of a portion of the South Saskatchewan River valley in 1967, after construction of the Gardiner and Qu'Appelle dams (Environment Canada, 1988). It is a major body of water on the Canadian prairies and supplies approximately 65% of Saskatchewan's drinking water. This multi-purpose reservoir also supplies water for industrial and agricultural purposes, aquaculture (Wild West Steelhead fish farm), hydroelectric power generation (Gardiner Dam), and maintains an important sport fishery. The majority (~95%) of the land bordering the reservoir is used for crop production (wheat, barley, canola) and cattle ranching (Hall et al., 1999).

Recent anecdotal evidence suggests that the occurrence and frequency of algal blooms have been increasing within the reservoir, possibly indicating decreasing water quality. Due to limited historical monitoring of the reservoir, few empirical data are available to assess current and past water quality conditions and trends. To set realistic management goals, management strategies require an understanding of historical environmental conditions, as well as long term trends. This study was designed to address these knowledge gaps through the use of paleolimnological techniques, which are commonly used to assess temporal trends in key variables within lake sediments. The main goal of this study was to answer the questions: has the nutrient status of Lake Diefenbaker changed over time, and has primary productivity within Lake Diefenbaker changed over time?

The limited availability of historical data regarding limnological conditions in Lake Diefenbaker, poses a problem for establishing environmental trends and determining the magnitude of any changes in environmental conditions (i.e., water quality) in the reservoir that may have occurred over time. Hecker et al. (2012) determined that phosphorus was the limiting nutrient of most concern for primary productivity within Lake Diefenbaker. The present study determined phosphorus concentrations and speciation within the vertical profile of depositional sediments from various locations along Lake Diefenbaker. This was done to better understand spatial and temporal trends in loading of this nutrient, as well as phosphorus dynamics within the reservoir. Total sedimentary phosphorus concentrations (TP) and three geochemical forms of phosphorus (apatite inorganic, non-apatite inorganic, and organic) contained in Lake Diefenbaker sediments (based on Williams et al., 1967a; Mayer et al., 2006; Hiriart-Baer et al., 2011) were investigated. Apatite inorganic phosphorus (AP) represents orthophosphates bound in a crystal lattice within apatite grains. Typically, this fraction is chemically stable and very insoluble in surface waters. Non-apatite inorganic phosphorus (NAIP) represents all remaining orthophosphates bound to particulate matter. This fraction typically consists of orthophosphates bound to metal oxides (iron, manganese and aluminum oxides) and hydroxide groups. This fraction tends to be redox sensitive. Organic phosphorus (OP) represents phosphorus associated with carbon. This fraction is typically made up of C-O-P or C-P bonds within the sediment.

The chemical speciation of phosphorus within the vertical profile of sediment cores can provide information regarding temporal trends in TP loading in lakes and reservoirs (e.g., Mayer et al., 2006; Williams et al., 1967a) and temporal trends in the loading of biologically available forms of phosphorus over time (Hiriart-Baer et al., 2011). Phosphorus in freshwater sediments can originate from either detrital or non-detrital sources (Bostan et al., 2000, Williams et al., 1967a). The AP form is typically derived from surface run-off events and erosional processes of banks of the water body and is in a similar chemical form to the surrounding soils, rocks and minerals in the watershed (Bostan et al., 2000; Williams et al., 1967a). This form tends to be quite insoluble in the water column and is typically not biologically available (Hiriart-Baer et al., 2011; Williams et al., 1976a; Williams et al., 1980). The NAIP and OP fractions are typically of non-detrital origin. As such, it is typically assumed that these fractions are in solution prior to either being mineralized or deposited to sediments in an organic form. Therefore, changes in concentrations of these fractions in the sediment profile can suggest temporal alterations in loading of more biologically available forms of phosphorus to aquatic environments (Hiriart-Baer et al., 2011).

Lake Diefenbaker is a man-made reservoir and, as such, water levels and thus water flow vary both temporally and spatially. These changes can greatly influence sediment deposition patterns, the erosion of banks surrounding the reservoir, and turbidity within the water column (Baxter, 1977). All of these factors can influence spatial and temporal patterns in phosphorus deposition, availability and sequestration.

Based on hydrological and limnological characteristics, reservoirs can often be divided into three zones. In long, narrow reservoirs such as Lake Diefenbaker, up-reservoir locations tend to be more like a river in character. Compared to down-reservoir sites, this region is characterized as being narrower, having greater flow rates, increased turbidity and an advective nutrient supply (Kimmel et al., 1990; Kimmel & Groeger, 1984). Down-reservoir locations closer to the outflow are typically more lacustrine, having features more similar to a lake. This zone is characterized by a wider and deeper basin, slower flow rates, having greater contributions of *in situ* nutrient cycling, and is typically less turbid than up-reservoir locations (Kimmel et al., 1990; Kimmel & Groeger, 1984). A transition zone is located between the up-reservoir riverine zone and the down-reservoir lacustrine zone and has features intermediate to the two (Kimmel et al., 1990; Kimmel & Groeger, 1984). The size and location of the transition zone can vary temporally due to changes in flow regimes. Different spatial conditions are present within most reservoirs. Temporal trends in the sediment profile must therefore be interpreted with this concept in mind.

In addition to phosphorus analyses, other variables were investigated to provide supporting data for trend interpretations. These included total organic carbon (TOC) and total nitrogen (TN) and the $^{15}N/^{14}N$ isotopic ratio ($\delta^{15}N$), all of which have been used extensively to investigate temporal trends in autochthonous primary productivity within lakes. The ratio between the TOC and TN (C:N ratio) can help differentiate between autochthonous and allochthonous organic matter sources (Meyers & Ishiwatari,1993; Meyers & Lallier-Vergès, 1999). Temporal decreases in the C:N ratio indicate increased input of autochthonous organic matter due to autochthonous sources containing less lignin (high aromatic carbon content) compared to allochthonous organic matter sources. Increases in lake primary productivity are also typically associated with enrichment in the ^{15}N isotope due to a decreased availability of the lighter ^{14}N isotope, which is preferentially incorporated by algae (Shelske & Hodell, 1995). Increases in primary productivity overwhelm the ability of surface waters to replace ^{14}N stores with dissolved N_2 from the atmosphere, and enrichment in the ^{15}N isotope occurs in the autochthonous organic matter. Temporal increases in sediment $\delta^{15}N$ values have also been associated with increased loading of anthropogenic inputs of nitrogen from fertilizers in surface run-off and municipal waste water effluents (Talbot, 2001; Sweeney & Kaplan, 1980; Heaton, 1986; Owens 1987).

2.3 Materials and methods

Lake Diefenbaker is a relatively large reservoir that currently covers 500 km^2 of previously prairie grassland and has a maximum storage capacity of $9.4x10^9$ m^3 of water. It reaches a maximum depth of 62 m and has an average annual water level fluctuation of 6.3 m (Hall et al., 1999). Sediment cores were collected from six locations along the reservoir between May and October of 2011 (sites 1, 2, 4, 5, 6, and 7) and two locations between July and August of 2012 (sites 3 and 8) (Figure 2-1). Sites were selected to assess spatial trends in nutrient dynamics and primary productivity within the reservoir. Sites 2 and 5 were in proximity to two possible point sources of nutrient contamination: Site 2 near the outflow of Swift Current Creek which contains municipal effluent from the City of Swift Current (population: 17,535), and Site 5 near the Wild West Steelhead Fish Farm, a substantial aquaculture facility (licensed annual fish production: 1,450 tonnes).

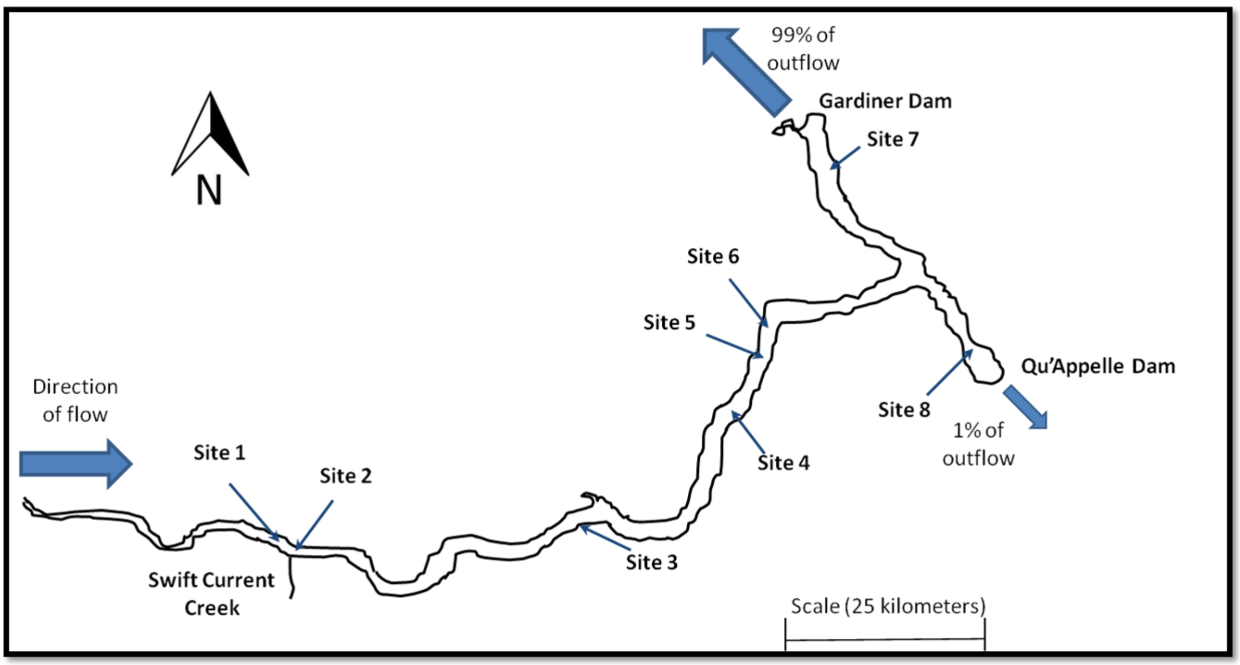

Figure 2-1. Lake Diefenbaker sediment core sampling locations (Saskatchewan, Canada) used in 2011 and 2012. All cores were collected from mid-channel locations.

All sediment cores were collected using a GLEW Gravity Corer (John Glew, Kingston, ON, Canada) and acrylic core tubes with a 7.5 cm diameter and 61 cm length. All cores were collected from mid-channel locations. Sediment core samples were capped on site and transferred into coolers engineered to hold the cores in an upright position during transport. The cores were transported on ice back to the Toxicology Centre at the University of Saskatchewan (Saskatoon, Saskatchewan, Canada) and stored in the dark at 4^{o}C prior to sectioning and analysis.

Sediment cores were sectioned under a nitrogen gas stream at 1-cm increments using a Glew core extruder. The sediment subsections removed for physicochemical analysis were then frozen at -20^{o}C and freeze-dried in a Dura-Dry multiprocessor corrosion control freeze-drier (FTS systems™, Stone Ridge, NY, USA). The freeze dried material was ground into a fine powder and stored in the dark in small plastic snap cap vials until analysis.

One limitation of this paleolimnological investigation was the inability to assign dates to the sediment core subsections. Due to the relatively recent creation of the reservoir in 1967, radiometric dating techniques (e.g., Pb^{210}, Cs^{137}) were not applicable. Down-reservoir sediment cores (sites 4, 5, 6, 7 and 8) all demonstrated a similar TP trend within their core profiles, indicating similar temporal coverage within their respected sediment core profiles. The year of reservoir formation (1967) was inferred in sediment Cores 5 and 7, based on an absence of diatom remains at a depth of 16 cm and 27 cm in their sediment core profiles, respectively. These results give confidence that these down-reservoir sampling locations provided a temporal profile covering the life span of the reservoir. The more up-reservoir sediment cores 1, 2 and 3 did not show the same increasing trend in TP as the down-reservoir sites and diatom remains persisted throughout all sediment sections within the sediment core profiles. Although these cores cannot be dated and the depth representing the date of reservoir formation was not established, the three collected sediment cores were 31 cm, 50 cm and 50 cm in length, respectively, and likely represent a substantial period of time relative to the life of the reservoir.

Sediment subsections were analyzed for total phosphorus concentrations, three sediment phosphorus species (AP, NAIP and OP), TOC, TN, TS, stable isotope content ($^{13}C/^{12}C$, $^{15}N/^{14}N$ and $^{34}S/^{32}S$), moisture content, total sediment metals, and particle size distribution. The following analyses were performed on freeze-dried material. Samples for analysis of total sediment phosphorus concentrations were first combusted at 550^{o}C followed by a 16 hour 1 M HCl extraction (Mayer et al., 2006). Total phosphorus concentrations in these extracts were determined using colorimetry (Harwood et al., 1967) with a Spectramax 190 spectrophotometer operated at 850 µm (Molecular Devices Corporation, Sunnyvale, CA, USA). The three sedimentary phosphorus species were determined using the harmonized extraction procedure outlined by Mayer et al. (2006) and quantification of extracts performed at 850 µm using a Spectramax 190 spectrophotometer. Total sediment metals were determined following complete sediment digestions using nitric acid, hydrogen peroxide, hydrofluoric acid and a MARS-5 microwave oven (CEM Corporation, Matthews, NC, USA), following standard procedures (Vonderheide et al., 2006; Dean, 2005; van de Wiel, 2004). This was followed by quantification of the digest using an X Series II ICP-MS (Thermo Electron Corporation, Winsford, Cheshire, UK). Particle size was determined with the mini-pipette method (Burt, 2009; Kaira & Maynard, 1991) and was performed by ALS laboratories Ltd., Saskatoon, SK, Canada. Due to limited remaining material following use in other sediment analyses, the top five 1-cm subsections from each site (1 to 8) were homogenized at equal masses to achieve a large enough sample to produce reliable particle size results. These results, as well as a detailed particle size profile of selected sediment core subsections from sites 2 and 6, are presented in Appendix C.

Prior to TOC, TN and stable isotope analyses, sediments were treated with 0.3 M HCl to digest inorganic carbonates. Samples were then oven-dried at 60^{o}C and approximately 30 mg of each sample added to tin capsules. Quantification of samples was performed on a Costech ECS4010 elemental analyser (Costech Analytical Technologies Inc., Valencia, CA, USA) coupled to a Delta 5 Advantage mass spectrometer (Thermo Scientific, Bremen, Germany. Total sulphur, and its stable isotopes ratios, were determined using a Carlo Erba NA1500 Series II Elemental Analyser **(**Costech Analytical Technologies Inc., Valencia, CA, USA) interfaced with a MAT 252 mass spectrometer (Thermo Scientific, Bremen, Germany) at the Stable Isotope Laboratory at Memorial University of Newfoundland (St. John's, NL, Canada). Total sulphur and δ^{34}S values are presented in Appendix A. δ^{13}C values are presented in Appendix B. TN and δ^{15}N values are presented in the following results of Chapter 2.

2.3.1 Statistics

Correlations between variables were determined using sediment cores 1 through 7. Sediment core 8, collected from the Qu'Appelle arm of the reservoir, receives a different flow regime (~1% of reservoir outflow; Saskatchewan Watershed Authority, 2012) and appears to be geochemically different compared to the other sites. All correlations were performed using the non-parametric Spearman rank correlation test ($p < 0.05$), with the exception of correlations involving distance down-reservoir. TP concentrations, TOC and δ^{15}N values in the top 1-cm of each sediment core (cores 1 through 7) were correlated with distance from Site 1, the upper most reservoir sampling site. These correlations were performed using the parametric Pearson product-moment correlation test ($p < 0.05$).

2.4 Results

Sediment TP concentration profiles (Figure 2-2) were similar in the sediment cores collected furthest up-reservoir (Sites 1 and 2). These up-reservoir sediment core samples showed relatively consistent TP concentrations throughout their entire core profiles with Site 1 averaging (± S. D.) 582 ± 44 mg of P/kg d.w. (dry weight) and Site 2 averaging 692 ± 50 mg of P/kg d.w. The concentrations of the NAIP, AP and OP fractions also showed relatively consistent concentrations throughout the core profiles. Site 1 had an average (± S. D.) of 64 ± 3 % AP, 24 ± 3 % NAIP, and 13 ± 3 % OP. Site 2 averaged (± S. D.) 52 ± 6 % AP, 23 ± 4 % NAIP and 24 ± 5 % OP.

A different trend was observed for TP and the three phosphorus fractions beginning at sampling Site 3 and included all the remaining down-reservoir sampling sites (4-8, Figure 2-2). At these down-reservoir locations, TP appeared relatively stable in the deepest sediment core subsections, but increased in the more recently deposited surface layers. In sediment core samples collected from Sites 3 to 7, the increase in TP concentrations in surficial sediment layers was driven primarily by increases in the NAIP fraction and to a lesser extent the OP fraction. NAIP fractions reached 54, 58, 44, 44 and 40% of the TP concentrations in the most surficial sediment subsection (0-1 cm) of Sites 3 to 7, respectively. OP fractions reached 21, 10, 31, 19 and 30% of the TP concentrations in the most surficial sediment layers (0-1 cm) of Sites 3 to 7, respectively. Apatite phosphorus concentrations were relatively constant throughout each core profile, with average concentrations (± S. D.) of 362 ± 40, 359 ± 37, 350 ± 28, 430 ± 37, and 385 ±30 mg of P/kg d.w. within sediment cores collected at Sites 3 to 7, respectively. Similar to other down-reservoir sites, Site 8, which was the only site sampled in the Qu’Appelle arm, displayed a similar increase in TP concentrations in surficial sediments as the main channel down-reservo

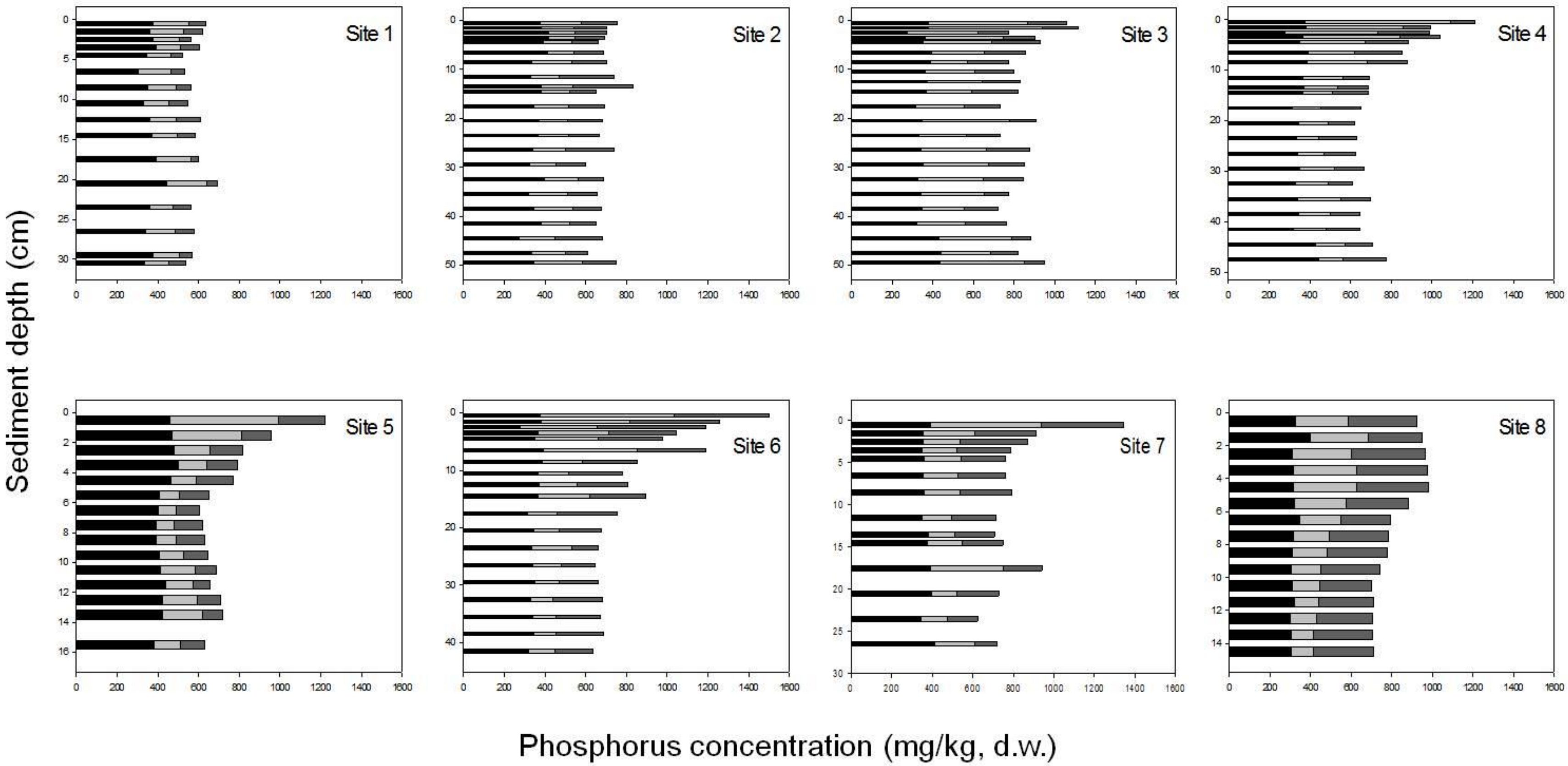

Figure 2-2. Total phosphorus and phosphorus species concentrations contained at specific depths within sediment cores collected from eight sites in Lake Diefenbaker, SK (2011-2012). Left to right, black bars represent AP, light grey bars represent NAIP, dark grey bars represent OP, and total phosphorus is represented by the summation of the three bars. Y-axis scale varies among sites.

sampling locations; however, the increase was driven to a greater extent by the OP fraction (48 % of TP in the 0-1 cm sediment subsection) and to a lesser extent by the NAIP fraction (17% of TP in the 0-1 cm sediment subsection). The historical trends in AP concentrations were similar to the other down-reservoir sampling locations and were relatively consistent throughout the length of the sediment core (340 ± 17 mg of P/kg d.w).

Sediment cores collected from Lake Diefenbaker showed both spatial and temporal trends in TOC content (Figure 2-3). All eight sediment cores showed temporal increases in TOC concentrations with the greater concentrations observed in most recently deposited sediments. This trend was exaggerated spatially and was most pronounced at down-reservoir sites, with the exception of Site 8. Sediment $\delta^{15}N$ values remained relatively constant at the two most up-reservoir sampling locations (Sites 1 and 2), but showed an increasing trend throughout the sediment core profiles within the remaining down-reservoir sampling sites (Site 3-8, Figure 2-3). The total organic C:N ratio (Figure 2-4) was relatively stable within the sediment cores collected from Sites 1 and 2. With the exception of Site 6, all down-reservoir sampling sites (3 to 8) showed a decreasing trend in C:N ratios in more recently deposited sediments.

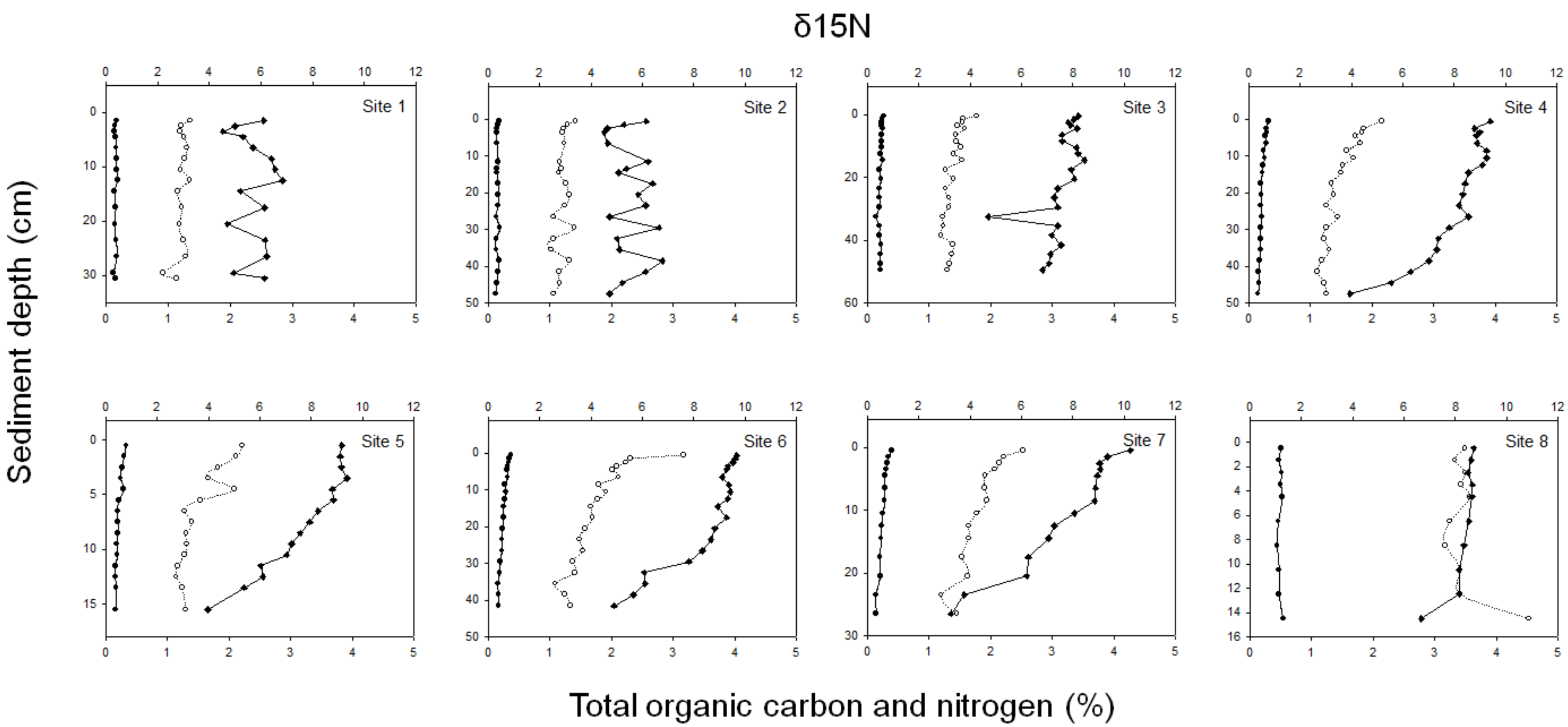

Figure 2-3.Total nitrogen (TN; black circles), total organic carbon (TOC; open circles) and $\delta^{15}N$ values (black diamonds) measured at selected depths within sediment cores collected from eight sites in Lake Diefenbaker, SK (2011-2012). Y-axis scale varies among sites.

Phosphorus enrichment factors were calculated by normalizing TP concentrations with sediment aluminum (Al) concentrations. Aluminum is a conservative metal and therefore normalization has been shown to be a good measure for assessing phosphorus loading trends and to aiding in the differentiation between phosphorus contributed from soils within the watershed (Kemp & Thomas, 1976) and phosphorus associated with non-natural sources, typically from anthropogenic activities (Mayer et al., 2006; Horowitz, 1991; Kemp & Thomas, 1976). The phosphorus enrichment factor (EF) was calculated using the following formula (Mayer et al., 2006):

$$EF = (P_x / P_d) \times (Al_d / Al_x)$$

Where P_x and Al_x are the total phosphorus and total aluminum concentrations, respectively, for the sediment section being calculated. P_d and Al_d are the total phosphorus and aluminum concentrations, respectively, in the deepest sediment subsection of the sediment core and thus represent historical conditions. An EF that is equal to 1 represents no change from historical conditions. An EF greater than 1 represents enrichment in phosphorus concentrations. Sites 1 to 3 displayed phosphorus enrichment factors consistently close to 1, suggesting no enrichment of phosphorus over time (Figure 2-5). Sites 4 through 8 had phosphorus enrichment factors greater than 1 in more recently deposited sediment, suggesting increased enrichment in phosphorus in recent years.

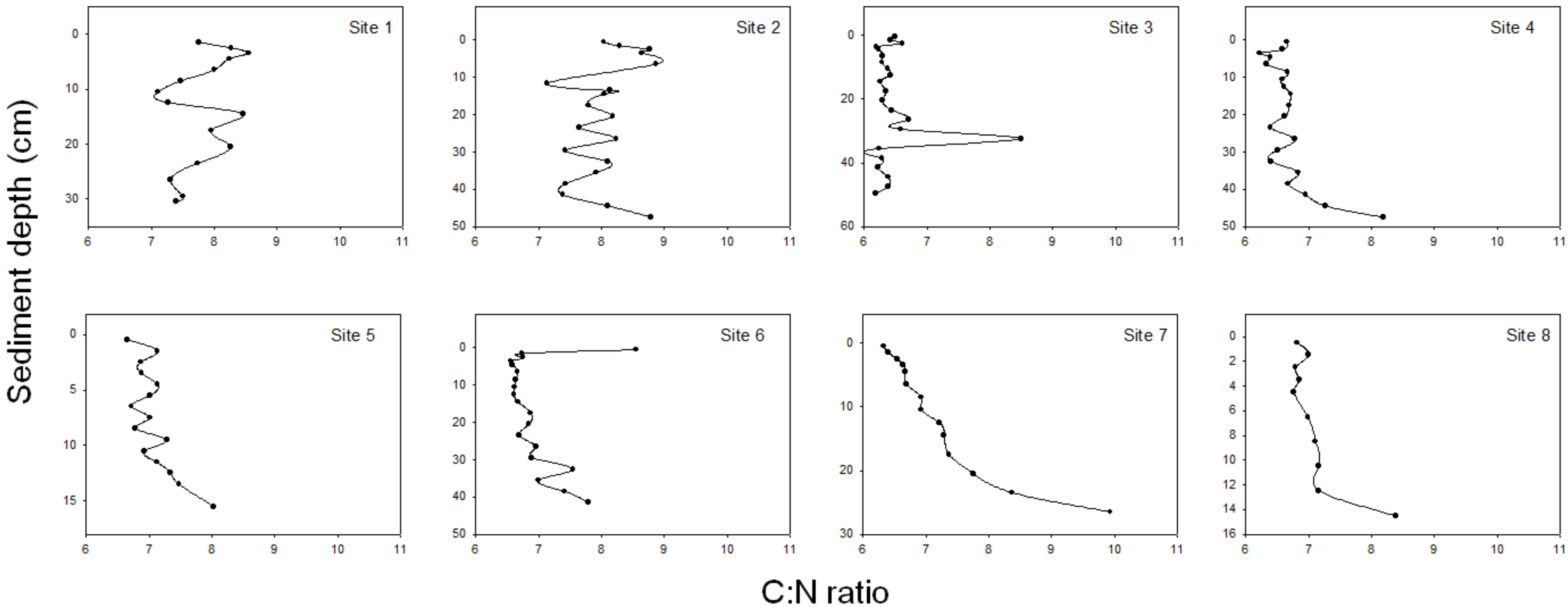

Figure 2-4. Total organic carbon to nitrogen (C:N) ratios of specific depths within collected sediment cores collected from eight sites in Lake Diefenbaker, SK (2011-2012). Y-axis scale varies among sites.

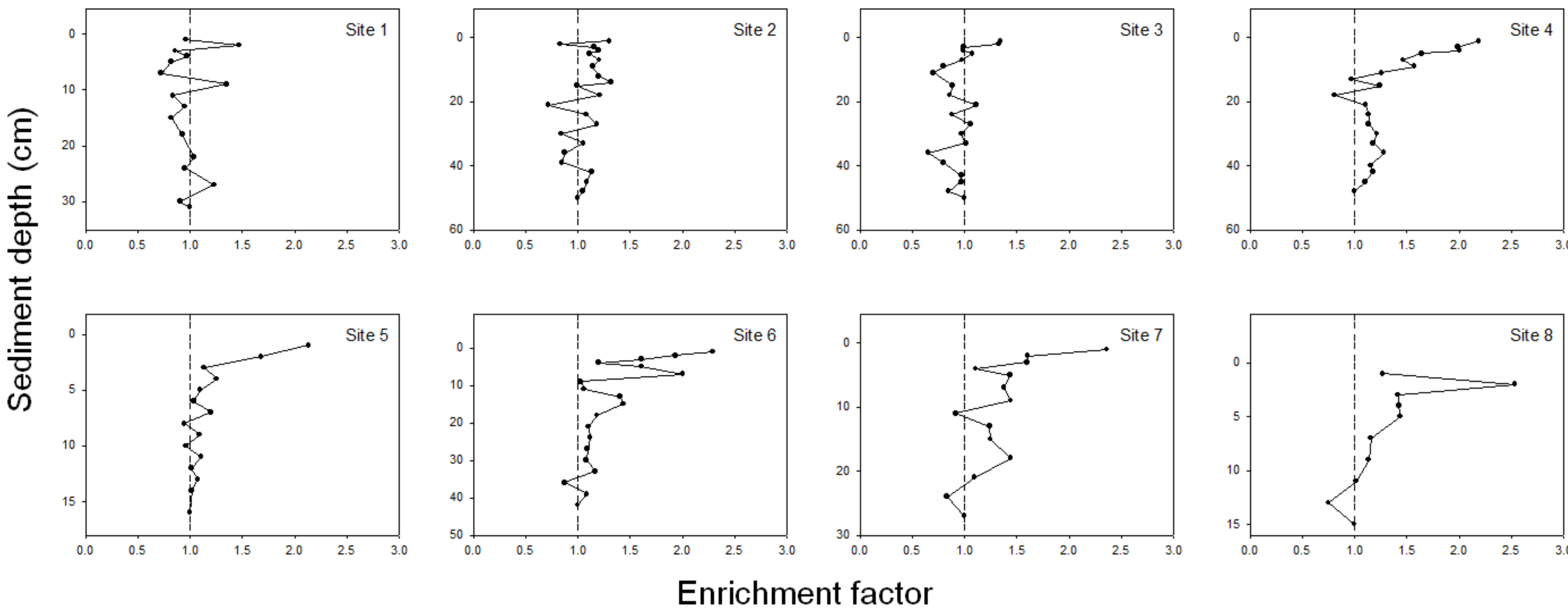

Figure 2-5. The phosphorus enrichment factor at specific depths of sediment cores collected from eight sites in Lake Diefenbaker, SK (2011-2012). An enrichment factor of 1 (dashed line) represents historical conditions. Y-axis scale varies among sites.

There was a strong and statistically significant correlation between TP and TOC (r = 0.643, $p < 0.0001$; Figure 2-6). OP and TOC displayed a lower correlation (r = 0.583, $p <$ 0.0001; Figure 2-6), while AP and TOC showed no significant correlation (r = 0.116, $p > 0.05$; Figure 2-6). Finally, the combined concentrations of the NAIP and OP fractions, the more biologically available phosphorus (Hiriart-Baer et al., 2011), were compared with TOC, and a similar correlation to that of the TP and TOC was observed (r = 0.633, $p < 0.0001$; Figure 2-6). Strong correlations were also observed with increasing distance down-reservoir (Sites 1-7) for TOC (r = 0.839, p = 0.0184), TP (r = 0.920, p = 0.0034) and $\delta^{15}N$ (r = 0.980, $p < 0.0001$) in the most surficial Lake Diefenbaker sediments (Figure 2-7).

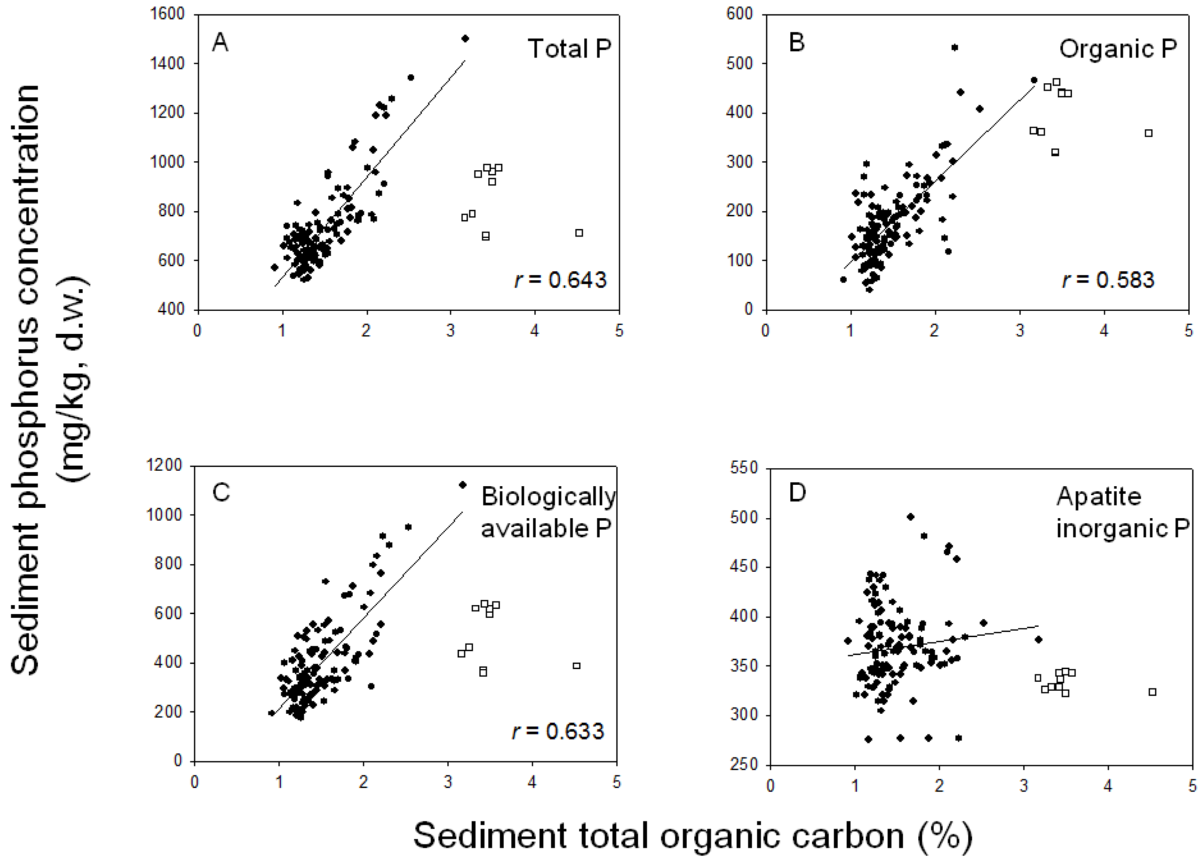

Figure 2-6. Correlations between sediment total organic carbon and sediment total phosphorus (A), sediment organic phosphorus (B), sediment biologically available phosphorus (NAIP + OP) (C), and sediment apatite inorganic phosphorus (D). All correlations were determined to be significant ($p < 0.05$), with the exception of total organic carbon versus apatite inorganic phosphorus ($p > 0.05$). Correlations were performed using data collected from Sites 1 to 7 (black circles). Data from Site 8 (white squares) are shown, but were not included in the correlation analysis. Y-axis scale varies.

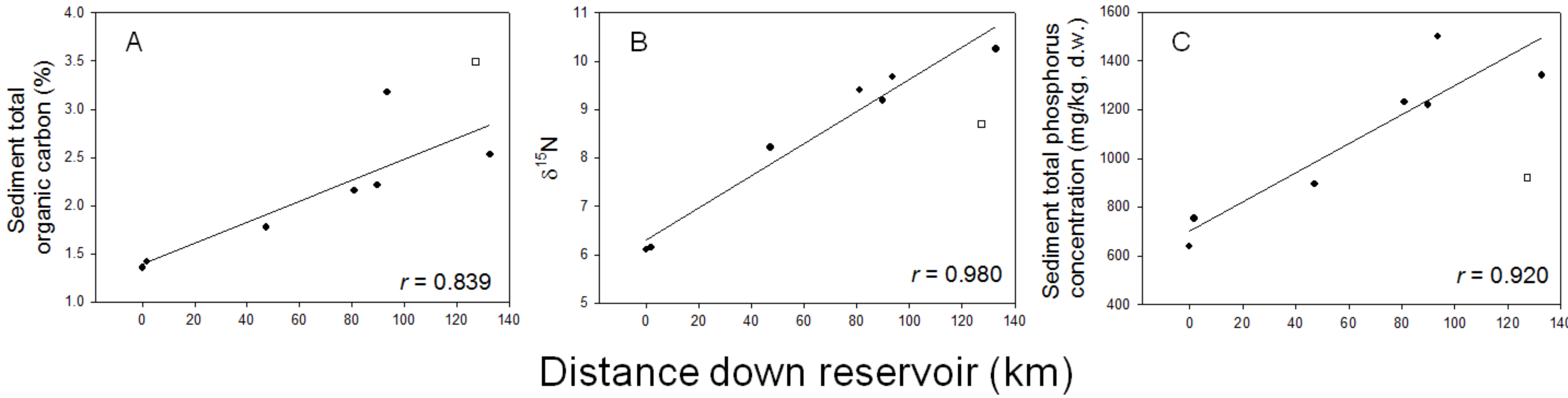

Figure 2-7. Correlation between distance down-reservoir and sediment total organic carbon (A), sediment $\delta^{15}N$ ratio (B), and sediment total phosphorus (C) in the top 1-cm subsection of collected sediment cores. All correlations were significant ($p < 0.05$) and were performed using data collected from Sites 1-7 (black circles). Data from Site 8 (white squares) are shown, but were not included in the correlation analysis.

2.5 Discussion

The physicochemical data from sediment cores collected along Lake Diefenbaker showed distinct spatial and temporal trends. Spatial trends are likely the result of hydrological and limnological processes common in reservoirs. Two regions were apparent and are referred to as up- and down-reservoir locations. Up-reservoir locations (Sites 1 and 2) have experienced relatively stable historical conditions. Down-reservoir locations (Sites 3 to 8) have undergone changes likely related to the aging of the reservoir.

Sediment total organic carbon content has increased over time at the majority of sites sampled in Lake Diefenbaker (Sites 1-7) and the magnitude of this increase was generally greater with distance down-reservoir (Figure 2-3). This is supported by the strong positive correlation between TOC in the top 1-cm of sediment and distance down-reservoir (Figure 2-7). This trend suggests increasing deposition of organic matter over time at down-reservoir locations. Although the Qu'Appelle arm (Site 8) had the highest TOC concentrations of all sites sampled, the relatively stable organic carbon concentrations at most measured depths suggests relatively consistent input of TOC to sediments throughout the temporal coverage of the sediment core.

The strong positive correlation between $\delta^{15}N$ values in surficial sediments and distance down-reservoir (Figure 2-7) further supports the conclusion that primary productivity has increased with increasing distance down-reservoir (Shelske & Hodell, 1995). Furthermore, the relatively stable C:N ratios and $\delta^{15}N$ values throughout the sediment core profiles of up-reservoir locations (Sites 1 and 2), suggest no major temporal shifts in the deposition of autochthonous organic matter (Meyers & Ishiwatari,1993; Meyers & Lallier-Vergès, 1999) and relatively stable in-lake primary productivity at these locations. Conversely, the decreasing trend in C:N ratio in more surficial down-reservoir sediments is consistent with a greater proportion of autochthonous organic matter being deposited to the sediment in more recent years (Meyers & Ishiwatari,1993; Tyson, 1995; Meyers & Lallier-Vergès, 1999). The enrichment in δ^{15}N in more recently deposited down-reservoir sediments is again consistent with increased primary productivity (Shelske & Hodell, 1995). Primary producers preferentially entrain the lighter ^{14}N isotope. However, increases in autochthonous primary productivity can overwhelm the capacity for dissolution of atmospheric ^{14}N. As a consequence, autochthonous organic matter becomes enriched with the ^{15}N isotope. Thus, based on multiple lines of evidence (Corg, C:N ratio and δ^{15}N values), primary productivity increases in magnitude along the length of Lake Diefenbaker. Temporally, stable primary production has been inferred up-reservoir, whereas primary productivity appears to be increasing at down-reservoir locations.

Sediment phosphorus deposition in surficial sediments also increased with increasing distance down-reservoir (Figure 2-7).The similar TP concentrations and phosphorus speciation profiles in the up-reservoir sediment cores (Sites 1 and 2; Figure 2-2) indicate relatively consistent nutrient loading to these sediments throughout the temporal period represented by the core profiles. Conversely, the increasing temporal trend in sediment TP concentrations observed in surficial down-reservoir sediments (sites 3 to 8; Figure 2-2) was driven primarily by increases in the more biologically available NAIP and OP fractions. The temporal increase of these phosphorus forms in down-reservoir sediments suggests increasing nutrient status down-reservoir and is consistent with a conclusion of increased primary productivity over time (Mayer et al., 2006; Hiriart-Baer et al., 2011).

The increase in the percent contribution of the OP fraction to TP concentrations in surficial sediments of the Qu'Appelle Arm of Lake Diefenbaker appear to support anecdotal observations of increased algal blooms occurring in and near this arm. On an annual basis, the

Qu'Appelle Arm of Lake Diefenbaker accounts for only about 1% of the main channel outflow from Lake Diefenbaker (Saskatchewan Watershed Authority, 2012). This results in more stagnant water and increased water clarity due to the settling of suspended solids, which could explain why OP increases are highest in this section of the reservoir. Alternatively, the reduced outflow and resulting thermal stratification within this arm, coupled with increased primary productivity, could lead to decreased oxygen concentrations at the sediment-water interface (Walker, 1979). Decreased oxygen levels could result in slower microbial decomposition rates and reduced conversion of OP into NAIP through microbial mineralization (Mayer et al., 2006). However, both hypotheses are speculative and cannot be differentiated by this study.

High turbidity can attenuate light and decrease depth of the photic zone. This could limit primary production in more turbid up-reservoir locations, even in the presence of high phosphorus availability (Kimmel et al., 1990; Kimmel & Groeger, 1984). This likely explains the relatively consistent primary productivity and nutrient status observed up-reservoir (Sites 1 and 2). Primary production at these sites has not increased overtime, possibly due to persistent light limitation (i.e., high turbidity) linked to reservoir morphology and hydrology.

The observed down-reservoir trends are likely linked to site location within the lacustrine zone, which generally has lower flow velocity, decreased turbidity due to the settling of suspended particulates, and a greater influence of *in situ* nutrient supply compared to the more riverine up-reservoir regions (Kimmel et al., 1990; Kimmel & Groeger, 1984). Regarding the latter, some portions of Lake Diefenbaker thermally stratify in the summer and fall (Environment Canada, 1988). Given that *in situ* nutrient cycling is typically more pronounced with distance down-reservoir (Kimmel et al., 1990; Kimmel & Groeger, 1984), internal loading of phosphorus from Lake Diefenbaker sediments may be a contributing factor to the inferred increases in primary productivity down-reservoir. Furthermore, the decreased turbidity historically observed at down-reservoir locations (Environment Canada, 1988) would increase the depth of the photic zone and thus reduce light limitation. Therefore, nutrients flowing from up-reservoir locations, or being remobilized from sediments into overlying waters, would theoretically be more accessible to phytoplankton, resulting in increased primary production compared to up-reservoir locations. This hypothesized increase in primary productivity at down-reservoir locations can be inferred based on increases in sediment TOC concentrations, increases in $\delta^{15}N$ values, and decreases in the C:N ratio in the most recently deposited sediments (Figure 2-7). The correlations between these variables and distance down-reservoir is consistent with continued settling of suspended sediments and increased water clarity further down-reservoir.

The observed increase in sediment TP concentrations at down-reservoir locations was likely driven primarily by increases in the more biologically available NAIP and OP fractions (Hiriart-Baer et al., 2011). Apatite inorganic phosphorus, which is mainly of detrital origin and typically not of biological significance, has remained constant both spatially and temporally within Lake Diefenbaker (Figure 2-2). It would be expected that with increasing primary productivity along the reservoir, that sedimentation of biologically incorporated phosphorus would increase at down-reservoir locations. This phosphorus fraction (NAIP + OP) should therefore proportionally increase in down-reservoir Lake Diefenbaker sediments compared to up-reservoir locations. This hypothesis was supported by the strong positive correlations observed between sediment TOC, a proxy for primary productivity, and both sediment TP concentrations and biologically available phosphorus (NAIP + AP) (Figure 2-6). Autochthonous organic matter sources tend to be more labile than allochthonous sources in lake sediments. Biological degradation of the more labile authochthonous sources, and mineralization of associated OP, has been implicated in contributing to increases in the NAIP fraction (Mayer et al., 2006). Therefore, increases in NAIP concentrations under certain conditions can be an indication of increased primary productivity. This likely explains why the NAIP fractions are increasing with increased distance down-reservoir and why the more biologically available phosphorus concentrations show a strong correlation to TOC within Lake Diefenbaker sediments.

The increasing concentrations of phosphorus in surficial sediments down-reservoir are most likely due to either increased anthropogenic loading of phosphorus over time, or to the aging process of reservoirs, or both. In the early years of reservoir formation, it would be expected that bank erosion would have contributed large amounts of suspended sediments to the water column (Baxter, 1977). The resultant high turbidity would likely have persisted for many years, eventually subsiding as suspended sediments settle (Nursall, 1952). This would have limited some phosphorus accumulation in sediments, as light limitation would have limited the ability of phytoplankton to sequester nutrients and deposit them to sediments. As water clarity has improved down-reservoir over time, phosphorus entrainment to sediments would have concomitantly increased due to increased primary productivity and settling of organic particles. The increasing trend in TP may also be influenced by increased anthropogenic loading of nutrients to the reservoir. The increase in phosphorus enrichment factors (Figure 2-5) in surficial sediments of down-reservoir sediment cores, of up to 2.5 fold that of historical concentrations, suggests phosphorus of anthropogenic origin is accumulating at down-reservoir locations (Mayer et al., 2006; Horowitz, 1991; Kemp & Thomas, 1976). Both mechanisms have merit and cannot be differentiated by this study. Future work should investigate their respective influences on nutrient dynamics in Lake Diefenbaker.

Complications can arise in primary productivity interpretations when diagenic decomposition of the organic matter within the sediment profiles occurs. However, this does not appear to be a major concern within Lake Diefenbaker sediments. Firstly, N-rich compounds contained within sediment organic matter tend to be some of the most labile constituents of sediment organic matter. This loss of nitrogen from the organic matter has the potential to increase the C/N ratio at depth within the sediment core profile, thus influencing conclusions made regarding organic matter sources (Bernasconi et al., 1997; Ostrom et al., 1998). This does not appear to be the case within Lake Diefenbaker as a diagenic loss of nitrogen would tend to cause enrichment of the $\delta^{15}N$ isotope with increased depth in the sediment profiles due to preferential uptake of ^{14}N by sediment bacteria (Wada, 1980). The case here was quite the opposite.

Complications in the interpretation of phosphorus loading trends can also result from diagenic processes that lead to upward migration of phosphorus within sediments as a result of changing redox potentials. Redox sensitive manganese in the sediment seem to influence phosphorus in Lake Diefenbaker sediments due to a significant correlation between manganese concentrations and TP (Data not shown; $r = 0.525$, $p < 0.0001$). This suggests that some orthophosphate species likely experience some upward migration within the sediment core profiles (Williams et al., 1967a). Deep water anoxia does not appear to be a current concern within Lake Diefenbaker (Rebecca North, University of Saskatchewan, 2013) and therefore remobilization of phosphorus from sediments into overlying waters is likely not a significant factor (Boyle, 2001). However, similar to the findings of Hiriart-Baer et al. (2011), the movement within the sediment profiles is likely transient due to the lack of a significant correlation between sediment TP and iron concentrations (Data not shown, $r = 0.079$, $p > 0.05$).

This suggests that significant upward movement of phosphorus is likely not occurring because of a lack of co-precipitation between iron and orthophosphates within the upper sediment core profiles (Carignan and Flett, 1981; Trolle et al., 2009; Hiriart-Baer, 2011). Furthermore, there was a strong correlation observed between TP and TOC, supporting conclusions that increased phosphorus deposition is likely associated with capture and sedimentation processes of primary producers (Trolle et al., 2009; Hiriart-Baer et al., 2011). Future research should be conducted to investigate the potential effects that changing dissolved oxygen concentrations at the sediment-water interface will have on the movement and dissolution of phosphorus from Lake Diefenbaker sediments.

2.6 Conclusions

Nutrient status and primary productivity within Lake Diefenbaker have exhibited spatial and temporal changes since reservoir formation. These changes largely appear to be a consequence of physical morphology and aging processes of the reservoir itself, rather than point sources of nutrient contamination. Primary productivity and nutrient entrainment in surficial sediments appear to be increasing with distance down-reservoir, likely due to differences in light availability as a result of decreasing turbidity with distance down-reservoir. Consistent organic matter and phosphorus concentrations accumulated in up-reservoir sediments suggest consistent primary productivity, nutrient input and mechanisms of entrainment over time. Increases in TOC content and $\delta^{15}N$ enrichment, and decreases in the C:N ratio all suggest increasing primary productivity at down-reservoir locations. The strong correlation between TOC and more biologically available phosphorus concentrations (NAIP and OP), suggest that the phosphorus entrainment within sediments is likely influenced by phosphorus availability, sequestration and subsequent sedimentation by primary producers. The resulting and ongoing increases in the redox sensitive NAIP fraction in surficial sediments is a concern, although anoxic conditions are not currently considered an issue within the hypolimnion of Lake Diefenbaker. Increased primary productivity and the resulting organic matter deposition and decay can lead to deep water anoxia, and therefore reduced redox potentials. Low redox potential could influence phosphorus remobilization. The potential for phosphorus remobilization under changing environmental conditions warrants further investigation.

CHAPTER 3:
Reconstructing historical diatom and chironomid community compositions to better understand trends in trophic status and primary productivity within a Great Plains Reservoir in Southern Saskatchewan, Canada[2]

3.1 Abstract

Following anecdotal reports of greater frequency and severity of algal blooms, a paleolimnological investigation of Lake Diefenbaker, a large reservoir in Southern Saskatchewan, Canada, was conducted to investigate spatial and temporal shifts in reservoir environmental conditions. Sediment core samples were collected along the length of Lake Diefenbaker to investigate spatial and temporal environmental trends. Sub-fossil remains of diatoms and chironomid larvae were isolated from selected subsections of sediment cores and identified to assess temporal shifts in community compositions and to infer historical changes in reservoir conditions. The compositions of diatom and chironomid communities were consistent over time at up-reservoir locations, with *Stephanodiscus parvus* dominating the diatom communities and *Procladius* dominating the chironomid communities. This suggests relatively stable and consistent trophic status and primary productivity in this region. Conversely, major shifts occurred in the diatom and benthic chironomid communities at down-reservoir locations. These shifts were consistent with typical reservoir ontogeny. A shift in dominance from *Stephanodiscus parvus* to *Asterionella formosa*, *Tabellaria flocculosa* and *Stephanodiscus medius* followed by a shift to *Aulacosiera ambigua* suggests an initial period of eutrophy, followed by a period of mesotrophy, and finally a transition into a more productive system in recent years. The increase in relative abundance of the chironomid tribe *Tanytarsini* suggests

[2] Lucas B.T., Liber K., L.E. Doig. Reconstructing historical diatom and chironomid community compositions in order to better understand trends in trophic status and primary productivity within a Great Plains Reservoir in Southern Saskatchewan, Canada. Journal of Great Lakes Research. (In preparation).

rising levels of organic matter sedimentation, likely due to increased autochthonous primary productivity. Up-reservoir locations are typically more riverine in character, whereas down-reservoir locations have more lacustrine characteristics. The more riverine locations appear to be more turbid than the down-reservoir locations, which appears to affect nutrient availability and thus primary production.

3.2 Introduction

Lake Diefenbaker is an important reservoir located in Southern Saskatchewan, Canada. It is a multi-purpose reservoir used for hydropower generation, aquaculture (Wild West Steelhead Fish Farm), sport fishing and recreation, and it provides high quality potable water for agriculture, industry and 65% of Saskatchewan's population. This reservoir was filled beginning in November of 1967 through the damming of the South Saskatchewan River with the Qu'Appelle and Gardiner dams (Environment Canada, 1988). Recent anecdotal evidence has suggested that the frequency and severity of algal blooms within the reservoir have increased over time, suggesting a potential overall decrease in water quality. Declining water quality is a concern due to its potential effects on the ecology of the reservoir and on the various intended uses of this water supply. Unfortunately, there are limited monitoring data available to assess historical and ongoing trends in the reservoir's water quality. Such data are necessary to effectively manage this water resource over the long term. Using a combination of paleolimnological techniques involving sub-fossil analyses, the goal of this investigation was to determine whether Lake Diefenbaker has undergone spatial or temporal shifts in primary production or trophic status since reservoir formation.

The analysis of sub-fossil remains (e.g., diatoms, invertebrates) preserved in sediments has been used extensively to interpret temporal changes in inland waters. Diatoms are single celled algae that possess a siliceous cell wall that tends to be well preserved in many freshwater sediments (e.g., Prat and Daroca 1983; Donar et al., 1996). Diatom remains are useful indicators of changes to lake trophic status (Bradbury, 1975; Batterbee, 1978a; Hall and Smol, 1992; Brugam, 1979, Whitmore 1989) because community composition responds quickly to changes in nutrient (Tilman et al., 1982; Kilham, 1984; Kilham et al., 1996) and light availability (Maberly et al., 1994; Talling, 1957). Lake Diefenbaker has been previously investigated (1995) using paleolimnological techniques, which included the analysis of diatom remains (Hall et al., 1999). However, Hall et al. (1999) limited their investigation to a single sediment core collected from the Qu'Appelle arm of Lake Diefenbaker. Three fundamental shifts in diatom species composition were observed over the temporal profile. These shifts were attributed to natural succession processes, driven by physical alterations due to anthropogenic flooding of the river valley. This investigation suggested high productivity and high nutrient status in the early years after reservoir formation due to the release of soluble nutrients from flooded prairie soils, rapid erosion of banks, high initial water residence time and the release of nutrients due to biodegradation of the flooded terrestrial organic matter sources (Hall et al., 1999; Ostrofsky and Duthie, 1978; Kennedy and Walker, 1990). This was followed by a period of decreased nutrient status and primary productivity, attributed to a decreased nutrient flux from the sediments (Hall et al., 1999; Nursall, 1952). Finally, the diatom remains in the most recently deposited sediments suggested that nutrient status and primary productivity have increased. It was hypothesized that these increases were most likely driven by either nutrient inputs from expanded aquaculture operations within the reservoir, or due to increased internal loading of nutrients (Hall et al., 1999). Given that the Qu'Appelle Arm of Lake Diefenbaker only receives approximately 1% of the annual flow of water through the reservoir (Saskatchewan Watershed Authority, 2012), the temporal trends within this arm might not be representative of the broader reservoir. The present study revisited the paleolimnological record of Lake Diefenbaker to assess temporal trends in nutrient status and primary productivity within the spatial context described below. Our primary objective was to determine if the diatom communities in Lake Diefenbaker have changed over time, and if so, what can be inferred from the observed changes regarding spatial and temporal trends in water quality.

Reservoirs come in many shapes and sizes, and have a multitude of hydrologic features. Nevertheless, some generalizations can be made. Kimmel and Groeger (1984) describe three regions that are typical in reservoir limnology; an up-reservoir riverine zone, a down-reservoir lacustrine zone and a transitional zone located between the two. The up-reservoir riverine zone has characteristics similar to a river, being relatively narrow and having a shallow basin, high flow velocity, high turbidity and an advective nutrient supply. The down-reservoir lactustrine zone has lake-like characteristics and is typically wider with a deeper basin, lower flow velocities, less turbidity and a greater contribution of *in situ* nutrient cycling. The characteristics of the transition zone are intermediate to the up-reservoir and down-reservoir regions. Because of the differences in limnological conditions that can occur spatially within reservoirs, spatial trends in reservoir conditions must be assessed, in addition to temporal trends, to best understand the system as a whole. In addition, by evaluating spatial trends in biological communities, the influence of point sources of nutrients, such as aquaculture facilities and urban effluents, can be assessed relative to that of non-point sources and processes, such as reservoir ontogeny.

In addition to the nutrient sources described above, the internal loading of nutrients from sediments could be increasing over time in Lake Diefenbaker. Sediments can act as sinks for various elements, including phosphorus. Depending upon phosphorus speciation and environmental conditions, sediments can change from a sink to a nutrient source. For example, when exposed to low redox potential at the sediment water interface, redox sensitive phosphorus can be liberated to the water column. With increased productivity comes an increase in deposition of organic matter to the sediment surface. When this organic matter breaks down, oxygen is consumed (Lukkari et al., 2007). Anecdotal observations of increased primary production suggest the possibility of decreasing dissolved oxygen (DO) concentrations over time at the sediment-water interface, thus possibly increasing seasonal internal loading of phosphorus. Increased nutrient availability can in turn further stimulate primary productivity and this process can have serious consequences for water quality (Lukkari et al., 2007)

Trends in chironomid remains preserved in the profiles of sediment cores can serve as reliable indicators of temporal changes in organic matter sedimentation and dissolved oxygen concentrations at the sediment water interface (Merilainen et al., 2000; Hofmann, 1971a; Hofmann, 1978; Warwick, 1980; Wiederholm, 1980; Kansanen, 1985; Olander et al., 1997; Itkonen et al., 1999). Certain chironomid taxa (e.g., *Chironomus*) can tolerate low oxygen concentrations through the use of haemoglobin, while others use behavioural adaptations (Little et al., 2000). Temporal trends in chironomid community composition can provide insight into the historical potential for low oxygen levels at the sediment water interface and thus the potential for increased internal loading of redox-sensitive nutrients. Our second objective was therefore to determine if the chironomid communities in Lake Diefenbaker have changed over time, and if so, what can be inferred from the observed changes regarding spatial and temporal trends in primary productivity and the potential for phosphorus remobilization.

Low chironomid head capsule counts have been previously observed in Lake Diefenbaker sediments (Hall et al., 1999). Therefore, there was a need to characterize the toxicity of Lake Diefenbaker sediments to chironomids to ensure that these low numbers were the product of the physical habitat (e.g., substrate, food availability), rather than a product of chemical toxicity. Therefore, this study also investigated the toxicity of key Lake Diefenbaker sediments to a model chironomid species, *Chironomus dilutus*. Two potential "worst case" sites were identified to investigate the potential for toxic effects, sediments in close proximity to the Wild West Steelhead Fish Farm and sediments near the outflow of Swift Current Creek, downstream of the city of Swift Current (Saskatchewan, Canada; population 17,535 as of 2011). Reference sites in proximity to these worst-case sites were also sampled for toxicity testing.

3.3 Methods and materials

Sediment core samples for diatom analysis were collected from eight locations along the length of Lake Diefenbaker (Figure 2-1). Sediment cores 1, 2, 4, 5, 6 and 7 were collected in September, 2011. Sediment cores 3 and 8 were collected in July, 2012. Six separate sediment cores were also collected from each of sites 1, 2, 5 and 6 in July, 2012. One sediment core from each of these four locations was processed for chironomid head capsule analysis. The remaining five cores for each site were used in a 10-day whole-sediment toxicity test (described below). Sampling sites 2 and 5 were chosen for toxicity testing as these sites are in proximity to anthropogenic point sources of waste input, the outflow of Swift Current Creek (Site 2, municipal effluent discharge) and adjacent to the Wild West Steelhead Fish Farm (Site 5, aquaculture activities). Sampling sites 1 and 6 were chosen as reference sites for the Swift Current Creek outflow and the Wild West Steelhead Fish Farm, respectively.

The banks of Lake Diefenbaker are generally steep and easily eroded. Therefore, all sediment cores were collected from main channel locations in order to minimize disruption of the sediment profile by the slumping of banks and wave action. All sediment cores were collected using a Glew gravity corer (John Glew, Kingston, ON, Canada) and acrylic core tubes having a 7.5-cm inner diameter and 61-cm length. After collection, sediment cores were capped, put on ice in an upright position and transported back to the Toxicology Centre (University of Saskatchewan, Saskatoon, SK, Canada) for storage in the dark at 4^oC. Sediment cores destined for diatom or chironomid head capsule analysis were later sectioned into 1-cm horizons under a constant nitrogen stream using a Glew core extruder. Sediment cores used in the whole-sediment toxicity tests were stored for a maximum of 32 days prior to testing.

3.3.1 Diatom sub-fossil remains

Subsamples (approximately 0.5g wet weight) of each 1-cm section of sediment core (sites 1 to 8) were placed in 20-mL glass vials and stored in the dark at 4^oC prior to digestion and mounting. Briefly, sediment subsamples were initially digested at room temperature in a small volume of 1M HCl and three drops of hexametaphosphate. This was followed by digestion at a temperature between 70 and 80^oC in a 1:1 mixture of concentrated HNO_3 and H_2SO_4. Once digestion was complete, each sample was rinsed with ultrapure water until the pH was neutral. Diluted sample slurries were dried onto glass microscope cover slips and then fixed onto glass microscope slides using Naphrax® (see methods of Hall and Smol, 1992). Diatom remains were identified using a Zeiss light microscope under 1000x magnification (Carl Zeiss Canada Ltd., Toronto, ON, Canada). A minimum of 300 diatom valves per sediment subsection were identified to the species or the lowest possible level of taxonomy.

The first five 1-cm sediment subsections of all eight sediment cores were analyzed for diatom remains, followed by every other subsection to a depth of 15 cm, and then every third 1-cm subsection until the bottom of the sediment core or until diatom remains were no longer present. The only exception to this was sediment core 5, where all sediment subsections were analyzed for diatom remains (remains ceased at a depth of 15 cm). Where diatoms ceased, this subsection was assumed to represent approximately 1967, the year of reservoir formation. Sediment cores 5 and 7 covered the entire temporal profile of the reservoir, as diatoms ceased prior to the end of the collected sediment cores. In all remaining sediment cores, diatom remains persisted to the bottom of the cores. Radiometric dating techniques (Pb^{210} and Cs^{137}) were not applicable in this study due to the relatively recent reservoir formation (1967). However, based on similar diatom profiles of key up- and down-reservoir sediment cores, all sediment cores collected likely represent a substantial period of time relative to the life of this reservoir.

3.3.2 Chironomid sub-fossil remains

A 30 g (wet weight) composite sample of every three 1-cm sediment subsections (10 g from each), from sediment cores collected from sites 1, 2, 5 and 6, were added to 50-mL polypropylene conical tubes and stored at 4^{o}C prior to analysis. Hall et al. (1999) previously found very low chironomid head capsule densities in the Qu'Appelle arm of Lake Diefenbaker. Therefore, large composite samples were used in this investigation to enhance the community composition analysis. Chironomid head capsule analysis was performed using standard procedures similar to those of Hall et al. (1999). Briefly, head capsules were isolated first through deflocculating composite sediment samples in 8-10% warm KOH. The samples were then rinsed with deionized water through 95-um Nitrex mesh (Wildlife Supply Company, Yulee, Florida, USA). The material retained was transferred to 50-mL polypropylene conical tubes for storage. The head capsules were then manually removed from the sieved material using a dissecting microscope and a Bolgorov counting tray (Wildlife Supply Company). All head capsules were mounted on glass cover slips and fixed to glass microscope slides using Entellan mounting medium (Electron Microscopy Sciences, Hatfield, PA, USA). Head capsules were then identified to genus or the lowest possible level of taxonomy and quantified by Aquatax Consulting (Saskatoon, SK, Canada) using light microscopy.

3.3.3 Whole-sediment toxicity test

Whole sediment toxicity tests were carried out in a controlled environmental chamber at a temperature of 23 ± 1^{o}C and a photoperiod of 16:8 light to dark hours (800 to 1300 lux).The top 5 cm of each core (5 replicates for each of the four sites) was extruded into an acrylic tube (diameter = 4.5 cm) and were both subsequently transferred to a 300-mL tall-form glass beaker. Care was taken to prevent disrupting the integrity of the upper sediment core profile. Test sediments and silica sand controls were then frozen in the dark at -20^{o}C for 48 hours to eliminate confounding factors associated with indigenous macro organisms inhabiting the sediment samples, as recommended by Day et al. (1995). Following thawing, sediments were tested for toxicity using ten 8 to 10-day old *Chironomus dilutus* larvae collected from a culture maintained at the Toxicology Centre. Tests were conducted following standard procedures (Environment Canada, 1997) for 10 days using a sediment testing intermittent renewal (STIR) system, modified after Benoit et al. (1993). Test units received temperature-controlled, carbon-filtered, bio-filtered, Saskatoon municipal water from a plexiglass head-tank and were gently aerated to maintain adequate oxygen concentrations. Water renewals were controlled by a timer and occurred every 6 hours for durations of 15-minutes. Each beaker containing test sediment had opposing 1.5-cm diameter holes in its side, at a height of 7-cm, that corresponded to opposing holes with an area of 16.5-cm^2 at a height of 4.5-cm in the acrylic tubes, to allow for water exchange. The beaker holes were covered with a stainless steel 25-um mesh and the acrylic tube holes were covered with 25-um nylon mesh. Test organisms were fed daily with 6 mg (d.w.) of Nutrafin^{TM} ground tropical fish food flakes, administered as a slurry to each glass beaker.

Overlying-water chemistry measurements, which included water hardness, alkalinity, conductivity, pH, and ammonia concentrations, were performed on days 0, 5 and 10. Temperature and dissolved oxygen concentrations were measured daily. Overlying-water and pore-water for analysis of dissolved metals concentrations were collected using miniature peepers (Doig and Liber, 2000). Six peepers were used in each treatment group, with three peepers being collected at the midpoint (day 5) of the toxicity test and the remaining 3 being collected at the completion of the test (day 10). Pore-water samples collected from the peepers (~1-mL) were added to pre-cleaned 8-mL Nalgene® bottles and acidified using 20 µL of 12 M nitric acid. Samples were stored at 4^{o}C prior to trace element analysis using an X Series II ICP-MS (Thermo Fisher Electron Corporation, Waltham, MA, USA). Upon test completion, all surviving organisms were collected, counted, and oven-dried (60^{o}C) overnight. Dry weight was determined for the pooled larvae for each replicate.

3.3.4 Statistics

Percent relative abundance of all diatom and chironomid sub-fossil remains were calculated for each sediment subsection analyzed. Taxa with greater than 5% relative abundance in at least one sediment subsection were stratigraphically analyzed using the TILIA v. 2.02 program (Illinois State Museum, Springfield, IL, USA). Percent relative abundance data were transformed using a square root transformation and variations in community composition subsequently identified through the use of constrained cluster analysis and a sum of squares test (CONISS).

Typically, a minimum of 50 chironomid head capsules should be identified per sediment subsection to reliably infer environmental conditions (Heiri and Lotter, 2001; Quinlan and Smol, 2001). Despite using large composite samples, the number of head capsules collected from each sediment subsection exceeded 50 head capsules in only three sediment subsections (mean number of head capsules per section was 24 ± 16). Nevertheless, stratigraphic analyses were performed using these data and the observed trends were quite distinct and consistent with trends observed in diatom community composition (described below).

Toxicity test endpoints were assessed for statistical differences between the control and treatment groups, as well as among treatment groups, using a one-way ANOVA followed by a Tukey's post-hoc test ($p < 0.05$). All data were tested to ensure that they met assumptions of normal distribution and homogeneity of variance. Data were log transformed when necessary. When data did not meet requirements for a one-way ANOVA test following transformations, these data were subjected to the non-parametric Kruskal-Wallis ANOVA test ($p < 0.05$).

3.4 Results

3.4.1 Diatoms

Similar to Hall et al. (1999), all Lake Diefenbaker sites sampled were dominated by planktonic diatom species. In the two upper-most reservoir sampling locations (sites 1 and 2) the diatom community composition was dominated by *Stephanodiscus parvus* throughout the core profiles of both sites (average percent relative abundance for sites 1 and 2 = 49 ± 9% and 53 ± 12%, respectively) (Figure 3-1). The sediment core profiles in cores 3 and 8 were consistently dominated by *Aulacoseira ambigua* (average percent relative abundance for sites 3 and 8 = 48 ± 15% and 40 ± 8%, respectively) (Figure 3-1).

Sediment cores 4, 5, 6 and 7 showed three similar major shifts in diatom community composition (Figure 3-2). The deepest sediment subsections were dominated by *S. parvus*. The middle subsections of the sediment core profiles showed relative increases in *Tabellaria* *flocculosa*, *Stephanodiscus medius*, *Asterionella formosa,* and *A. ambigua*. *A. ambigua* dominated community composition in the more surficial sediments of the sediment core profiles, with *T. flocculosa* co-dominating at Site 7.

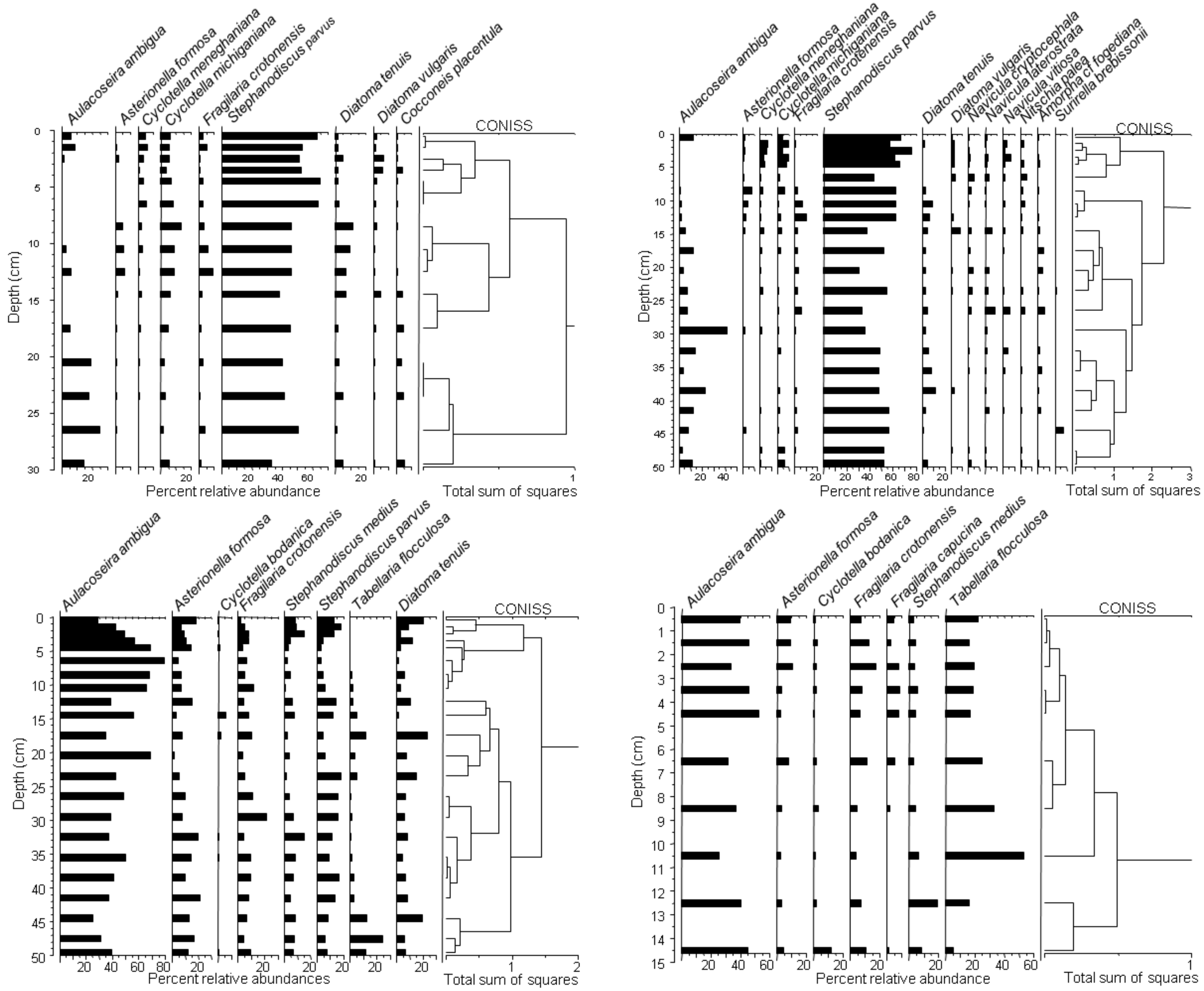

Figure 3-1. Diatom sub-fossil stratigraphy for sediment cores collected from Sites 1 (top left), 2 (top right), 3 (bottom left), and 8 (bottom right). The zonation was determined using constrained cluster analysis (CONISS) based on Euclidean distances (total sum of squares).

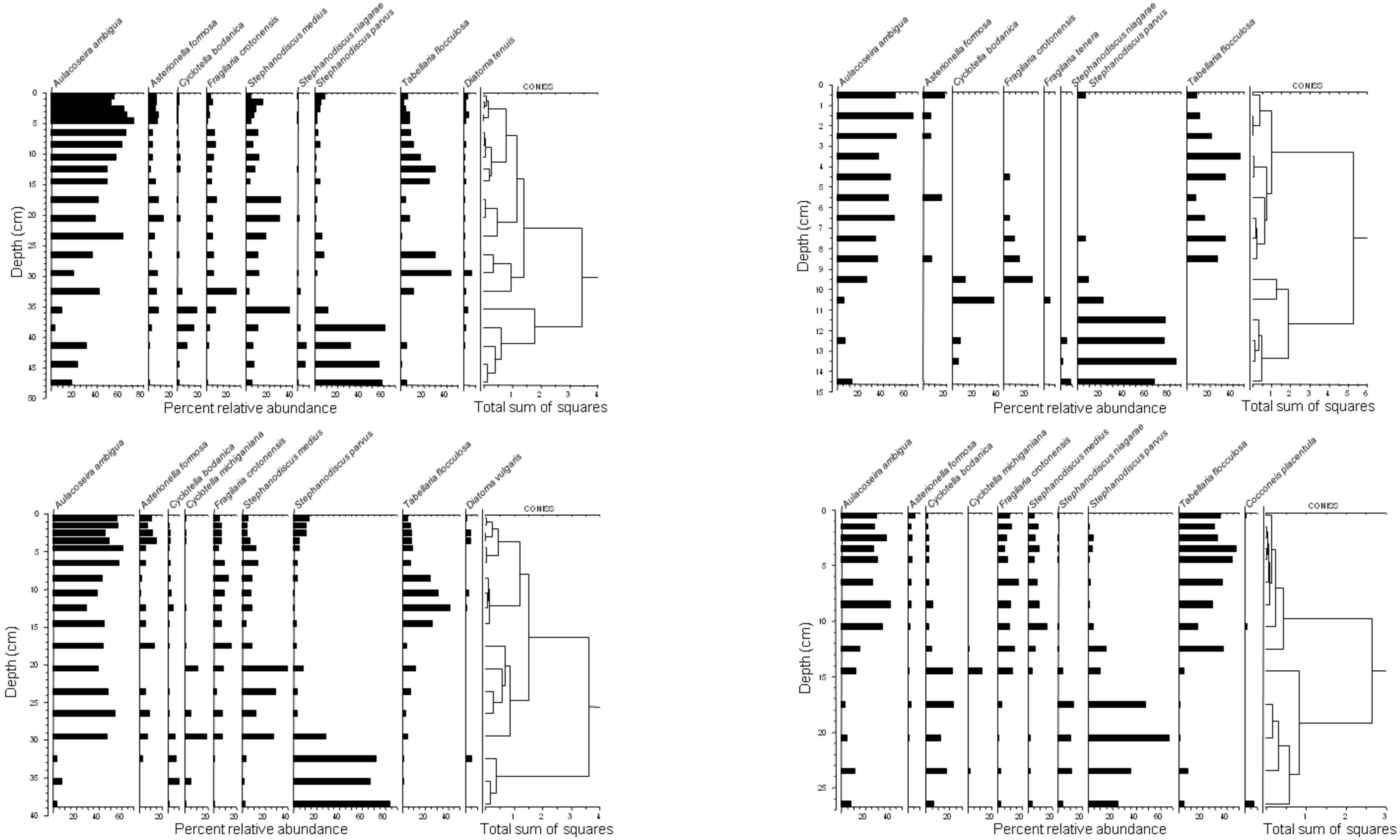

Figure 3-2. Diatom sub-fossil stratigraphy for sediment cores collected from Sites 4 (top left), 5 (top right), 6 (bottom left), and 7 (bottom right). The zonation was determined using constrained cluster analysis (CONISS) based on Euclidean distances (total sum of squares).

3.4.2 Chironomids

In terms of the historical trends in chironomid community composition, the two most up-reservoir sampling sites (sites 1 and 2) showed a relatively consistent domination of the entire sediment core profile by the genus *Procladius* (Figure 3-3). This genus averaged 49 ± 26% and 62 ± 10% of all chironomid remains identified within each 3-cm composite sample collected at sites 1 and 2, respectively.

The more down-reservoir sites (sediment cores 5 and 6) showed two and three major shifts in species composition, respectively, throughout their sediment core profiles (Figure 3-4). Community composition in sediment core 5 was dominated by the genus *Procladius* in the deepest sediment subsections, which was followed by an increase in relative abundance of the tribe Tanytarsini in the upper, more recently deposited sediment subsections. Community composition at site 6 was dominated by the genus *Chironomus* in the deepest sediment subsections. This was followed by an increase in percent relative abundance of the genus *Procladius* and the tribe Tanytarsini in the middle sediment subsections. Finally, in the most surficial sediment subsections, the tribe Tanytarsini increased in percent relative abundance to between 54% and 85% of the community composition.

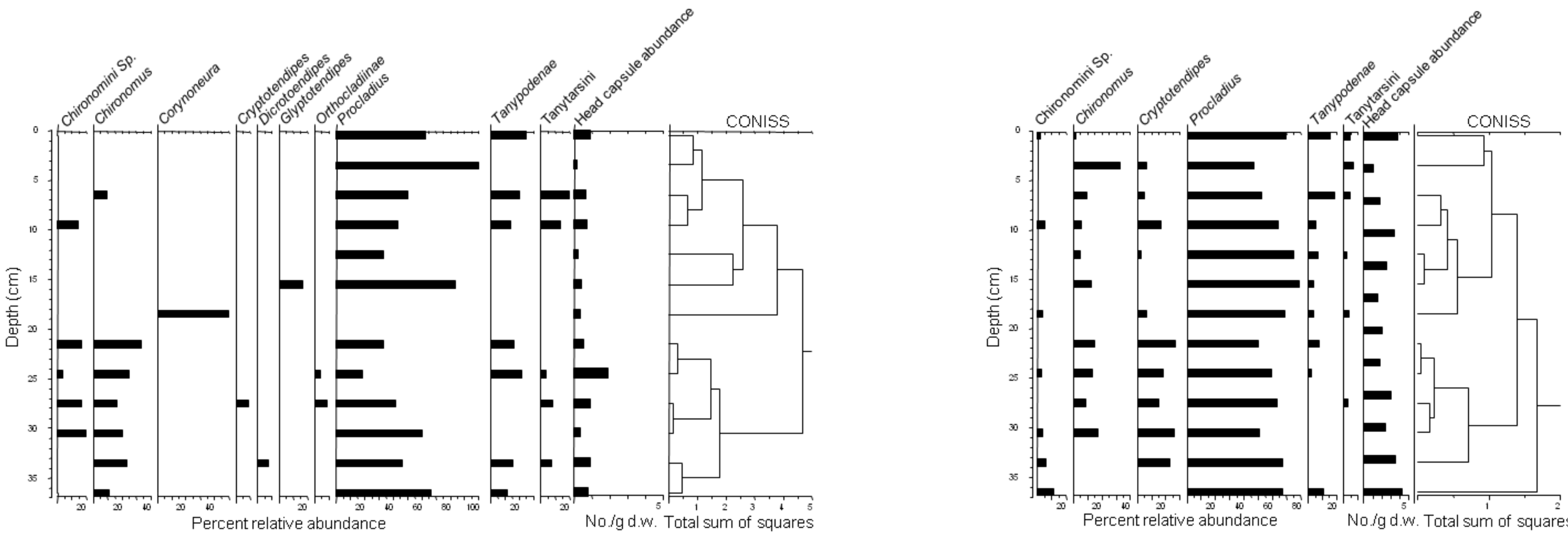

Figure 3-3. Chironomid sub-fossil stratigraphy for sediment cores collected from Sites 1 (left) and 2 (right). The zonation was determined using constrained cluster analysis (CONISS) based on Euclidean distances (total sum of squares).

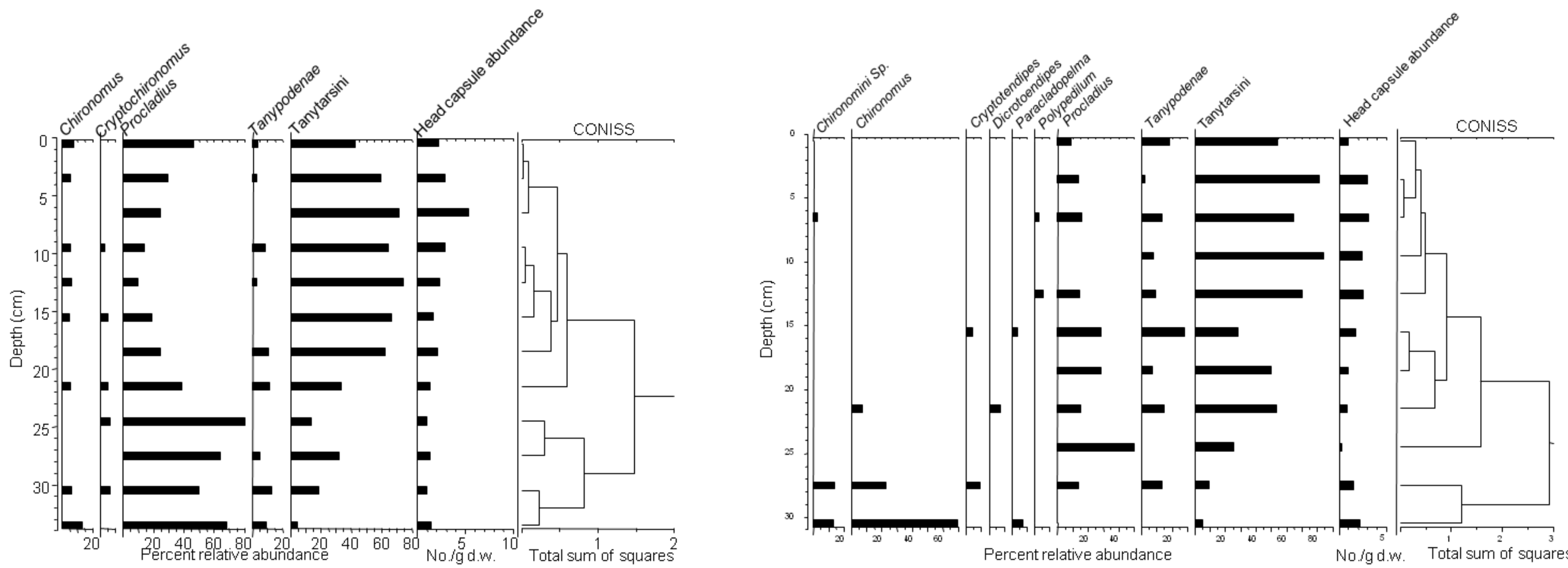

Figure 3-4. Chironomid sub-fossil stratigraphy for sediment cores collected from Sites 5 (left) and 6 (right). The zonation was determined using constrained cluster analysis (CONISS) based on Euclidean distances (total sum of squares).

3.4.3 Toxicity test

Overlying water quality was similar among the experimental groups. The mean ± S.E. for each variable calculated across treatment groups was as follows: temperature = 21.6 ± 0.1^{o}C, dissolved oxygen concentration = 7.8 ± 0.1 mg/L, conductivity = 439 ± 2 μS/cm, pH = 8.0 ± 0.1, hardness = 156 ± 2 mg/L $CaCO_3$, alkalinity 112 ± 2 mg/L $CaCO_3$, and ammonia concentration = 0.27 ± 0.01 mg/L .Source water for this study was carbon filtered, bio-filtered, municipal Saskatoon water drawn from the South Saskatchewan River, which is supplied by Lake Diefenbaker. All water quality parameters fell within the recommended tolerance ranges for *Chironomus dilutus* toxicity testing (Environment Canada, 1997).

Table 3-1 shows overlying- and pore-water metals concentrations (mean ± SE) measured from peeper samples. Metals that exceeded the recommended CCME guidelines for the protection of aquatic life are shown in bold. These guideline values are meant to protect all forms of aquatic life over the long term (CCME 1999) and tend to be conservative. They are best used as a screening tool to identify those elements unlikely to cause chronic toxicity in a long-term exposure (i.e., those elements having total concentrations below CCME guideline values). Iron and arsenic concentrations were in excess of CCME guidelines for both overlying- and pore-water from all treatment groups. Since there were no significant differences observed in survival and in dry weight of *Chironomus dilutus* between the majority of the treatment groups and the control group, and since the control group displayed no adverse response, these exceedances are likely not biologically significant. Cadmium concentrations were in excess of CCME guidelines in the overlying-water of the control group and were in excess in the overlying-water of the Fish Farm Reference site and both the Swift Current Exposure site. Because cadmium concentrations were greatest in control groups, and both survival and growth in these control groups met test validity thresholds proposed by Environment Canada (1997), the biological significance to *C. Dilutus* is likely minimal. Copper concentrations were in excess of CCME guidelines in the control group and the Swift Current Reference site overlying water, and in the Fish Farm Reference site overlying- and pore-water. Neither of these sites showed significant differences in survival or growth of test organisms exposed and thus exceedances of the guidelines are likely not biologically significant.

At the completion of the 10-day whole-sediment toxicity test, there were no significant differences in survival among any of the reference or exposure site sediments, or between the silica sand control and any of the exposure site sediments ($p>0.05$) (Figure 3-5). Survival exceeded 74% in all cases. There was, however, a significant difference in *C. dilutus* growth observed between the silica sand control and the Swift Current Exposure site sediment (Site 2) ($p<0.05$). However, larval growth in the Swift Current Exposure group was not significantly different from growth in the Swift Current Reference group (Site 1), or any of the other treatment groups (the Fish Farm Exposure group and the Fish Farm Reference site) ($p>0.05$) (Figure 3-5). There were no other significant differences observed in *C. dilutus*.

Metal (µg/L)	Control		Site 1		Site 2		Site 5		Site 6	
	OW	PW	OW	PW	OW	PW	OW	PW	OW	PW
Aluminum	24.9 ± 3.7	14.4 ± 5.1	65.6 ± 4.4	31.4 ± 4.5	24.2 ± 3.2	54.5 ± 4.1	19.9 ± 4.8	12.7 ± 4.6	24.8 ± 3.9	57.1 ± 3.0
Titanium	4.5 ± 0.0	10.9 ± 2.2	12.9 ± 2.7	23.3 ± 7.4	18.0 ± 6.2	48.1 ± 5.1	30.3 ± 2.2	60.1 ± 3.1	17.7 ± 6.5	49.7 ± 8.3
Vanadium	0.6 ± 0.2	0.6 ± 0.1	1.1 ± 1.0	2.1 ± 1.0	2.1 ± 0.7	3.1 ± 1.0	2.8 ± 0.1	3.1 ± 0.1	1.7 ± 0.8	3.1 ± 0.8
Chromium	5.9 ± 3.0	17.3 ± 5.2	18.4 ± 7.1	38.1 ± 12.1	9.9 ± 7.7	22.8 ± 7.5	25.8 ± 5.0	23.9 ± 7.7	45.2 ± 11.5	68.4 ± 11.7
Manganese	27 ± 15	441 ± 106	530 ± 293	1510 ± 385	1071 ± 399	2364 ± 458	2416 ± 91	4501 ± 79	949 ± 1088	6333 ± 1357
Iron	20 ± 5	130 ± 19	**504 ± 157**	**3917 ± 694**	**468 ± 131**	**6454 ± 145**	**426 ± 30**	**5152 ± 26**	**538 ± 1105**	**5959 ± 1549**
Cobalt	0.4 ± 0.0	1.2 ± 0.2	0.8 ± 0.1	1.5 ± 0.1	0.8 ± 0.4	1.7 ± 0.3	1.3 ± 0.2	1.8 ± 0.4	0.7 ± 0.3	2.4 ± 0.4
Nickel	2.3 ± 0.5	5.6 ± 1.2	3.1 ± 0.4	3.4 ± 0.3	2.9 ± 1.2	4.4 ± 1.1	4.5 ± 1.2	4.6 ± 1.5	4.0 ± 0.5	7.2 ± 0.6
Copper	**9.2 ± 5.2**	2.2 ± 5.4	**9.3 ± 0.7**	3.0 ± 0.6	1.9 ± 0.7	2.4 ± 0.7	3.1 ± 0.5	2.7 ± 0.4	**6.0 ± 0.7**	**4.0 ± 0.7**
Zinc	3.4 ± 0.9	3.3 ± 0.5	5.2 ± 1.2	2.0 ± 0.4	2.9 ± 1.0	2.0 ± 1.1	1.8 ± 0.4	1.1 ± 0.4	2.2 ± 0.4	7.9 ± 0.4
Arsenic	1.6 ± 0.4	3.3 ± 0.6	**6.0 ± 5.2**	**22.3 ± 7.8**	**10.9 ± 2.9**	**40.9 ± 2.8**	**16.3 ± 0.5**	**61.4 ± 0.4**	**14.1 ± 13.2**	**95.6 ± 22.0**
Selenium	< 1.9	< 1.9	< 1.9	< 1.9	< 1.9	< 1.9	< 1.9	< 1.9	< 1.9	< 1.9
Strontium	213 ± 2	221 ± 2	232 ± 10	262 ± 20	225 ± 10	261 ± 10	240 ± 4	287 ± 5	244 ± 21	324 ± 30
Molybdenum	2.6 ± 0.1	3.3 ± 0.1	2.4 ± 2.1	3.0 ± 1.8	2.3 ± 2.0	3.0 ± 2.1	4.8 ± 0.3	4.8 ± 0.4	5.2 ± 1.8	10.1 ± 1.8
Silver	< 0.03	< 0.03	< 0.03	< 0.03	< 0.03	< 0.03	< 0.03	< 0.03	< 0.03	< 0.03
Cadmium	**0.2 ± 0.1**	< 0.04	< 0.04	< 0.04	**0.1 ± 0.0**	< 0.04	< 0.04	< 0.04	**0.1 ± 0.0**	< 0.04
Tin	0.4 ± 0.2	0.2 ± 0.2	0.1 ± 0.0	0.1 ± 0.0	0.1 ± 0.0	0.1 ± 0.0	0.1 ± 0.0	0.1 ± 0.0	0.2 ± 0.0	0.2 ± 0.0
Antimony	0.30 ± 0.02	0.30 ± 0.02	0.33 ± 0.06	0.37 ± 0.04	0.33 ± 0.09	0.33 ± 0.08	0.50 ± 0.02	0.46 ± 0.04	0.42 ± 0.04	0.55 ± 0.04
Barium	37.5 ± 0.2	48.6 ± 1.6	69.4 ± 9.2	90.4 ± 12.5	65.3 ± 9.5	168.6 ± 10.0	80.1 ± 2.3	120.0 ± 2.6	68.6 ± 10.7	129.1 ± 14.1
Mercury	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
Thallium	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Lead	0.3 ± 0.1	0.7 ± 0.5	0.4 ± 0.0	0.3 ± 0.0	0.1 ± 0.1	0.2 ± 0.0	0.1 ± 0.5	0.1 ± 0.5	0.3 ± 0.0	0.1 ± 0.0
Uranium	1.8 ± 0.3	3.2 ± 2.5	1.6 ± 1.3	1.3 ± 1.3	1.4 ± 0.4	1.2 ± 1.3	3.0 ± 2.5	1.5 ± 2.5	1.9 ± 0.3	1.3 ± 0.3

Table 3-1. Total dissolved overlying- (OW) and pore-water (PW) metals concentrations collected from peepers during the 10-day whole sediment toxicity test. Metals concentrations represent the mean ± standard error concentrations for peepers collected on day 5 and at the completion of the 10-day toxicity test. Concentrations in bold depict means that exceeded CCME water quality guidelines for the protection of aquatic life (Iron > 300 µg/L; Arsenic > 5 µg/L; Copper > 3.31 µg/L; Cadmium > 0.046 µg/L). Measurements that were consistently below the limit detection (L.D.) are listed as < L.D.

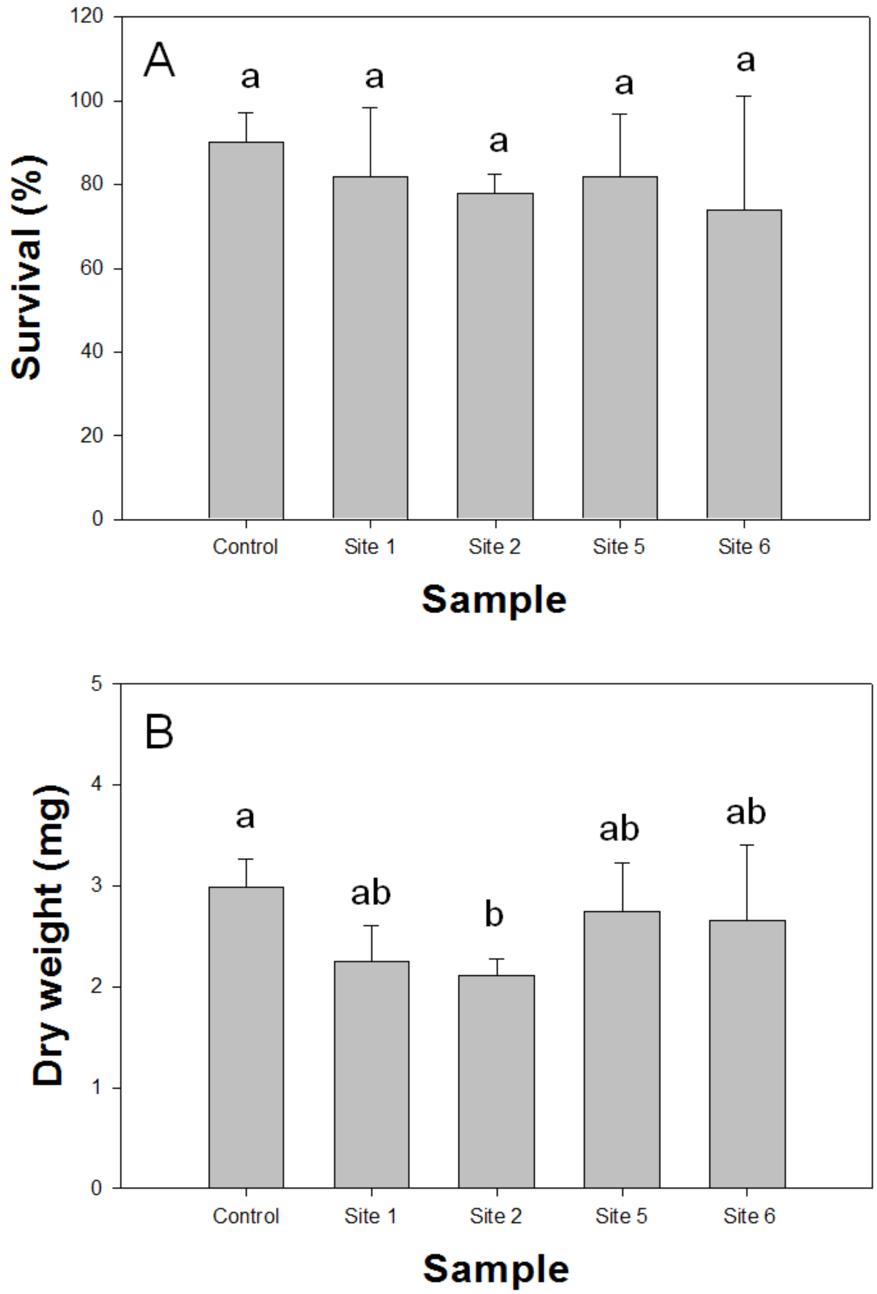

Figure 3-5. The mean (± S.D.) percent survival (A) and dry weight (B) of *Chironomus dilutus* larvae for each treatment group. Statistical differences ($p < 0.05$) are indicated by different letters above the bars.

3.5 Discussion

3.5.1 Diatom community trends

The consistent domination of the diatom community composition at the up-reservoir sampling locations (Sites 1 and 2) by *S. parvus* suggests relatively stable long-term nutrient status and ecological conditions. *Stephanodiscus parvus* is generally regarded as a higher nutrient status species, suggesting consistently high nutrient status up-reservoir (Hall et al., 1999; Hall and Smol, 1992). The major shifts in community composition in sediments from down-reservoir locations (Sites 4, 5, 6 and 7) suggest associated changes in nutrient status and ecological conditions over time. The domination of *S. parvus* within the deepest sediment subsections is consistent with conditions observed in the up-reservoir sediment cores, suggesting that similar environmental conditions were observed at down-reservoir locations in the early years of reservoir formation (i.e., high nutrient availability). This is likely the result of typical reservoir ontogeny, where the initial flooding of the prairie landscape would most likely have mobilized soluble nutrients from soils. This, coupled with biodegradation of soil organic matter in the early years after flooding, would have contributed to elevated nutrient levels (Ostrofsky and Duthie, 1978; Kennedy and Walker, 1990; Hall et al., 1999), which is known to promote high relative abundance of *S. parvus* (Hall et al., 1992, 1999).

The shift in community composition to a greater proportion of *A. formosa*, *T. flocculosa*, and *S. medius* in the middle sections of the down-reservoir sediment cores suggests a subsequent decrease in nutrient status to more mesotrophic conditions (Hall et al., 1999; Hall and Smol, 1992). The initial high erosion of bank materials and the subsequent settling of this material would cause the burial of the decomposing soil organic matter (Hall et al., 1999, Nursall, 1952). This, coupled with depletion of the soluble soil nutrient stores, would progressively result in decreased availability of nutrients down-reservoir over time resulting in a shift to mesotrophic conditions.

Finally, the more surficial down-reservoir sediment subsections showed increasing community dominance by *A. ambigua*, suggesting an increased nutrient status in more recent years (Hall et al., 1999; Hall and Smol, 1992). Sediments from Sites 3 and 8 showed consistent domination of their core profiles by *A. ambigua*, with no signs of early domination by *S. parvus*. It is likely that community composition trends at these locations were in fact similar to the other down-reservoir sites, but that only more recent sediments were collected in these cores. The core from Site 8, the Qu'Appelle Arm, was collected in close proximity to the site used in 1995 by Hall et al. (1999). Due to the physical properties of the sediment in this location (Site 8), the longest intact core collected was limited to only 15 cm. Had collection of a longer sediment core been possible, similar trends to those observed in the other down-reservoir cores and the core collected by Hall et al. (1999) may have been observed. Similarly, the absence of a community dominated by *S. parvus* at Site 3 was likely due to limitations to the sediment depth that our equipment could sample (diatom remains were present at the bottom of the Site 3 core). Regardless, the high relative abundance of *A. ambigua* at Site 3 suggests historical and recent trophic conditions similar to down-reservoir locations.

Hall et al. (1999) proposed that increased abundance of *A. ambigua* in more recently deposited sediments in the Qu'Appelle arm of Lake Diefenbaker could have resulted from either increased nutrient loading from aquaculture, or due to increased internal loading of nutrients from Lake Diefenbaker sediments. Based on the increased relative abundance of *A. ambigua* in sediments from Sites 3 and 4, which are both up-reservoir of the Wild West Steelhead fish farm, nutrient loading from the fish farm is most likely not a major contributor to the observed changes in diatom community composition over time in the down-reservoir region. Nevertheless, the increase in nutrient status at down-reservoir locations over time could be due to increased loading of nutrients from other sources in the watershed. With regard to internal nutrient loading, enhanced light penetration down-reservoir over time would have allowed phytoplankton progressively greater access to nutrients in the water column. This would suggest that phosphorus is being retained down-reservoir by sedimentation of phytoplankton and that retention of phosphorus by this mechanism has increased over time. This trend was not observed in up-reservoir sediments. Increased accumulation of organic matter and phosphorus within sediments, especially the redox sensitive phosphorus fractions observed in Lake Diefenbaker, increase the potential for internal loading of phosphorus. As such, both increased loading of phosphorus to Lake Diefenbaker from the surrounding watershed and increased deposition and subsequent remobilization of phosphorus from the sediment are possible mechanisms for the increasing trophic status of Lake Diefenbaker. It is likely that both mechanisms may have contributed to the observed trend.

Both *S. parvus* and *A. ambigua* are species observed to dominate diatom community composition at high phosphorus conditions (Hall et al., 1992, 1999). The observed domination of one or the other provides insight into spatial and temporal environmental processes and trends in Lake Diefenbaker. Spatially, *S. parvus* presently dominates the diatom community in up-reservoir regions, whereas *A. ambigua* dominates the down-reservoir community. Although water quality characteristics (pH, hardness, alkalinity) are very similar between regions (Environment Canada, 1988), turbidity decreases with distance down-reservoir (Environment Canada, 1988). Whereas both species are known to inhabit nutrient rich waters, *A. ambigua* has a higher light requirement and thus tends to thrive in environments where light limitation is less of a factor (Kilham et al., 1986). As particulates tend to settle out along the longitudinal gradient of reservoirs, down-reservoir sites typically experience less light attenuation than up-reservoir locations (Kimmel et al., 1990; Kimmel & Groeger, 1984). Recent investigation of Lake Diefenbaker has confirmed that turbidity and suspended sediment concentrations decrease with distance down-reservoir (Rebecca North, University of Saskatchewan, 2013, Personal Communication). A higher light requirement likely explains why *A. ambigua* dominates the diatom community only in the clearer, down-reservoir locations. Similarly, light requirement likely also explains why *S. parvus* initially dominated the historical communities both up- and down-reservoir. In addition to high nutrient concentrations, turbidity would also have been high down-reservoir in the early years after reservoir formation due to bank erosion (Baxter, 1977). During this period the down-reservoir portion of the reservoir would have been environmentally similar to up-reservoir, and this likely explains why *S. parvus* dominated the diatom community across the entire reservoir. *Aulacosiera ambigua* emerged as the dominant species down-reservoir only after abatement of bank erosion (i.e., reduced turbidity) and water column nutrient concentrations once again increased. Conversely, and likely due to the consistently high flow velocities, high tubidity and advective nutrient supply, the up-reservoir riverine zone appears to have remained ecologically stable over time, as demonstrated by stable diatom and chironomid community composition with sediment depth. The high flow velocity has been shown to maintain higher levels of turbidity (Environment Canada, 1988) and hence has a more limited photic depth. The advective nutrient supply due to high flow velocity would be expected to maintain relatively high nutrient concentrations in this region, as were observed in 1984 and 1985 (Environment Canada, 1988). Therefore, although nutrient concentrations may fluctuate over time, primary productivity is limited in the up-reservoir region by the availability of light, the availability of which has likely remained reasonably similar over time.

3.5.2 Chironomid community trends

Hall et al. (1999) observed that Lake Diefenbaker sediments have low chironomid head capsule concentrations. Similarly, this study only produced an average chironomid head capsule concentration of 1.76 ± 1.17 head capsules/g dry weight, despite the large composite samples (30 gram wet weight). Based on toxicity test results, sediment toxicity even at expected "worst case" sites, did not appear to be a factor in the interpretation of the chironomid head capsules data for Lake Diefenbaker sediments. Instead, the low chironomid head capsule concentrations are most likely a result of poor physical habitat conditions within Lake Diefenbaker (e.g., high clay content, low organic matter content).

The relatively consistent historical domination of the chironomid community at Sites 1 and 2 by the genus *Procladius* (Figure 3-3) suggests poor environmental conditions for other taxa. *Procladius* is a predatory chironomid genus that is able to out compete other chironomid taxa when food is scarce for non-predatory (i.e., deposit-feeding) chironomid taxa (Kajak, 1980). *Procladius* can meet its dietary needs through predation on other macrobenthos and therefore does not require sustenance from organic matter sedimentation. This conclusion is supported by the relatively low total organic carbon (TOC) concentrations observed in the different sediment layers at up-reservoir locations (Sites 1 and 2) within Lake Diefenbaker (TOC mean ± S.D. = 1.21 ± 0.11%, d.w.).

At the two down-reservoir sampling locations there were two (Site 5) and three (Site 6) major shifts in chironomid community composition (Figure 3-4), similar to that observed in diatom community composition. *Chironomus*, which dominated community composition in the deepest sediment subsections, are known to tolerate low dissolved oxygen concentrations and are typically the only species present during anoxic conditions (Little et al., 2000). Therefore, the high percent relative abundance (69%) in the deepest sediment subsection suggests low oxygen concentrations during this time period. This is consistent with the conclusions derived from diatom sub-fossil remains at these down-reservoir sites, which suggested high productivity in the years following reservoir formation. The high levels of biodegradation of soil organic matter and the sedimentation of autochthonous organic matter sources as a result of the initially high nutrient levels likely resulted in decreased oxygen concentrations at depth (e.g., Kennedy and Nix, 1987).

During the mesotrophic period suggested by the diatom remains in the middle sediment subsections, there was a shift in chironomid community composition from *Chironomus* to an increased relative abundance of the predatory genus *Procladius*. This change suggests decreased organic matter sedimentation and is consistent with decreased primary productivity and a more mesotrophic period. It also suggests that oxygen concentrations were improving due to *Procladius* requiring a higher dissolved oxygen threshold for survival than *Chironomus* (Heinz and Davids, 1993; Reiss and Fittkau, 1971).

Finally, the shift towards a higher proportion of the tribe Tanytarsini in the more recently deposited sediment suggests an increase in organic matter sedimentation, but an absence of anoxic conditions (Heinz and Davids, 1993). It has been shown that Tanytarsini tend to thrive in more eutrophic lakes when hypoxic conditions are absent (Heinz and Davids, 1993). However, under similar eutrophic conditions where thermal stratification has resulted in anoxic conditions, numbers of Tanytarsini decrease rapidly (Heinz and Davids, 1993). The conclusion that increased organic matter sedimentation in recent years has driven the increased relative abundance of *Tanytarsini* is supported by an increasing trend in organic carbon content in more recently deposited sediments.

3.6 Conclusions

This study has shown that an understanding of spatial differences in limnological conditions is required to fully understand reservoir ontogeny and trends in environmental quality. Based on consistent diatom and chironomid community composition, it was inferred that primary productivity has remained stable for a substantial period of time at the up-reservoir locations in Lake Diefenbaker. This is in contrast to temporal changes observed down-reservoir where shifts in diatom and chironomid community composition over time suggest an initial increase in nutrient status following reservoir formation. This was followed by a period during which primary productivity decreased to more mesotrophic conditions. Finally, in more recent sediments an increased relative abundance of the diatom *A. ambigua* and the chironomid tribe Tanytarsini suggest increasing trends in primary productivity and nutrient status down-reservoir, but without hypolimnion anoxia. The upward trend in nutrient status is consistent with anecdotal observations of an increased frequency and severity of algal blooms in this region of Lake Diefenbaker. This is a concern given that increased primary productivity can lead to a decline in water quality and impairment of its intended uses. Future work should investigate the mechanism driving the increased nutrient availability in down-reservoir locations. This study suggests that aquaculture is likely not the reason for recent changes in primary productivity and nutrient status (inferred from diatom community composition) down-reservoir. Although anoxic conditions have not been observed in Lake Diefenbaker to date, the potential for remobilization of phosphorus from down-reservoir sediments should be characterized under various dissolved oxygen regimes. Such data would facilitate the modeling of internal loading of phosphorus under observed and future scenarios. Lake Diefenbaker is of high value to municipal, industrial, commercial, recreational and agricultural sectors in Saskatchewan. To better manage this important resource, the inferred increases in nutrient status and primary productivity in down-reservoir sites should be more thoroughly investigated and nutrient sources identified.

CHAPTER 4:
Discussion

4.1 General discussion

Based on spatial and temporal trends in physicochemical and biological sub-fossil remains in sediments cores collected along a spatial gradient in Lake Diefenbaker, SK, Canada, two regions were identified, an up-reservoir and a down-reservoir region. Spatial differences in sediment physicochemistry and biological sub-fossil remains between these two regions are likely due to differences in reservoir morphology and hydrology. Sediments from up-reservoir locations suggest relatively consistent primary production, nutrient loading and trophic status throughout the temporal coverage of the collected sediment cores. Conversely, sediments from down-reservoir locations suggest increasing primary production and nutrient loading in more recent years. These sediments also suggest three major shifts in trophic status since reservoir formation in 1967.

Primary production appears to increase with increasing distance down-reservoir based on strong correlations between distance down-reservoir and primary productivity proxies ($\delta^{15}N$ and TOC) in surficial sediments. This is likely explained by typical reservoir limnology whereby up-reservoir locations have increased turbidity and light attenuation compared to down reservoir locations (Kimmel et al., 1990; Kimmel and Groeger, 1984). Down-reservoir locations would likely experience less turbidity due to the settling of particulates as the reservoir transitions into a more lacustrine environment, and thus less light attenuation. The reduced light attenuation at down-reservoir locations likely explains the inferred increases in primary productivity with distance down-reservoir.

Surficial TP concentrations followed a similar increasing spatial trend with distance down-reservoir. This is likely due to less availability and sequestration of phosphorus by primary producers at up-reservoir locations due to light limitation. Further down-reservoir, the reservoir likely transitions into a more lacustrine environment where turbidity decreases as suspended sediments settle. The greater light penetration at these down-reservoir locations would reduce light limitation for phytoplankton and result in greater phosphorus sequestration and deposition to sediments.

Phosphorus loading to Lake Diefenbaker sediments also appears to be influenced historically by autochthonous primary productivity based on strong correlations between sediment TOC and both sediment TP concentrations and the more biologically available phosphorus fractions (NAIP + OP). As a result, up-reservoir sediments showed relatively consistent TP concentrations and relatively consistent concentrations of AP, NAIP and OP over time. Down-reservoir, an increasing trend in TP concentrations, driven primarily by increases in the NAIP and OP fractions, suggests increased phosphorus loading to the sediments in recent years. This likely resulted from accumulation in primary producers and subsequent deposition. Autochthonous organic matter tends to be more labile in aquatic environments than allochthonous organic matter (Mayer et al., 2006). As a result, OP associated with autochthonous organic matter tends to be mineralized by microbial communities into the NAIP fraction within the sediments. This is consistent with the observed increases in NAIP within surficial sediments and the strong correlations between the more biologically available sediment phosphorus and TOC, within Lake Diefenbaker sediments. Therefore, the increasing phosphorus loading trend observed down-reservoir is likely a result of temporal increases in primary productivity at these locations.

The increased concentrations of NAIP in surficial sediments are worrisome since NAIP is a redox-sensitive phosphorus fraction. If ongoing trends continue, increases in primary productivity down-reservoir increase the potential for anoxia in the hypolmnion which would remobilize this phosphorus fraction. This does not yet appear to be happening in Lake Diefenbaker based on chironomid sub-fossil remains data that show the tribe Tanytarsini to dominate the community composition within the most recently deposited sediments. Tanytarsini tends to be sensitive to low oxygen concentrations (Heinz & Davids, 1993) and therefore the high relative proportion of Tanytarsini in recently deposited sediments suggests that deep water anoxia is likely not currently occurring in Lake Diefenbaker. The future potential of Lake Diefenbaker sediments to act as an internal source of phosphorus is discussed below.

4.2 General implications

This work has implications for management and monitoring of other long river valley reservoirs like Lake Diefenbaker, as it illustrates the need for the understanding of spatial trends along the reservoir in addition to temporal trends. Reservoir physical morphology and hydrology generally differs longitudinally in this type of reservoir which leads to spatial differences in nutrient dynamics, primary productivity, ecology (e.g., diatom and chironomid community structure), and reservoir ontogeny. The different conditions observed between up- and down-reservoir sampling locations appear to be consistent with existing knowledge of reservoir limnology (Kimmel et al., 1990; Kimmel & Groeger, 1984), where up-reservoir regions are relatively shallow and narrow, have relatively high flow velocities, increased turbidity and a greater contribution of advective nutrient supply compared to down-reservoir regions. In comparison, down-reservoir regions tend to be wider and deeper, have a lesser flow velocity, decreased turbidity and a greater contribution of *in situ* driven nutrient supply.

In terms of reservoir ontogeny, river valley reservoir aging at down-reservoir locations has been well documented (Hall et al., 1999; Baxter, 1977; Thornton et al., 1990; Kennedy & Nix, 1987). At such down-reservoir regions, an initial up-surge in trophic status, such as that inferred from the high community composition of the diatom species *Stephanodiscus parvus* and the chironomid genus *Chironomus* in the deepest sediment profiles of Lake Diefenbaker sediment cores, is typical due to dissolution of soluble soil nutrients, rapid decomposition of terrestrial organic matter, high biological oxygen demand, and long initial water residence times (Ostrofsky and Duthie, 1978; Kennedy and Walker, 1990). This is typically followed by a decrease in trophic status as a result of depletion of soluble nutrients and burial of organic matter with the sedimentation of suspended particles (Nursall, 1952). This is consistent with inferred conditions from Lake Diefenbaker sediment sub-fossil remains in the middle sections of the sediment profiles of down-reservoir sediment cores. In these sections community composition of the lower nutrient status diatom species *Asterionella formosa*, *Stephanodiscus medius*, *Cyclotella bodanica*, and *Tabellaria flocculosa* (Hall et al., 1999; Hall et al., 1992) increased in relative abundance. Furthermore, the predatory chironomid genus *Procladius* increased in relative abundance, suggesting lower organic matter sedimentation and thus a less productive system (Kajak, 1980). Finally, as is common in down-reservoir portions of many river valley reservoirs, it appears that nutrient status and primary productivity are increasing within Lake Diefenbaker based on the increasing relative abundance of the diatom species *Aulacoseira ambigua* and the chironomid tribe Tanytarsini (Hall et al., 1999; Baxter, 1977).

Aging of the more riverine up-reservoir regions of reservoirs has been characterized far less in the literature. Up-reservoir regions experience different flow rates, water residence times, turbidity and basin morphology than down-reservoir regions, and knowledge of how these regions age in terms of nutrient dynamics, primary productivity and trophic status is important intrinsically, and due to its potential influence on down-reservoir regions. The present study suggests that up-reservoir regions within Lake Diefenbaker have experienced relatively little change in nutrient dynamics, primary productivity and trophic status. It is believed that this is in part due to high light attenuation as a result of increased turbidity, which has resulted in a decreased photic zone and limitation of primary productivity. Results of the present study also suggest that accumulation of the more biologically available phosphorus (NAIP and OP) in sediments seems to be driven by accumulation of autochthonous organic matter and subsequent sedimentation (Hiriart-Baer et al., 2011; Mayer et al., 2006) down-reservoir. Light limitation up-reservoir likely limits the accumulation of the more biologically available phosphorus at these locations. Therefore, unused nutrients are able to flow down-reservoir where they can be incorporated by autochthonous primary producers and entrained in sediments. Without characterization of up-reservoir regions, the increasing primary productivity trend associated with distance down-reservoir due to decreasing turbidity and light limitation would have been difficult to decipher. Therefore, this study suggests that in order to properly characterize a reservoir an understanding of spatial trends is required.

4.3 Specific implications

Given the importance of Lake Diefenbaker as a source of water for municipal, industrial, agricultural and recreational purposes, the increases in trophic status and primary productivity inferred from the most recently deposited down-reservoir sediments should be a concern. For example, water discharged from Lake Diefenbaker into the South Saskatchewan River has been valued at 8.1 to 11.1 million dollars annually based on domestic water use in Saskatoon alone (Kulshreshtha & Gillies, 1993). The river’s value was also estimated to be between 12.3 and 16.7

million dollars annually in terms of waste assimilation (Kulshreshtha & Gillies, 1993). Therefore, the deterioration in water quality associated with the inferred increases in primary productivity and nutrient status at down-reservoir locations could have consequences on Saskatchewan's economy and future water use if the observed trends continue.

Increasing primary productivity and nutrient status could also have consequences for biota that inhabit this large water body (maximum storage capacity of $9.4x10^9$ m^3) (Hall et al., 1999). Increased primary productivity can result in decreased oxygen concentrations at depth within the water column as a result of increased organic matter (e.g., algal blooms) decomposition and subsequent microbial organic matter degradation (Lukkari et al., 2007). Although deep water anoxia does not currently appear to be occurring within Lake Diefenbaker, if primary productivity continues to increase, then increasing microbial degradation rates of the deposited organic matter could lead to decreased oxygen concentrations at depth. Decreased oxygen concentrations can result in changes in benthic community structure and can lead to fish kills. Due to the social and economic importance of Lake Diefenbaker's sport fishery, large scale fish kills are a concern. Such changes could obviously also have serious consequences for aquaculture activities, which currently rely on the deeper, cooler waters during the hot summer months to culture rainbow trout.

Reduced oxygen concentrations at depth in the water column, coupled with increased concentrations of redox sensitive phosphorus species in surficial sediments, is a further concern due to the potential for remobilization of sediment phosphorus (i.e., internal loading) into the water column. Increased primary production within Lake Diefenbaker could lead to an increased release of phosphorus from the sediments, thus increasing the potential for primary production in a self-perpetuating cycle of decreasing water quality. Another concern would be that if conditions continue to worsen and phosphorus remobilization becomes a major factor in fueling algal primary productivity, then remediation efforts could potentially become more difficult in the future.

4.4 Future research

If the inferred trend of increasing primary production and increases in the redox sensitive phosphorus fraction of Lake Diefenbaker sediments escalate, then low oxygen concentrations would be expected in the hypolimnion at down-reservoir locations due to an increase in algal decay. The microbial breakdown in sediment of this excess organic matter from algal decay is generally an aerobic process and can thus lead to anoxic conditions at the sediment water interface (Lukkari et al., 2007). These anoxic conditions result in a decrease in redox potential and can lead to the dissolution of redox sensitive metal forms, such as manganese and iron oxides, as well as the release of associated phosphorus (NAIP fraction). This dissolved phosphorus concentrates in the hypolimnion of thermally stratified lakes, such as Lake Diefenbaker, and can become available to further fuel autochthonous primary productivity during fall turnover. This cycle of internal loading of phosphorus from sediment fueling increased primary production during fall turnover can escalate from year to year and produce annual decreases in water quality and gradually more eutrophic conditions. This is a worst case scenario, however, if no steps are taken to mitigate the inferred trends of increasing primary productivity, increasing nutrient status and increasing concentration of redox sensitive phosphorus species in surficial sediments, then there is the potential that conditions within Lake Diefenbaker could deteriorate rapidly (i.e., an increase in trophic status) when redox thresholds are exceeded.

With respect to reservoir management, if environmental conditions continue to deteriorate and internal loading becomes a significant nutrient source for algal productivity, then efforts to remediate eutrophication within Lake Diefenbaker become increasingly more challenging. Instead of only having to remediate surface water phosphorus concentrations, reduction of algal productivity would also require steps to increase phosphorus retention within sediments (Burley et al., 2001; Welch & Cooke, 1995; Boers et al., 1998). Remediation methods for increasing phosphorus retention in Lake Diefenbaker sediments are available, but, as is the case with any remediation strategy, would require balancing effective control measures with both the resulting adverse effects and economic feasibility (Burley et al., 2001). Alum, lime, and oxidizing treatments of either O_2 or $FeCl_3$ have all been effective remediation strategies for reducing sediment phosphorus remobilization in hard water prairie lakes under certain conditions (Burley et al., 2001). A proper understanding of lake and sediment chemistry is required to properly characterize the issue and administer the proper remediation strategy, should measures be required.

Currently, the internal loading potential of phosphorus from Lake Diefenbaker sediments has yet to be characterized. Given that low dissolved oxygen concentrations (e.g., 3 mg/L) have been observed in Lake Diefenbaker (Rebecca North, University of Saskatchewan, 2013), future work should investigate thresholds regarding current and potential phosphorus release from Lake Diefenbaker sediments under different oxygen concentrations. Although chironomid data suggest that deep water anoxia is not currently a concern, if primary productivity continues to escalate, seasonal lows in oxygen concentrations could decrease further and thus have significant effects on sediment phosphorus release.

Another source of uncertainty that requires characterization is the turbidity patterns along the reservoir. As the down-reservoir inferred increases in primary productivity, trophic status, and phosphorus loading to the sediments are all likely influenced by decreasing turbidity with distance down-reservoir, a proper characterization of seasonal and spatial turbidity along the reservoir is important.

4.5 Conclusions

In conclusion, primary productivity and nutrient status up-reservoir appears to have remained relatively consistent over time. Conversely, down-reservoir locations appear to have experienced trophic status shifts, increased primary productivity and increased nutrient loading since reservoir formation. With changing conditions and inferred increases in primary productivity and nutrient loading down-reservoir, the potential for deteriorating water quality within Lake Diefenbaker exists. More research is required to understand the role sediments play in the nutrient dynamics of this system and assess if and what management actions are necessary to ensure the long-term health and quality of water of Lake Diefenbaker.

CHAPTER 5:
References

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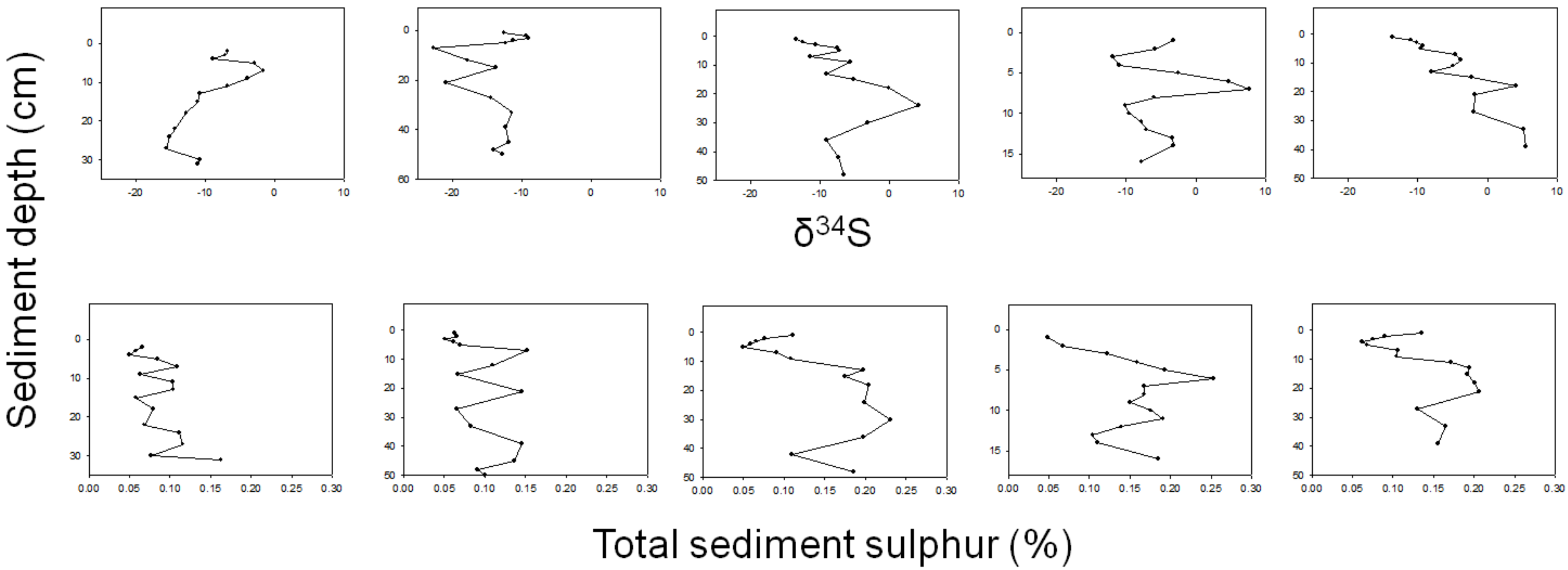
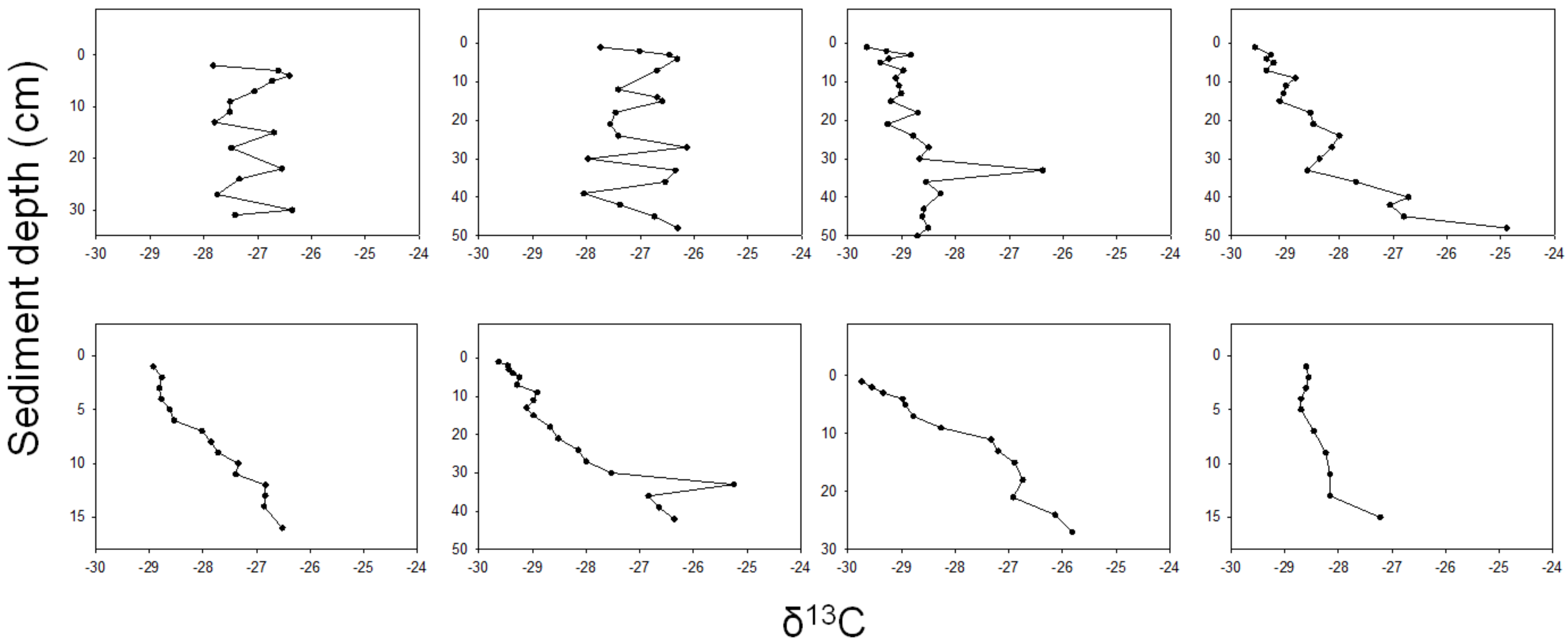
Appendix A



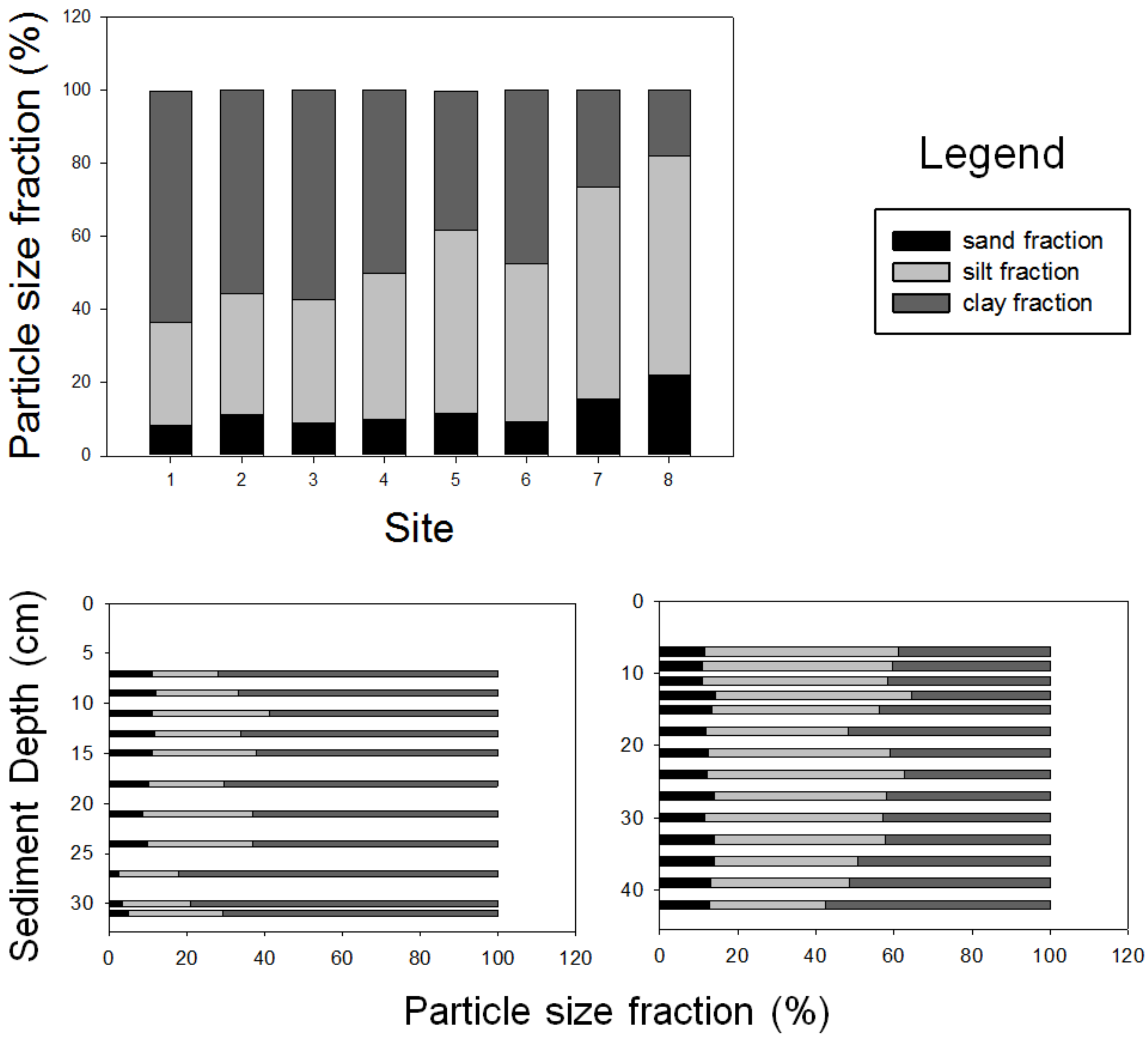
$\delta^{34}S$ values (above) and total sulphur (below) measured at selected depths within sediment cores collected from five sites along Lake Diefenbaker, SK (2011-2012). From left to right, for both $\delta^{34}S$ values and total sediment sulphur are Sites 1, 2, 4, 5, and 6. Y-axis varies among sites

Appendix B



$\delta^{13}C$ values measured at selected depths within sediment cores collected from eight sites in Lake Diefenbaker, SK (2011-2012). Top figures from left to right represent Sites 1, 2, 3 and 4. Bottom figures from left to right represent Sites 5, 6, 7, and 8. Y-axis scale varies among sites.

Appendix C



The top figure represents sediment particle size distributions for a composite sample of the top 5 cm within sediment cores collected from eight sites in Lake Diefenbaker, SK (2011-2012). The bottom two figures represent the particle size distributions of selected sediment sections within cores collected at Sites 2 (left) and 6 (right). In both figures, black bars represent sand, light grey bars represent silt, and dark grey bars represent clay. Y-axis scale varies among the bottom two figures.