University of Alberta

Biogeochemical responses of lake ecosystems to nutrient subsidies and climate change: paleolimnological investigations of selected western Canadian lakes

by

William Oliver Hobbs ©

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ABSTRACT

Biogeochemical changes in lake ecosystems over time can be investigated with paleolimnology. This work presents recent (< 300 years) lake sediment records where nutrient subsidies, silica cycling, and the rate of biological responses to recent anthropogenic forcing are the focus of study.

The ability of paleolimnology to record marine-derived nutrient (MDN) subsidies in three salmon nursery lakes within the Fraser River Basin, BC, Canada is explicitly tested. Multiple sediment proxies of lake production, as well as nitrogen isotopes, all portray relatively complacent stratigraphies, despite well-monitored changes in salmon returns. In all three lakes the sediment record failed to register the series of landslides in 1913-14, which prevented spawning salmon migration. The low proportion of MDN in the lake's annual budget and high flushing rate of the lakes are probable reasons the influence of MDN is not expressed in lake sediments.

The complete dissolution of diatom microfossils, the recycling of silica, and the diagenetic loss of fossil algal pigments are investigated in alpine lake sediments from Banff National Park, AB, Canada. Silica is rapidly dissolved and recycled within the lake water and surface sediments, with only ~1% of the total biogenic silica ($BSiO_2$) permanently buried in the lake sediments. The loss of extracellular polymeric substances (EPS) coating the diatoms, appears to lead to exposure of the frustules, and complete dissolution of the diatom microfossils. Fossil pigments exhibit signs of diagenesis, although the pigment record extends below the depth of diatom dissolution. This work is the first to place quantitative constraints on internal silica cycling in an alpine lake ecosystem.

Fifty-two diatom-based paleolimnological records are synthesized from North America and west Greenland, where diatom compositional turnover (β-diversity) is quantified over the last ~450 years. Arctic and alpine lakes exhibit significantly greater β-diversity during the 20th century than the previous 350 years. Regional temperature

increases during the 20th century correspond to the latitudinal trend of diatom β-diversity in arctic lakes, whereas a southward increase of anthropogenic N deposition suggests that biogeochemical impacts are most pronounced in mid-latitude alpine lakes.

Ultimately, this body of work shows the effectiveness of paleolimnology in explicitly testing questions over variable temporal and spatial scales, while detailing some limitations of the discipline.

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The mentorship, freedom, and support given to me by Alex Wolfe allowed me to explore the nature of scientific thought. I am also indebted to my immediate supervisory committee members Rolf Vinebrooke and Duane Froese for their guidance and support. A visit to the University of Bergen greatly expanded my comprehension of the world of multivariate statistics and I thank Richard Telford and John Birks for passing on their knowledge. A large synthesis of lake sediment records could not have been possible without the contributions of John P. Smol, Marianne S.V. Douglas, Reinhard Pienitz, Brian Cumming, Kathleen Rühland, Kathleen Laird, Dermot Antoniades, Neal Michelutti, and Bronwyn Keatley. Numerous friends and colleagues shared their experience, wisdom and time with me during this research. I am grateful to Colin Cooke, Alberto Reyes, Jo Ann Conan, Stefan Lalonde, Larry Amskold, Bianca Perren, Tyler Hauck, Britta Jensen, Roderick Hazewinkel, Chantel Nixon, Paul Weidman, Kris Hadley, Vanessa Phillips, Todd Kristensen, and Erin Doxsey-Whitfield.

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CHAPTER 1: INTRODUCTION

Paleolimnology is the study of lake histories using the sediment record. Lakes are at the receiving end of drainage basins and as such integrate the biological, geochemical and sedimentological nature of the basin over time. The sediment matrix is therefore composed of mineral and organic components derived from within the lake (autochthonous) and external to it (allochthonous). The biological remains of aquatic organisms are incorporated into the sediments and offer insights as to how the ecosystem has varied through time. Likewise geochemical parameters reflect changes within the lake, but also in the allochthonous contribution from within the drainage basin. Retrieval of undisturbed sediment records is clearly a crucial step in any paleolimnological study and techniques have matured with the science (Glew et al., 2001). Multivariate statistical analysis of paleolimnological data have developed rapidly in the last 15 years and is now an important part of data interpretation. A conceptual overview of the information used and attained in this dissertation is presented in Figure 1.1. The field of paleolimnology has been important in elucidating insights into climatic change, lake ecosystem evolution and human impacts to aquatic ecosystems.

This introductory chapter is not intended to be a comprehensive literature review of paleolimnology and associated methods, but rather an overview of those aspects which bear directly on the content of the papers contained herein. Reviews and texts on the field of paleolimnology are numerous and a few can be recommended here: Binford et al., 1983; Haworth and Lund, 1984; Last and Smol, 2001a, 2001b; Smol et al., 2001a, 2001b; Smol, 2008.

Paleolimnology and temporal scale

Paleolimnology has evolved dramatically from its conception by E. S Deevey and others

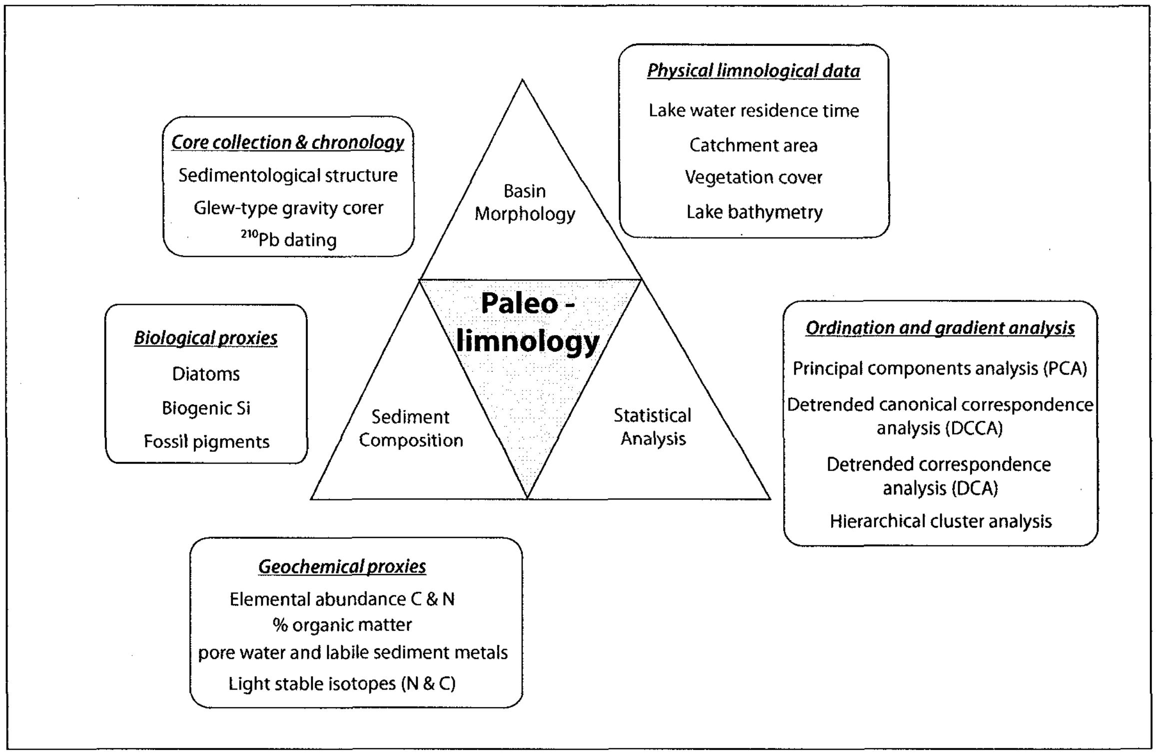

Fig. 1.1 Conceptual overview of the proxies, data, and techniques used within the paleolimnological studies of this dissertation.

(namely G.E. Hutchinson and D. Livingstone) in the mid-1900s, to become a stand-alone discipline. The use of sedimentary archives in a lake to conduct 'experiments' (Deevey, 1969) has given the limnologist access to a history which is not limited by the same temporal scale monitoring is (Figure 1.2). Working on sediment records from Linsley Pond, CT, USA, Deevey interpreted records of both the terrestrial and aquatic ecosystems, recognizing associations between catchment changes (climatic, hydrological, or human influences) and aquatic community structure (benthic invertebrates, zooplankton, and diatoms) (Deevey, 1942). In the absence of known ecological history, testing the stability of aquatic ecosystems over periods of climatic instability is a central 'experiment'. One of the early utilities of paleolimnology was to model lake ontogeny and senescence (Deevey, 1984). This question continues to be revised as our understanding of lake histories has evolved to recognize that lake development is not unidirectional (Livingstone, 1957; Renberg, 1990; Engstrom et al., 2000). The ability to observe lake aquatic communities prior to and after the industrialization of most of the northern hemisphere, has enabled scientists to explicitly show the impact of human activities on lakes, such as acidification (Charles and Smol, 1990), eutrophication (Hall et al., 1997; Lotter, 1998), anthropogenic climate change (Smol et al., 2005), and atmospheric nitrogen deposition (Wolfe et al., 2003). It is important, however, to acknowledge the complete temporal variability of the lake sediment record (Renberg, 1990; Fritz, 2008). An additional challenge of scale is recognizing local versus regional change over time, or spatial variability.

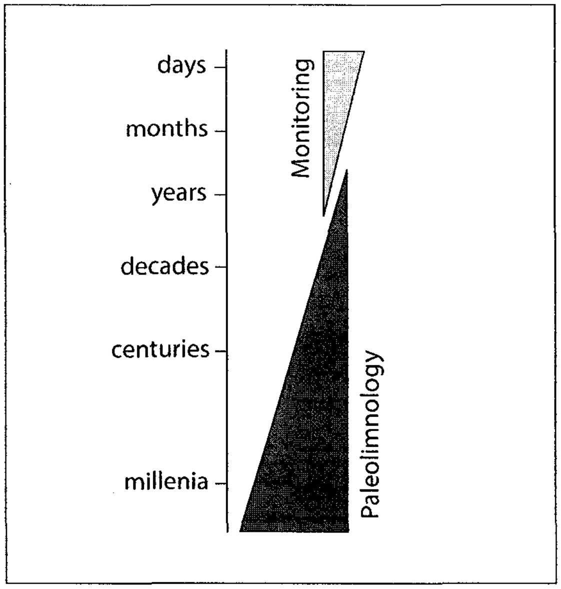

Fig 1.2 Conceptual timescale model of the overlap of environmental monitoring and paleolimnology. Adapted from Smol (2008).

Spatial scale and the importance of regional studies

The non-linearity of lake response to climate or anthropogenic forcing can make changes or biological shifts observed in local scale paleolimnological investigations difficult to put into context (Fritz, 2008). It is therefore most desirable to evaluate whether there is any spatial structure to the paleolimnological results. In a survey of 250 studies from the *Journal of Paleolimnology* (1988-present) over 55% of them were at the local (lake) level, while a considerable 27% were at the regional scale (Figure 1.3). This ratio seems to have remained fairly consistent through time, suggesting that paleolimnologists have long recognized the importance of regional studies. Large regional studies have produced sound evidence of anthropogenic impacts in recent lake histories (~300 years). Two examples of this include the lake acidification projects of North America

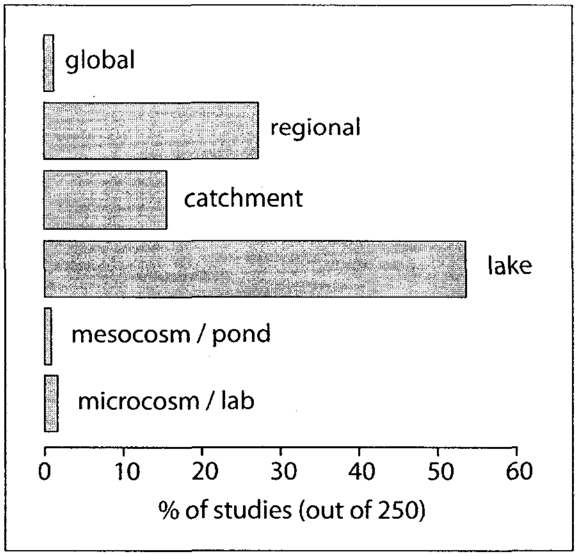

Fig. 1.3 Barplot of study spatial scale used in paleolimnology from a survey of 250 articles in *Journal of Paleolimnology*. Results are in percentages. Regional encompasses two or more catchments and ponds were considered as mesocosm scale.

(PIRLA: Paleoecological Investigation of Recent Lake Acidification) and Europe (SWAP: Surface Water Acidification Program), where interrogation of lake sediment records was able to delineate biological shifts to acidophilous taxa both temporally and spatially in response to acidic rainwaters from industrial activities. Regional studies have also been key in demonstrating the extent of impacts due to anthropogenic climate change in alpine and arctic regions (Battarbee et al., 2002; Smol et al., 2005) and atmospheric nitrogen deposition in alpine regions (Wolfe et al., 2003).

As paleolimnological methods have developed over time there has been an increasingly widespread use of quantitative inference models (transfer functions) (Birks, 1998). Inherent to the methodology of these assessments is a greater understanding of regional modern limnology. This can allow for an overview of any spatial heterogeneity in lake characteristics (e.g. hydrologic setting) which might be useful in interpreting temporal variations among a number of sediment records (Fritz, 2008). The failure to recognize the regional context of a paleolimnological record is a self-imposed limitation on the analysis.

Limits of paleolimnology

Arguably the most important aspect of paleolimnology is the preservation of modern biogeochemical states within the sediment archive. Post-depositional alteration, or lack thereof, of biological communities (e.g. diatom frustule dissolution) and geochemical parameters (e.g. redox sensitive metals) can be verified through various techniques (e.g. scanning electron microscopy). Furthermore, experimental approaches have been helpful in identifying conditions or environments which can lead to a poorly preserved record (Lewin, 1961; Engstrom and Wright, 1984; Flower, 1993). Binford et al. (1983) appropriately describe this limitation; "… diagenesis is at best an annoyance and at worst a nightmare, weakening nearly every generalization that investigators may wish to make (pg 271)". It is therefore important the paleolimnologist confirm reliable preservation of sedimentary proxies. This aspect of paleolimnology is explored in-depth in chapter 4 of this dissertation.

The basis for any sediment record and interpretations of it rely on a well-established chronology. Recent paleolimnology is dependant on the presence and reliable decay of ^{210}Pb, a short-lived radioisotope (half-life 22.3 years) which is part of the ^{238}U decay series. Abundant atmospheric supplies of ^{222}Rn (the parent isotope of lead) in the temperate regions of the globe result from the plentiful supply through diffusion in soils (Appleby, 2001). The limits of this approach can be strained at high latitudes, where permafrost can retard the release of ^{222}Rn and long ice cover inhibit the transfer of ^{210}Pb to the lake (Wolfe et al, 2004). At southern high latitudes the lower hemispheric land mass decreases the available ^{222}Rn. Assumptions of this dating method include: (1) ^{210}Pb supply has remained constant over time, (2) deposition of ^{210}Pb occurs within a closed lake system, and (3) there is no re-distribution by post-depositional processes (e.g. sediment mixing) (Appleby, 2001). Ages are modeled from the decay of the excess or unsupported ^{210}Pb (that which is above the background or supported sediment concentration, Bq g^{-1}). Excursions from the desired exponential decay of unsupported ^{210}Pb with sediment depth can be addressed through analysis of alternative short-lived radioisotopes (^{231}Cs and ^{241}Am) or further investigations (e.g. hydrologic data) of changing sedimentation rates within the lake. Instances of non-exponential decay are detailed within chapter 2 of this dissertation.

Assumptions in paleolimnology

In any paleoecological study the main assumption being made is that the modern ecology of the organism remains constant over time. This is particularly important for quantitative inferences, but also for qualitative studies such as those presented here. Clearly this is also more relevant to longer timescales and is a reason why multiple biological proxies are often used in paleolimnology. We must also make the assumption that the diagenetic environment has remained constant over time. This is perhaps a bit of a leap of faith, as we know that a lake's thermal structure and changes in productivity can affect the reduction potential boundary within the sediments (Deevey, 1955; Mackereth, 1965). However, it is possible to try and interpret changes in periods of diatom dissolution (Hickman and Reasoner, 1998; Stone and Frtiz, 2006) and in redox states through the analysis of geochemical parameters (Engstrom and Wright, 1984).

Other assumptions often mentioned in association with paleolimnology include: one core is sufficient to represent the entire lake and neolimnological aquatic communities are represented by biological fossils. Consensus that the profundal sediments of a lake are relatively homogenous (geochemically and biological fossil communities) has been reached from numerous studies (Binford et al., 1983; Charles et al., 1991; Brock et al., 2006). This does not translate into constant sediment accumulation rates over the profundal regions of a lake and flux calculations need to bare this in mind (Rowan et al., 1995). Sedimentary diatom assemblages have been shown to reflect the neolimnological communities in a number of studies (Haworth, 1980; Leavitt et al., 1994; Lotter and Bigler, 2000). It is therefore well-founded to assume that these conditions are true for a given lake.

Biogeochemical proxies

In each of the chapters that follow a variety of biogeochemical proxies were used and are described in introductory and methods sections therein. Diatom microfossils are common throughout and are described in more detail below. Further discussions and applications on the use of paleolimnological proxies are found in the following reviews: Leavitt and Hodgson (2001) (fossil pigments), Meyers and Teranes (2001) (sediment organic matter), and Petersen and Fry (1987) and Talbot (2001) (nitrogen stable isotopes).

In a survey of the *Journal of Paleolimnology*, the fossil remains of diatoms are the most commonly used biological proxy (Figure 1.4). The responsiveness, abundance, taxonomic diversity and preservation make this class (Bacillariophyceae) of algae a reliable bio-indicator of environmental change. The elegant construction of the diatom's siliceous cell walls (frustules) makes its morphological identification relatively straightforward. As a freshwater organism they are unicellular photo-autotrophs which can have distinct ecological tolerances to water quality (e.g. pH or total phosphorus). Paleoecological studies have shown that the organism is capable of rapid morphological evolution (Theriot and Stoermer, 1984; Theriot et al., 2006) and endemism (Bradbury et al, 1994). Applied studies based on diatom ecology have enlightened many areas of environmental science (Stoermer and Smol, 1999). A total of 351 species were identified during this thesis. A complete species list of diatoms and associated authorities identified during the completion of this dissertation is presented in Appendix A.

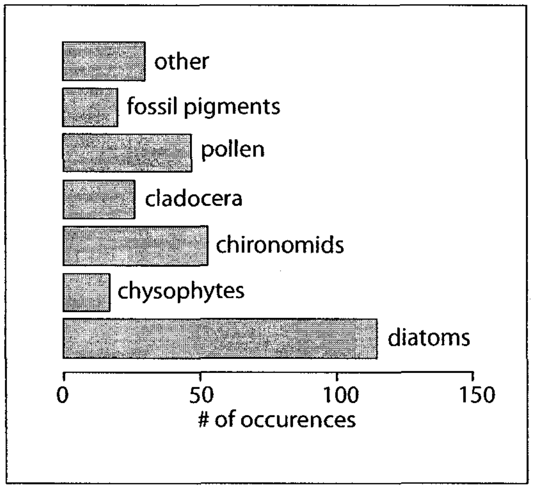

Fig. 1.4 Barplot of biological proxies used in paleolimnology from a survey of 250 articles in *Journal of Paleolimnology*. Results are in number of occurrences.

Fig. 1.5 Location of lake sediment records used in this dissertation. Stars indicate original study lakes, while points are contributed data (see Chap 5 and references within). Lakes from chapter 2 and 3 are: 1 (Fraser), 2 (McKinley), and 3 (N. Barrière). Lake 4 (Pipit) is found in chapter 4 and lakes 5 (Curator), 6 (McConnell), and 7 (Crater) are found in chapter 5. The dark shaded area represents the approximate extent of the Rocky Mountains.

Progression of papers

This dissertation offers an assessment of the biogeochemical responses of lakes to two different environmental forcing mechanisms in seemingly disparate geographical regions (Figure 1.5): (1) marine-derived nutrient subsidies to montane lake ecosystems in British Columbia, Canada, and (2) recent climate change and atmospheric nitrogen deposition in alpine and arctic regions of North America. The paleolimnological records presented herein represent the very recent history of the lakes (~300 years) and therefore focus entirely on the transition into a period of time where global biogeochemical cycles have been influenced by anthropogenic activities (Crutzen, 2002).

Chapter 2 presents an assessment of the ability of lake sediments to archive the biogeochemical changes associated with nutrient subsidies from spawning anadromous salmon (marine-derived nutrients or MDN) in the interior of British Columbia, Canada. Collated data from other studies is also statistically analyzed to ascertain those lake characteristics where MDN is evident in the paleolimnological record. Chapter 3 then expands on this study and presents results from additional lakes within the same drainage basin, using a well-documented human-induced crash of the returning salmon stocks as an independent chronological and biogeochemical marker. Both these chapters are published and reprinted with permission (Hobbs and Wolfe, 2007; 2008).

Chapter 4 looks in detail at the dissolution of diatoms and regeneration of Si from sediments within an alpine lake in the Canadian Rockies (Banff National Park). A holistic approach of water quality, sediment geochemistry, sediment pore waters, and microscopic analysis of diatom fossils are presented. Chapter 5 presents a synthesis of 52 faithful diatom records from alpine and arctic regions over North America. The rate of change of the diatom assemblages during the 20th century are placed in the context of the previous 350 years, allowing us to compare biological shifts during different periods of climatic change. Chapter 4 is unpublished and co-authored with S.V. Lalonde, R.D. Vinebrooke, K.O. Konhauser, R.P. Weidman, and A.P. Wolfe, all affiliated with the University of Alberta. Chapter 5 is unpublished and co-authored with A.P. Wolfe (University of Alberta), R. J. Telford and H.J.B. Birks (University of Bergen), J.E. Saros (University of Maine), R.R.O. Hazewinkel (Alberta Environment), B.P. Perren (University of Toronto), and É. Saulnier-Talbot (Université Laval). The code used for statistical analysis carried out in Chapter 5 using the open source program R can be found in Appendix B.

The main objectives of this body of work are to: (1) ascertain whether paleolimnology is meaningful in the discussion of historical salmon abundance within the Fraser River Basin, British Columbia, Canada, (2) determine if diatom microfossils can be used in recent alpine paleolimnology within the Canadian Rocky Mountains, and (3) quantitatively assess the amount of biological change in alpine and arctic regions of North America through sedimentary diatom records. In effect, objectives 1 and 2 highlight potential limitations in paleolimnology, while objective 3 demonstrates the effectiveness of paleolimnology in describing environmental change over varying temporal and spatial scales.

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CHAPTER 2: CAVEATS ON THE USE OF PALEOLIMNOLOGY TO INFER PACIFIC SALMON RETURNS *

Introduction

Pacific salmon (*Oncorhynchus* spp.) are important elements of the natural, economic, and cultural fabric of British Columbia. Changes in Pacific salmon populations have been attributed alternately to overfishing, habitat loss, and climate-driven oceanographic changes. Salmon life histories link marine and freshwater ecosystems, and thus they represent keystone organisms. For example, semalparous spawning salmon provide an essential source of marine-derived nutrients (MDN, mainly nitrogen (N), and phosphorus (P)) to nursery lakes and rivers (Finney et al., 2000; Naiman et al., 2002). The importance of these nutrient subsidies is sufficient to influence riparian and terrestrial production adjacent to salmon spawning habitats (Reimchen et al., 2002; Helfield and Naiman, 2006). In the case of sockeye salmon (*O. nerka*), lakes are exclusively used as rearing habitat during the first year, where parr benefit from nutrients accrued by the disarticulation and decomposition of adult carcasses in upstream spawning reaches. Via these mechanisms, there is potential for positive feedback between annual adult returns and eventual juvenile migration to the ocean as smolts.

Variability of sockeye MDN subsidies are tracked by lake phytoplankton production. Elevated MDN can induce dominance by eutrophic taxa such as diatoms of the genus *Stephanodiscus* (Finney et al., 2000). Because salmon accrue 95% of their biomass at sea (Groot and Margolis, 1991), where they occupy an elevated trophic position, there is enrichment in their nitrogen stable isotopic composition (^{15}N:^{14}N) relative to a purely freshwater life history. Dead salmon enrich the isotopic signature

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of N in spawning grounds, so that entire drainages, including nursery lakes, become geochemically distinct from non-salmon bearing counterparts, to degrees that are proportional to the numbers of salmon that return and die (Naiman et al., 2002). As a result, the combination of biological and geochemical proxies in lake sediments has been used successfully to reconstruct historical sockeye salmon abundance in a number of Alaskan lake basins (Gregory-Eaves et al. 2004; Schindler et al., 2005).

The applicability of paleolimnological techniques for inferring salmon populations has not been comprehensively assessed outside Alaska. Holtham et al. (2004) presented results from a nursery lake on Vancouver Island (British Columbia, Canada) that did not record the influence of MDN subsidies, leaving open the possibility that paleolimnology may not be universally applicable to the reconstruction of sockeye salmon abundances. There have been no prior studies from nursery lakes of the Fraser River drainage in the BC interior, where salmon travel up to 1000 km to reach spawning habitat. The Fraser River is among the world's most productive salmon fisheries (Groot and Margolis, 1991). Here, we present results of paleo-salmon investigations from Fraser Lake, a large nursery lake near the distal range of sockeye migration in the Fraser River Basin (Figure 2.1). These results are considered in the context of additional unpublished results from BC, as well as previously published sites from Alaska and coastal BC. Together, these findings provide guidance for future investigations by specifying site characteristics that appear to maximize the probability that meaningful salmon signatures are preserved in lake sediments.

Study site

Fraser Lake (54°05'N, 124°45'W) has a 6707 km^2 catchment that incorporates several additional large lakes, namely François, Decker, Burns, and Tchesinkut (Figure 2.1). The entire region falls within the Sub-Boreal Spruce biogeoclimatic zone, characterized by

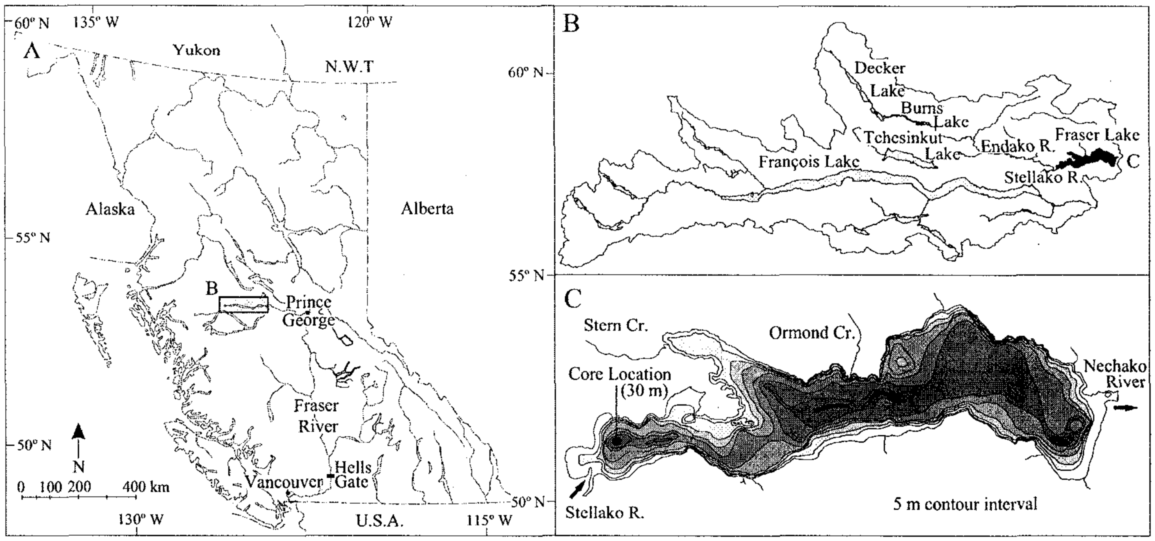

Fig. 2.1 (A) Site location map of Fraser Lake, British Columbia, Canada. (B) Fraser Lake catchment and (C) bathymetry of the lake showing location of the sediment core from the western basin.

englemann-white spruce, subalpine fir, and lodgepole pine. Approximately 92% of drainage into Fraser Lake is contributed by the Endako and Stellako rivers. The lake is dimictic, clear, and has a photic zone of 12 m during summer stratification (Carmichael, 1985). The residence time of lake water is less than a year (Table 2.1). Primary and secondary production in Fraser Lake is somewhat higher than other BC salmon nursery lakes. Fraser Lake is currently mesotrophic and experiences a depletion of N during the growing season, in addition to persistently high P concentrations and stable thermal stratification. Fraser Lake appears to have switched from P-limitation to N-limitation in the 1970s (Shortreed et al., 2001).

Of the 17 most important sockeye nursery lakes in the Fraser River basin, Fraser Lake has the fifth highest mean number of returning salmon (escapement), and the second highest spawner density behind Chilko Lake (Shortreed et al., 2001). Salmon migrate an estimated 820 km from the mouth of the Fraser River to spawning grounds primarily in the Stellako River, but also the Endako River and Ormond Creek (Figure 2.1). Department of Fisheries and Oceans Canada records for the Stellako date back to 1938 and document an increase in escapement post-1970, with highs of ~370,000 fish in 1988 and 2000. Prior to 1938, significant impacts to the run occurred with the onset of commercial

Table 2.1 Fraser Lake morphometry, water chemistry (1992-1993), and sockeye salmon escapement abundance (DFO, 1938-2004).

Lake Morphometry		Water Chemistry[a]	
Longitude	124°45'W	Mean NO_3^- ($\mu g\ L^{-1}$)	3.3
Latitude	54°05'N	Spring overturn NO_3^- ($\mu g\ L^{-1}$)	3
Elevation (m a.s.l.)	670	Seasonal minimum NO_3^- ($\mu g\ L^{-1}$)	0.9
Z_{max} (m)	30.5	Mean TP ($\mu g\ L^{-1}$)	15.4
Z_{mean} (m)	13.4	Spring overturn TP ($\mu g\ L^{-1}$)	17.8
Lake volume (x 10^9 L)	725.3	Chlorophyll *a* ($\mu g\ L^{-1}$)	4.2
Catchment area (km^2)	6707.1	pH	7.5
Lake area (km^2)	54.6		
Catchment:lake ratio	121.8		
Water residence time (yr)	0.8		
Sockeye salmon escapement (10^3 fish)			
Mean escapement	91.6		
Minimum escapement	2.6		
Maximum escapement	372.5		
Spawner density (10^3 km^{-2})	1.7		

[a] Shortreed et al., 2001; (*n*=12)

fishing and the establishment of Fraser River canneries in the late 1800s, and following a series of catastrophic landslides at Hells Gate in 1913-1914 (Figure 2.1). The first fishway that bypasses the Hells Gate slide was completed in 1917, allowing for slow recovery of all upstream runs in the Fraser River basin (Thompson, 1945).

Methods

Core collection and chronology

A 41 cm sediment core was recovered from the western basin of Fraser Lake on 27 May 2004 (Figure 1). A modified Kajak-Brinkhurst gravity corer was used to collect a continuous sediment record with an intact sediment-water interface (Glew et al., 2001). The core was extruded and sub-sampled at 0.25 cm intervals for the first 10 cm and 0.5 cm thereafter, using a high-resolution sectioning device (Glew et al., 2001). Core

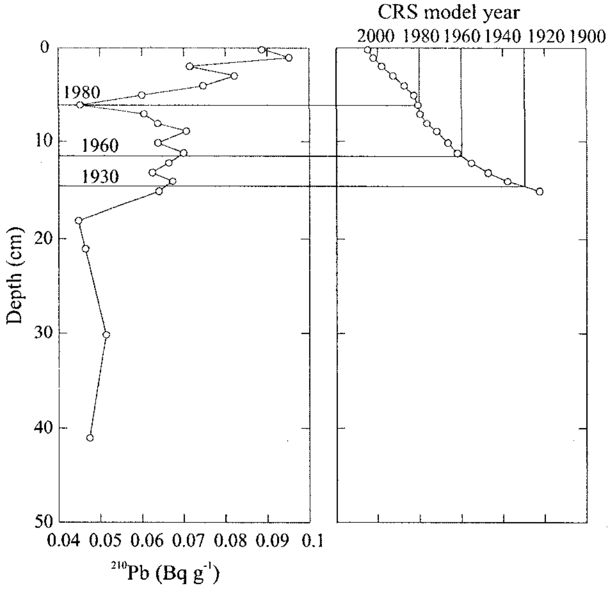

Fig. 2.2 ^{210}Pb chronology from the Fraser Lake gravity core. Sediment ages are estimated using the constant rate of supply (CRS) model.

chronology was established using the inventory of unsupported ^{210}Pb activity measured by alpha spectroscopy, to which the constant rate of supply (CRS) model was applied (Appleby and Oldfield, 1978). Because the inventory of unsupported ^{210}Pb becomes exhausted at 18 cm (Figure 2.2), sedimentation rates from the lower dated portion of the core (10-15 cm) were extrapolated to predict the age of deeper sediments, resulting in an estimated age of ~1820 AD at 41 cm depth.

Sediment geochemistry

Isotopic ratios and elemental abundances of N and C were determined from 0.25 cm increments taken every 2 cm from the Fraser Lake core, in order to ascertain the applicability of $\delta^{15}N$ as a proxy for MDN in Fraser Lake and to provide indications of the source of organic matter from molar C:N ratios. This sampling provides approximately decadal temporal resolution for the core, which should be sufficient to identify impacts associated with major events, such as the legacy of the Hells Gate slides in 1913-14, which depressed stocks for several decades. Natural abundances of stable carbon (^{13}C:^{12}C) and nitrogen isotopes (^{15}N:^{14}N) are reported as per mil (‰) using delta notation ($\delta^{13}C$; $\delta^{15}N$). $\delta^{15}N$ is reported relative to air ($\delta^{15}N = 0‰$), and $\delta^{13}C$ relative to the Vienna Pee Dee Belemnite (VPDB) marine-carbonate standard for carbon and oxygen. Samples were analyzed by continuous-flow isotope-ratio mass spectrometry, following pyrolysis and gas chromatographic separation in a coupled elemental analyzer. Analytical precision for isotopic analyses was ±0.15‰ ($\delta^{15}N$) and ±0.03‰ ($\delta^{13}C$), as calculated by the analysis of laboratory standards. In addition to %C and %N obtained from elemental analysis, total organic matter content (%OM) was estimated by loss on ignition following Heiri et al. (2001).

Organic matter separations

Following initial nitrogen isotopic measurements that failed to reveal an interpretable MDN signal in Fraser Lake bulk sediments, a density separation of sediment organic matter was undertaken to isolate a fraction representative of solely autochthonous sources. This was undertaken in an attempt to remove the potential overprinting of the aquatic isotopic signature, including that attributable to salmon, from terrestrial organic matter. The density separation protocol followed that of Hamilton et al. (2005), in which a slurry of sediment (100-200 mg) is slowly introduced to colloidal silica medium at a density 1.27 g cm^{-3}. The light organic matter (LOM) recovered from the supernatant, deemed to reflect primarily in-lake algal and microbial production, was then analyzed for $\delta^{15}N$. Both LOM and the remaining fraction were microscopically examined, which confirmed that different compositions were indeed separated from each other.

Diatom preparation, identification and enumeration

For diatom analysis, aliquots of 100 mg dry sediment were oxidized with 30% H_2O_2 to remove organic matter in preparation for identification and enumeration. General slide preparation and diatom enumeration protocols are presented elsewhere (Battarbee et al., 2001). Microscope slides were permanently mounted using Naphrax®. Between 400 and 500 diatom valves were counted from each sample under oil immersion at 1000x, using differential interference contrast optics. Diatom taxonomy followed Krammer and Lange-Bertalot (1986-1991), Cumming et al. (1995) and Fallu et al. (2000), with genus-level nomenclatural revision according to Round et al. (1990). Diatom counts are expressed as frequencies (%) of taxa relative to the sum of valves counted in any one sample.

Spectrally-inferred chlorophyll a

Fossil chlorophyll *a* (Chl *a*) in lake sediments provides an indication of total algal production within the lake. A non-destructive method of inferring Chl *a* concentrations from the spectral properties of freeze-dried lake sediments was applied to Fraser Lake samples (Wolfe et al., 2006). This method exploits sediment red reflection (650-700 nm) to estimate concentrations of Chl *a* and its degradational pheopigments (primarily pheophytin *a* and pheophorbide *a*). The description and protocols of this method can be found in Wolfe et al. (2006).

Statistical methods

Diatom stratigraphic zones were determined objectively by stratigraphically-constrained cluster analysis, using the squared chord distance metric. Compositional changes in diatom assemblages were summarized by ordination, using a detrended correspondence analysis (DCA) performed on the relative frequencies of each taxon >1% in any one sample (Hill and Gauch, 1980). This amounts to the inclusion of between 8 and 15 taxa per sample, more than are illustrated for some intervals (Figure 3). Plotted stratigraphically, the diatom DCA axis 1 sample scores graphically depict down-core diatom assemblage compositional changes (Birks et al., 2000). The sample scores are expressed in standard deviation (or turnover) units along the primary axis. Eigenvalues of the DCA axes 1 through 4 were: 0.15, 0.06, 0.05, and 0.03, respectively. Prior to DCA, all data were square-root transformed, detrended by segments, and rare species were downweighted.

A second ordination was undertaken to compare new results with previously published data pertaining to sediment MDN records in relation to lake features. For a series of 10 lakes in Alaska and BC the following parameters were tabulated: catchment:lake ratio, catchment area, sockeye escapement, spawner density, mean sediment C:N and $\delta^{15}N$.

Data for 5 of these lakes are published (Finney et al., 2000; Gregory-Eaves et al., 2004; Holtham et al., 2004). The remaining lakes include Fraser and the authors' unpublished data from four additional lakes in the interior (N. Barrière and McKinley) and coast of BC (Nahwitti and Clayoquot). Principal components analysis (PCA) was applied to a correlation matrix based on these data, thereby providing a synthetic overview of how reliably the MDN signature is transferred to lake sediments. Lake parameters were centered and standardized and ordinations were conducted with CANOCO v.4.

Results

^{210}Pb chronology

Supported levels of ^{210}Pb were attained in the Fraser Lake Glew core at a depth of 18 cm. However, the unsupported inventory does not decline exponentially with depth, but rather contains several intervals of moderately to strongly diluted ^{210}Pb activity (Figure 2.2). The most plausible explanation for these dilutions is short-lived events of accelerated inorganic sedimentation, given that the most pronounced depletions of the unsupported ^{210}Pb inventory (2 and 7 cm) coincide with reduction in sediment organic content (Figure 3). Extensive land-use changes in the basin, coupled to exceptionally high fluvial discharges into Fraser Lake during several years in the 1980s and 90s (Carmichael, 1985), are the most likely causes of irregular sedimentation patterns at the coring site. Nonetheless, the ^{210}Pb results can be accommodated by the CRS model to produce a realistic age model for the last ~75 years. This model (Figure 2.2) depicts a rapid increase in sediment accumulation rate after ~1980. At this time, the average accumulation rate of 1.6 mm yr^{1} for the 1930-1980 interval rose to 2.6 mm yr^{1} for 1980-2005. Previous results from the west basin of Fraser Lake documented similar sedimentation increases in the upper-most 10 cm of the core (Cumming, 2001). Hydrological monitoring of the Stellako River by Environment Canada shows peak mean annual flows in 1976, which correspond to the estimated ^{210}Pb age (within 1σ) of the noted excursions.

Diatom stratigraphy

Diatom valves were well preserved in the sediments of Fraser Lake, with no indications of dissolution. A total of 195 diatom taxa were identified, of which only taxa exceeding 3% in any sample are illustrated (Figure 2.3). Diatom assemblages show few major changes over the period of deposition. There is a clear dominance throughout the core by the planktonic diatom *Aulacoseira subarctica,* a meso- to eutrophic taxon (Figure 2.3). Phytoplankton samples taken during the growing season from the water column of Fraser Lake, show an early spring and late summer dominance of *A. subarctica* with *Asterionella* spp. and *Stephanodiscus* spp. (Carmichael, 1985).

Despite the dominance by one species of diatom, there are subtle changes significant enough for a cluster analysis to define 3 zones of similarity. The first zone extends from the bottom of the core (41 cm) to 26 cm. Sub-dominant taxa include the planktonic diatoms *Stephanodiscus parvus* and *S. minutulus*, both eutrophic diatoms, and *Staurosirella pinnata*, a benthic species with a wide tolerance of nutrient conditions (Christie and Smol, 1993; Reavie, 1995). The high percent abundance of *A. subarctica* (> 60%) translates into the low observed total benthic sum in zone 1. The second zone is essentially the remainder of the core, extending from 26 cm to 2.5 cm and starts at approximately the mid 1800s. At the bottom of this zone *A. subarctica* declines in concordance with increases in the *S. parvus / S.minutulus* complex and other planktonic spp. (*Fragilaria capucina* and *Tabellaria flocculosa*). Optimum nutrient conditions for *F. capucina* and *T. flocculosa* are eutrophic, however a large tolerance has also been observed suggesting more meso- to eutrophic conditions (Reavie, 1995). The percent abundance of the benthic taxa, *Cocconeis placentula* and *Achnanthes minutissima,* which have a wide tolerance to nitrogen and phosphorus concentrations (Christie and Smol, 1993; Stevenson, 1995), also increase in zone 2. Diatom DCA scores show that the

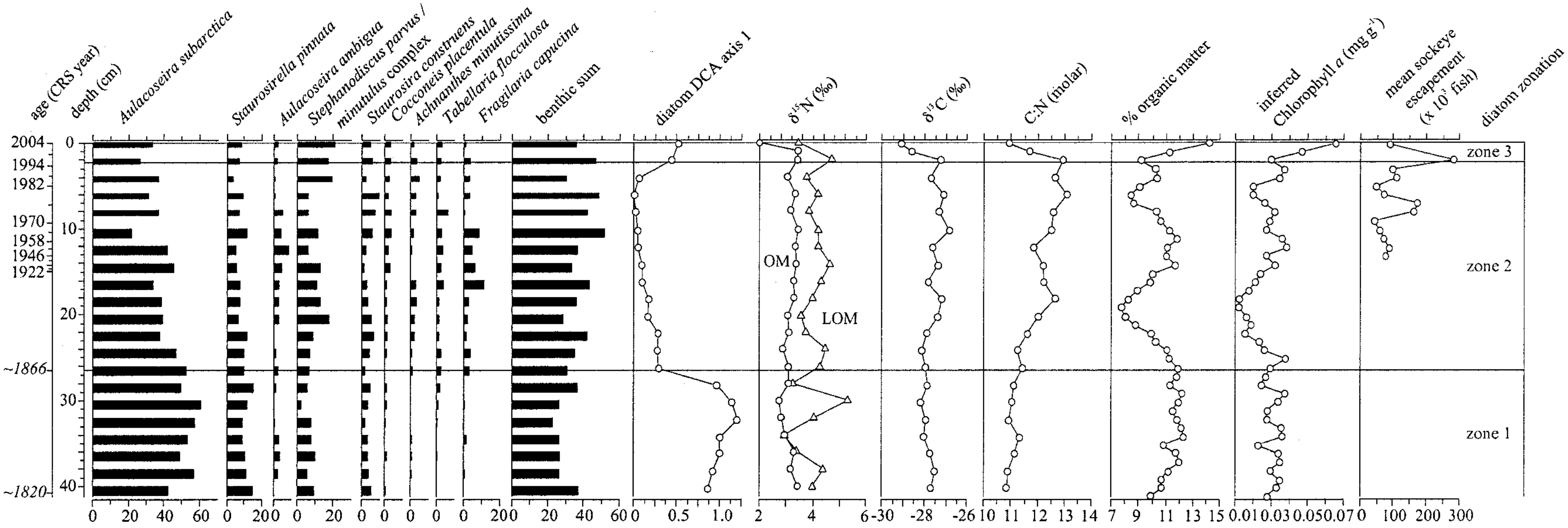

Fig. 2.3 Diatom and geochemical stratigraphy of the Fraser Lake sediment core. Relative abundances of diatom taxa are shown as black solid bars, where the thickness of the bars is proportional to sample thicknesses. DCA axis 1 scores summarize diatom compositional changes. $\delta^{15}N$ results from bulk OM (open circles) and LOM (open triangles) are shown on the same plot, alongside $\delta^{13}C$, C:N, %OM, inferred Chl a, and sockeye escapement (1938-2004) averaged over dated sediment intervals. Extrapolated CRS model ages are included in italics.

assemblages exhibit very low compositional changes throughout this zone (Figure 2.3). The uppermost zone 3 (2.5 cm to surface) shows the largest percent abundance in the *S. parvus / S.minutulus* complex (21.6%), suggesting increasingly eutrophic conditions. Other planktonic diatoms (*A. subarctica, F. capucina,* and *T. flocculosa*) decrease in percent abundance during this time period, while the benthic taxa remain similar to zone 2. This zone represents an estimated age of 1997 to present.

Geochemistry, spectrally-inferred chl a and sockeye escapement

The $\delta^{15}N$ of organic matter from sediment core samples ranged from 2.02‰ to 3.44‰ (Figure 2.3). There is only a subtle variation of ~ 0.30‰ throughout most of the core, with the exception of the uppermost surface sample which is isotopically depleted by 1.4 ‰ relative to the underlying sample. In order to explore relationships between $\delta^{15}N$ and sockeye escapement, the annual sockeye escapement data were averaged over the intervals represented by individual sediment slices, according to the ^{210}Pb dating results (Figure 2.2). In so doing, the escapement data represent integrations of time that are directly compatible with the resolution of the sediment record (multi-annual to decadal). No clear relationship was found between $\delta^{15}N$ and salmon escapement.

The $\delta^{13}C$ of bulk organic sediment shows some variation down-core (-26.88‰ to –29.13‰; $\sigma = 0.48$‰), including a 1.87‰ depletion in the upper 2 cm of the core (Figure 3). The C:N exhibits a range of 10.8-13.1, suggesting that Fraser Lake organic matter is mainly aquatically-derived, which is also confirmed by the strong relationship between %OM and Chl *a* (Figure 3; n=42, r=0.77, p<0.001). The reliability of C:N as a proxy for organic matter source is also supported by the diatoms: DCA axis 1 scores are correlated to sediment C:N (n=21; r=-0.78; p<0.001), with the lowest C:N values associated with the greatest abundances of planktonic taxa.

Stratigraphically, geochemical variables vary very little in diatom zone 1 (26–40 cm) of the core, with the exception of the depletion of $\delta^{15}N$ synchronous to a positive excursion in the diatom DCA axis 1 (28-34 cm; Figure 3). The second diatom zone (2.5-26 cm), beginning in approximately the mid-1800s, displays increased variation in %OM coincident with Chl *a* and an increase in C:N. The third diatom zone shows the greatest amount of change geochemically, evidenced by isotopic depletions and increased algal-derived OM.

Organic matter separations

Microscopic inspection of the LOM and remaining (ρ >1.27 g cm^{-3}) fractions revealed two different compositions; while LOM contained diatom frustules and green to grey amorphous organic matter, the denser fraction comprised charcoal, plant ligneous tissues, abundant pollen grains, and relatively few diatom frustules. These observations strongly suggest that the density separation was highly successful in separating aquatic from terrestrial sediment organic matter (Hamilton et al., 2005).

Isotopically, $\delta^{15}N_{LOM}$ is enriched on average 1‰ relative to $\delta^{15}N_{BULK}$, whereas $\delta^{13}C_{LOM}$ is depleted on average by 1‰ relative to $\delta^{13}C_{BULK}$. The co-isotopic plot of LOM and BULK fractions reveals that they are indeed distinct (Figure 2.4). Consistently low $\delta^{13}C_{LOM}$ values imply that primarily aquatic OM was recovered by the density separation, which is supported by the lower C:N of this fraction (ΔC:N$_{BULK-LOM}$=1.0-2.1; *n*=19). The stratigraphic record of $\delta^{15}N$ for both fractions (Figure 2.3) shows that, with the exception of three intervals (28, 34, and 36 cm), the $\delta^{15}N_{LOM}$ is significantly enriched (by ≥ 0.30‰, or twice instrument precision) relative

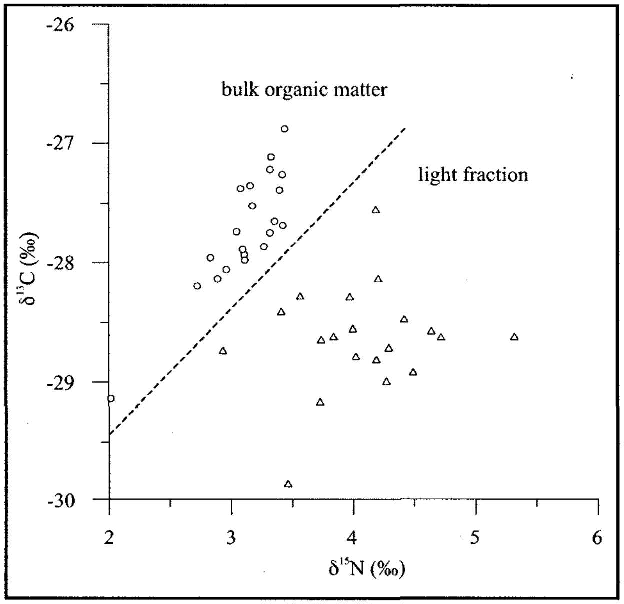

Fig. 2.4 Co-isotopic plot ($\delta^{13}C$ and $\delta^{15}N$) of bulk organic matter (open circles) and the density-separated light fraction (open triangles) from the Fraser Lake core. The dashed line separates the two fractions.

to $\delta^{15}N_{BULK}$. Neither the primarily aquatic LOM nor the bulk fraction produce N-isotopic results that can be interpreted with respect to salmon escapement (Figure 2.3).

Discussion

Paleo-salmon proxies

The use of lake-sediment $\delta^{15}N$ as a proxy of sockeye salmon abundance in nursery lake ecosystems has been applied with success in coastal Alaska (Finney et al. 2000, Gregory-Eaves et al. 2004; Schindler et al. 2005). The most striking difference between studies from Alaska and our data is the upper range of sediment $\delta^{15}N$ values. Finney et al. (2000) have reported $\delta^{15}N$ in sediment OM from Karluk Lake, Alaska ranging from 6.20‰–9.75‰, whereas Fraser Lake exhibits a narrower range of 2.02‰–3.44‰. The $\delta^{15}N$ of *O. nerka* is reported to be 11.2 ± 0.45‰ (Schindler et al., 2005). Studies have shown there is little diagenetic fractionation of the $\delta^{15}N$ of lake seston, indicating the sediments are reliable archive of $\delta^{15}N$ of primary OM (Hodell and Schelske, 1998; Teranes and Bernasconi, 2000). The more depleted $\delta^{15}N$ of Fraser Lake sediments, combined with the absence of correlation to sockeye escapement, suggest that variability of the MDN subsidy to this lake is not registered.

The most probable explanation for the absence of an MDN influence to Fraser Lake is the estimated proportion it contributes to the annual nutrient budget of the lake. An approximate annual nutrient budget from fluvial inputs to Fraser lake suggested that only 3% N and 7% P was attributable to sockeye salmon (Carmichael, 1985). In comparison, sockeye contribute >50% N, and ~60% P, to Karluk Lake (Koenings and Burkett, 1987; Finney et al. 2000).

Summer lake-water chemistry shows complete utilization of the Fraser Lake N pool for much of the growing season (Shortreed et al., 2001). We thus consider the possibility that periodic N-limitation may have stimulated cyanobacterial N-fixation, in turn accruing isotopically-light OM to sediments, and inducing relatively low sediment $\delta^{15}N$ values (Peterson and Fry, 1987). The main source of N for Fraser Lake is via the Endako - Stellako River basins, which are influenced by surrounding forests and agricultural land use. Nitrate and ammonium fertilizers tend to have a $\delta^{15}N$ ranging from –3‰ to 3‰ (Macko and Ostrom, 1994), while the $\delta^{15}N$ of forest litter and surface soils are ≤ 0‰ (Nadelhoffer and Fry, 1994). Because terrestrially-derived N is isotopically depleted relative to sockeye salmon, we interpret the low $\delta^{15}N$ of Fraser Lake sediments to reflect a large terrestrial contribution to sediment OM.

The main compositional change in diatom assemblages over the last ~190 years is in the mid to late-1800s (Figure 2.3). Having established that Fraser Lake is not responding to changes in MDN, the observed change in diatom assemblages can be attributed to either human disturbance within the catchment, through forestry and agricultural activities, or regional warming following the Little Ice Age (LIA) (Wilson and Luckman, 2003). The increased presence of meso- to eutrophic species (i.e. *Fragilaria capucina, Stephanodiscus parvus/minutulus*), suggests an increased nutrient load. Elevated sediment C:N values in diatom zone 2 are consistent with sustained terrestrial inputs (Kaushal and Binford, 1999). A second compositional change in the 1980s, highlighted by further increase in *S. minutulus/parvus*, seems to track further anthropogenic enrichment of Fraser Lake. However, none of these changes can be reliably tied to the lake's salmon history, unlike the diatom signatures observed in Alaskan counterparts (Finney et al., 2000).

Paleolimnology and sockeye salmon

To investigate the first-order controls on the likelihood of success using paleolimnology to infer historical salmon abundances, we analyzed known key variables in site selection (sockeye escapement, spawner density, catchment area, catchment:lake ratio) and subsequent analytical results (mean $\delta^{15}N$ and C:N), for a number of salmon nursery lakes on a latitudinal gradient from Kodiak Island, Alaska to southern coastal BC (Figure 2.5). PCA loadings of the collated parameters reveal that variability among the sites on the primary axis is strongly influenced by C:N, $\delta^{15}N$, and sockeye escapement (Figure 2.5A). The first axis explains 50% of variability within the data set. Catchment area and catchment:lake ratio are associated with the second PCA axis (29%). The PCA biplot shows Alaskan lakes to be most closely associated with sockeye escapement, spawner density, and sediment $\delta^{15}N$ (Figure 2.5B). Coastal and interior lakes from BC are more influenced by catchment area and catchment:lake ratio. Coastal BC lakes are inversely correlated to salmon escapement and strongly loaded by sediment C:N (Figure 2.5B), further attesting to the high allochthonous inputs they receive. The PCA analysis reveals that C:N and $\delta^{15}N$ load strongly in opposite directions on axis 1. BC

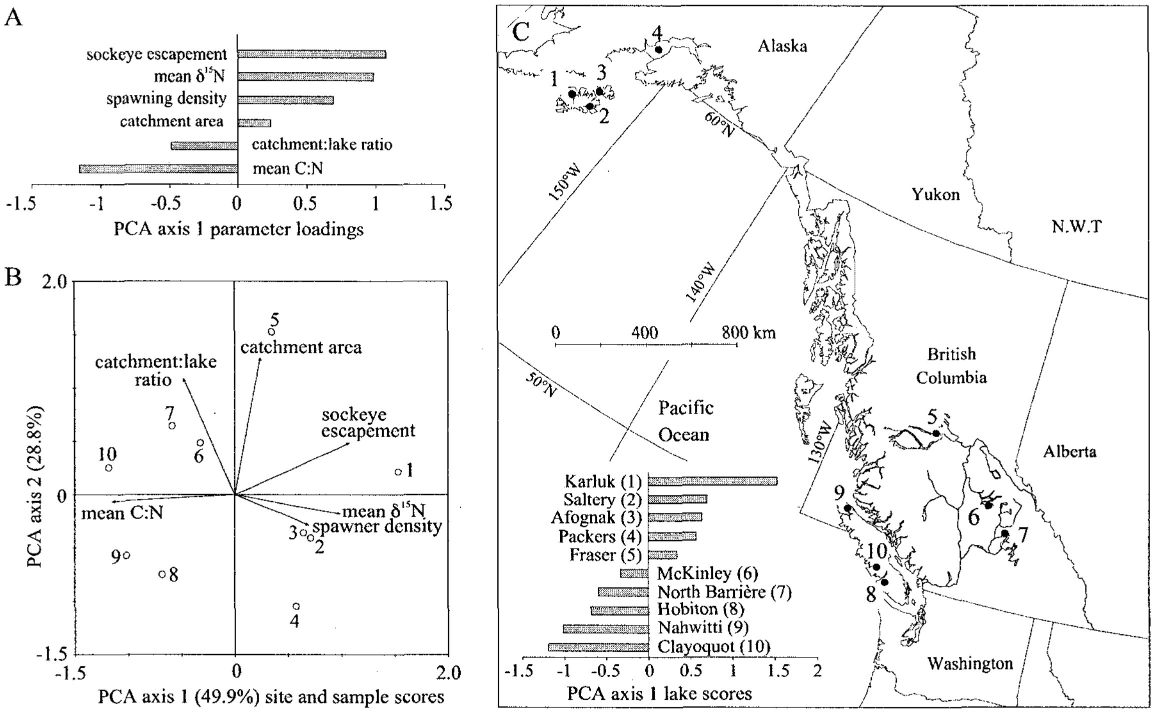

Fig. 2.5 PCA ordination results using catchment characteristics and paleo-salmon proxies from ten sockeye salmon nursery lakes. (A) Parameter loadings on the primary PCA axis. (B) PCA biplot of lake parameters (arrows) and sample locations (numbered open dots) for the first 2 PCA axes. Proximity of samples to a given variable implies strong loading by that parameter. (C) Locations of the analyzed lakes and their loadings on axis 1, showing the progression from the BC coast, to the BC interior, and finally to coastal Alaska. Sources are: N. Barrière, McKinley, Clayoquot and Nahwitti Lakes (Hobbs, unpubl. data); Packers Lake (Gregory-Eaves et al., 2004); Hobiton, Afognack and Saltery Lakes (Holtham et al., 2004); and Karluk Lake (Finney et al., 2000).

coastal lakes, in a general sense, are 'high C:N-low $\delta^{15}N$', whereas Karluk Lake might be considered a representative 'low C:N-high $\delta^{15}N$' site. Although this provides only a general set of guidelines based on currently available data, this direction of sediment C:N and $\delta^{15}N$ variability is supported by additional results from coastal BC (Brahney et al., 2006). Catchment:lake ratio, as used here, is a proxy for water residence time. BC lakes, especially from the interior, are most strongly influenced by this parameter, which dominates PCA axis 2 (Figure 2.5B). Shorter residence times imply faster flushing of any MDN accrued in the ecosystem, which may represent another fundamental difference between the BC and Alaskan lakes considered in this analysis. The responsiveness of lakes to MDN appears to vary geographically over a primary gradient of latitude (Figure 2.5C). Sediments from lakes situated in southern Alaska may thus archive a clearer response to past variability of MDN, relative to lakes from interior and coastal BC. In BC, the signals investigated appear either highly muted or completely absent. These lakes are more heavily subsidized by catchment-derived organic matter, whether of natural or anthropogenic provenance.

Conclusion

Studies from southern Alaska have demonstrated the reliability of paleolimnology to infer historical populations of sockeye salmon. Inherent to this success is the positive feedback between MDN and juvenile salmon in the nursery lake. A sediment record from Fraser Lake, BC failed to track the well-documented shifts in sockeye escapement over the past ~60 years. The proportion of this lake's annual nutrient supply contributed by sockeye appears to be small, compared to lakes which successfully record MDN variability in their sediments. Catchment-derived nutrients appear to dominate the sediment geochemical records from lakes within the interior and coastal regions of BC, in addition to shaping their diatom records. These findings corroborate the observation that juvenile salmon need not be completely reliant on MDN subsidies (Schindler et al., 2005). This assessment in no way dismisses the acknowledged importance of MDN in these ecosystems, but rather places caveats on how reliably they stand to be preserved in sedimentary archives.

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CHAPTER 3: RECENT PALEOLIMNOLOGY OF THREE LAKES IN THE FRASER RIVER BASIN (BC, CANADA): NO RESPONSE TO THE COLLAPSE OF SOCKEYE SALMON STOCKS FOLLOWING THE HELLS GATE LANDSLIDES *

Introduction

The use of paleolimnology to track changes in marine-derived nutrients (MDN) from sockeye salmon (*Oncorhynchus nerka*) nursery lakes has provided reliable estimations of historical populations in southern coastal Alaska (Finney et al. 2002; Gregory-Eaves et al. 2004; Schindler et al. 2005). The life history of sockeye sustains nutrient subsidies to natal lacustrine ecosystems, following spawning. Variations in MDN with sockeye population size can be tracked by fossil phytoplankton and zooplankton (Finney et al. 2000). Sockeye gain approximately 95% of their body mass during the marine portion of the life cycle at an elevated trophic level (Groot and Margolis 1991), yielding an enriched nitrogen stable isotopic composition (hereafter $\delta^{15}N$) compared to solely freshwater salmonids. Spawning sockeye have been observed to retain a body tissue $\delta^{15}N$ of $11.2 \pm 0.45‰$ (Schindler et al. 2005). As a result, the sediment $\delta^{15}N$ of organic matter in nursery lake systems can be isotopically-enriched relative to non-migratory systems, to degrees that relate to the abundance of spawned-out returns.

The sockeye salmon stocks of the Fraser River drainage provide the second most productive sockeye fishery in the world, after Bristol Bay, Alaska. Sockeye return to nursery lakes to spawn and die on an approximate four-year cycle. The individual runs must navigate a diverse and arduous terrain, with a maximum migratory distance of ~1100 km. With the exception of a small number of lakes in the southern extension of the Fraser River, sockeye must pass through the narrow portion of the Fraser canyon

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known as Hells Gate (49°46,75”N, 121°26.5”W; 106 m.a.s.l). Construction of the Canadian Pacific Railway (CPR) into the bedrock of the canyon (Early-Tertiary quartz diorites) caused a series of landslides at Hells Gate between 1913-1914 (Figure 3.1A). The constrained channel prevented the passage of nearly all returning sockeye, causing an almost complete collapse of the upstream runs. Effort was made immediately following and in subsequent years to clear and bypass the obstruction (Figure 3.1B). However, the legacy of the slides was felt for years to come, depressing stocks well into the 1940s (Figure 3.1C) (Thompson 1945). With the possible exception of commercial fishing, no single greater impact to Fraser River sockeye salmon is documented historically.

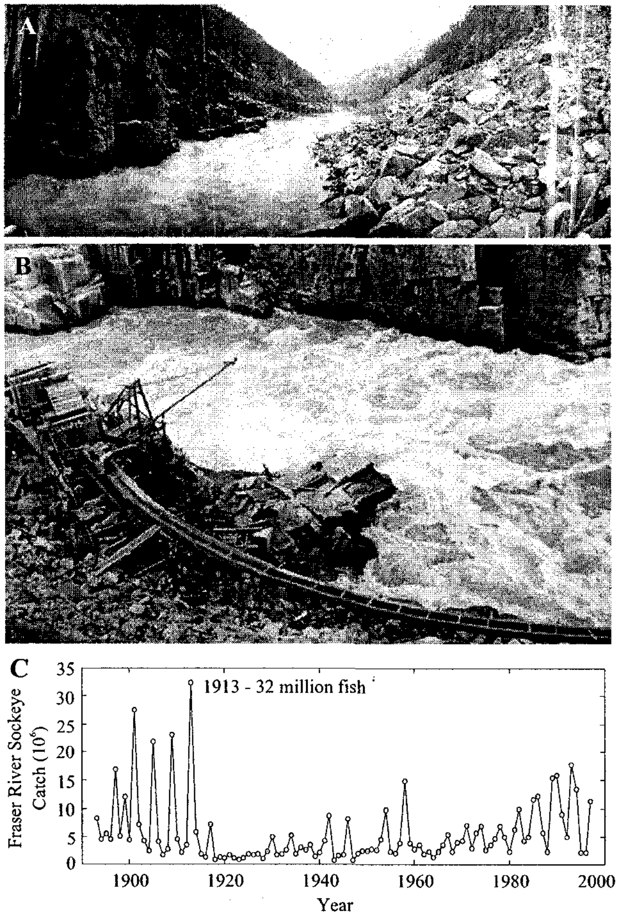


Fig. 3.1 Photographs of Hells Gate, Fraser Canyon, showing the channel immediately following a major slide in 1914 (A) and post-slide clean-up and construction of a temporary wooden fishway/sluiceway in 1915 (B); Photos reproduced with permission from BC Archives, Royal BC Museum (#A-04680) and Per Saxvik, Engineering Department of the International Pacific Salmon Fisheries Commission (www.saxvik.ca). Fraser River sockeye catch records from the Pacific Salmon Commission, detailing the collapse and slow recovery of salmon following the slides (C)

Previous paleolimnological investigations into sockeye nursery lakes in British Columbia (BC), Canada have focused solely on coastal lakes (Holtham et al. 2004; Brahney et al. 2006). Holtham et al. (2004) have suggested that high flushing rates, terrestrial inputs, and low salmon spawning densities in a coastal BC lake and two coastal Alaskan lakes resulted in a sedimentary δ^{15}N record which did not track salmon abundance variations. In this study we present paleolimnological findings from three sockeye nursery lakes upstream of Hells Gate in the Fraser River Basin located in the interior of BC. We selected lakes which vary in spawning density, migratory length (420-820km), and catchment characteristics. Typically, BC interior lakes have a nival-dominated hydrology with peak inflows during the summer months, before sockeye run and spawn. This contrasts rain-dominated coastal catchments which receive the majority of their hydrologic input during winter, well after all spawning activity (Stockner 1987). The main focus of this paper is to investigate the association between sediment geochemical parameters (δ^{15}N and C:N), diatom compositional changes, and the Hells Gate slides, in three well-dated cores. The Hells Gate event is not represented in the three records. Furthermore, we failed to identify paleolimnological trends that may be associated with other features of the documented record, namely the onset and intensification of the Fraser River commercial fishery after 1890. Escapement records exist for between 35 and 65 years for the 3 tributaries considered here, allowing further comparisons to the sediment record.

Study sites

Fraser Lake

Fraser Lake (124°45'W, 54°05'N; 670 m.a.s.l; Figure 3.2B) is situated within the Sub-Boreal Spruce biogeoclimatic zone, which is characterized by Englemann-white spruce and subalpine fir, with some lodgepole pine. Approximately 92% of the drainage to Fraser Lake is via the Endako and Stellako Rivers, producing water residence times under a year (Carmichael 1985). The geology of the Fraser Lake catchment is highly variable and fractured, consisting of minor mid-late Jurassic intrusive granites and quartzites and breccia, basalt, sandstone and shales (Massey et al. 2005).

Fraser Lake is dimictic and currently mesotrophic experiencing a depletion of N during the growing season, with high P concentrations and stable thermal stratification

(Table 3.1; Shortreed et al. 2001). The clearing of land for agricultural activities and residences has been the main effect on water quality. Of the 17 main sockeye salmon nursery lakes in the Fraser River Basin, Fraser Lake has the fifth highest mean escapement and the second highest spawner density behind Chilko Lake (Shortreed et al. 2001). Sockeye salmon primarily use the Stellako River (migratory distance of 820km) for spawning, but also the Endako River and to a lesser extent Ormond Creek (Figure 3.2C). Department of Fisheries and Oceans Canada (DFO) escapement records for the Stellako date back to 1938 and document an increase in escapement post-1970, with highs of ~370,000 fish in 1988 and 2000 (Table 1).

McKinley Lake

McKinley Lake (120°56'W, 52°15'N; 865 m.a.s.l; Figure 3.2B) straddles the Interior Cedar-Hemlock and Englemann Spruce-Subalpine Fir biogeoclimatic zones within the Horsefly River Basin. The surrounding forests are composed of Western Hemlock,

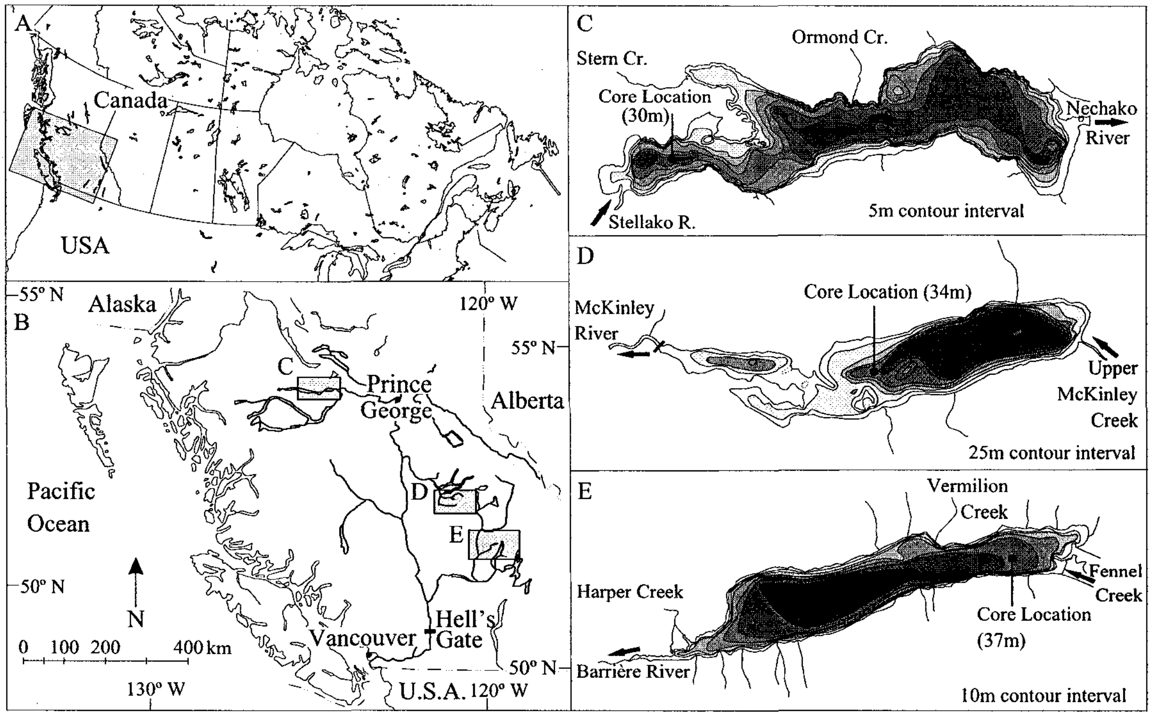


Fig. 3.2 Location maps (A-B) of the three sockeye nursery lakes in the Fraser River drainage (bold lines). Bathymetry and coring locations for Fraser (C), McKinley (D), and North Barrière (E) lakes

Western Cedar, Englemann Spruce, Subalpine Fir and Lodgepole Pine. The McKinley Lake catchment is composed mainly of Triassic to Jurassic volcanic bedrock with sandstone, shales, argillite, draped by Quaternary alluvium (Massey et al. 2005).

McKinley Lake is impacted almost exclusively by forestry, with the exception of a number of lakeside cabins. The lake appears to be oligotrohic (Table 3.1), however long-term water monitoring has not been carried out. It is situated in the Horsefly River Basin,

Table 3.1 Sockeye salmon nursery lakes within the Fraser River drainage, BC: lake morphometry, water chemistry (1992-1993; 2004) and sockeye salmon escapement abundance (DFO Salmon Escapement Database System)

Lake Morphometry	Fraser Lake	McKinley Lake	North Barrière Lake
Longitude	124°45'W	120°56'W	119°50'W
Latitude	54°05'N	52°15'N	51°20'N
Elevation (m.a.s.l)	670	865	634
Z_{max} (m)	30.5	65	52.6
Z_{mean} (m)	13.4	24	24.7
Lake volume (x 10^9 l)	725.3	123.8	112.1
Catchment area (km^2)	6707.1	401.3	517.7
Lake area (km^2)	54.6	5.1	4.5
Catchment:lake	121.8	77.4	113
Water residence time (yr)	0.8	0.8[a]	0.3[a]
Sockeye Escapement (x 10^3 fish)			
Mean escapement	95.6	3.6	5.8
Min. escapement	2.6	0	0
Max. escapement	371.5	15.8	33
Spawner density (10^3 km^{-2})	1.8	0.7	1.3
Max. spawner density (10^3 km^{-2})[b]	6.8	3.1	7.3
Water Chemistry[c]			
Mean NO_3 ($\mu g\ l^{-1}$)	3.3	0.01[d]	16
Spring overturn NO_3 ($\mu g\ l^{-1}$)	3	Unk	21
Seasonal minimum NO_3 ($\mu g\ l^{-1}$)	0.9	Unk	<1.0
Mean TP ($\mu g\ l^{-1}$)	15.4	1.85[d]	4.2
Spring overturn TP ($\mu g\ l^{-1}$)	17.8	unk	5.7
Chlorophyll ($\mu g\ l^{-1}$)	4.2	unk	5
pH	7.5	7.2	6.6

a. Estimated from Environment Canada Water Survey outflow data.

b. Based on the maximum sockeye escapement recorded

c. Fraser and North Barrière Lakes data from Shortreed et al., 2001

d. Represents a single sample at the time of coring.

which provides habitat for one of the largest and most important sockeye runs within the Fraser River Basin. The lake is organically stained and there has been hydrologic control of the outflow to McKinley River during the sockeye spawning season since 1969. In response to pre-spawning thermal-stress and mortality, a pumping system was built at the outflow of McKinley Lake which discharges cold hypolimnetic waters from the western basin into McKinley Creek, lowering the stream temperature during spawning (Cooper 1973). The potential biogeochemical impacts to the lake from the water extraction have not been studied. DFO escapement records for Upper McKinley Creek (Figure 3.2D), the main inflow to the lake, only date back to 1969 with recorded highs of ~15,000 fish in 1981 and 1985 (Table 3.1).

North Barrière Lake

North Barrière Lake (119°50'W, 51°20'N; 634 m.a.s.l) is located in the North Thompson drainage basin, which joins the Fraser River 60 km north of Hells Gate (Figure 3.2B). The lake catchment is within the Interior Cedar-Hemlock and Englemann Spruce-Subalpine Fir biogeoclimatic zones, where Western Hemlock, Western Cedar, Englemann Spruce, Subalpine Fir and Lodgepole Pine trees compose the surrounding forests. North Barrière Lake is surrounded by Quaternary till and alluvium, while catchment bedrock is composed of Cretaceous quartz monzonite and minor amounts of siliceous phyllite, quartz-schists, slate, breccia and tuffs (Massey et al. 2005).

The oligotrophic North Barrière Lake is the only sockeye salmon nursery lake within the North Thompson River Basin. The summer epilimnetic nitrate concentrations drop below instrumental detection limits (Table 3.1). The catchment is impacted mainly by forestry, in addition to agriculture and lakeside cabin septic systems. Sockeye spawning takes place exclusively in Fennel Creek at the east end of the lake (Figure 3.2E). Anecdotal evidence confirms that spawned-out salmon carcasses generally reach the lake every year, and can be deposited on the lakeshore midway down the lake. DFO escapement records for Fennel Creek date back to 1958 and show a high of ~32,000 fish in 1996 and ~26,000 fish in 1988 (Table 3.1).

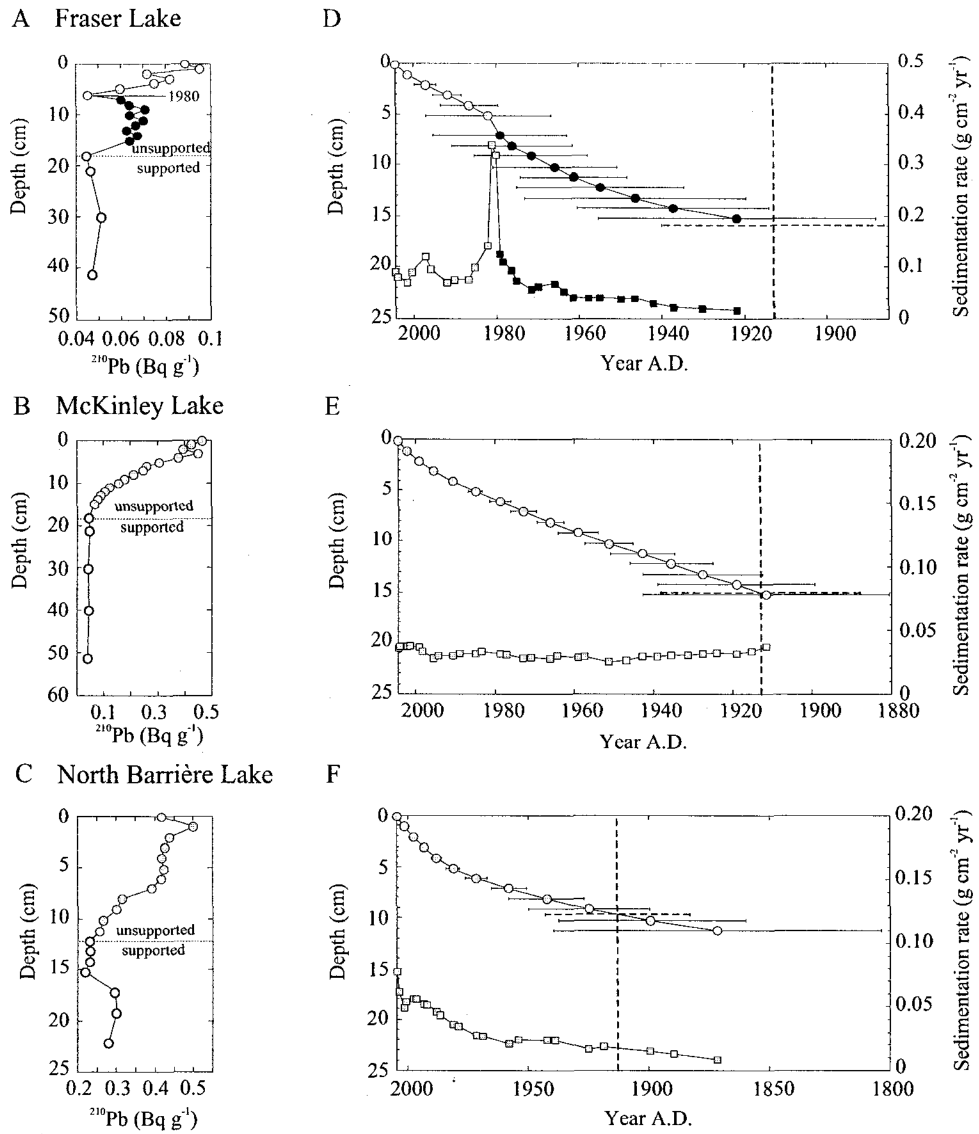
Methods

Sediment core collection, chronology, and sockeye salmon escapement

Sediment coring took place between May 18 and May 27, 2004 using a modified Kajak-Brinkhurst gravity corer to collect a continuous sediment record with an intact sediment-water interface (Glew et al. 2001). A 42 cm sediment core was recovered from the western basin of Fraser Lake, while 22 cm and 51cm cores were retrieved from North Barrière and McKinley Lakes, respectively (Figure 3.2C-E). All cores were sub-sampled on shore following collection and extruded at 0.25 cm intervals for the first 10 cm and 0.5cm thereafter, using a high resolution sectioning device (Glew et al. 2001). Relatively little spatial variation has been documented in both diatom and sediment $d^{15}N$ records from multiple-core paleolimnological studies from a number of lakes, justifying use of a single core per nursery lake (Wolfe 1996; Brock et al. 2006).

Chronostratigraphy of the cores was established through analysis of ^{210}Pb (measured as ^{210}Po) by alpha spectroscopy (Figure 3.3A-C). Calculation of ages are based on unsupported ^{210}Pb inventories and the constant rate of supply (CRS) model (Figure 3.3D-F; Appleby and Oldfield 1978). Sedimentation rates from the lower portions of the cores were extrapolated to give an estimated age for the base of each core. The log ^{210}Pb activity (Bq g^{-1}) was plotted against the cumulative dry mass for each of the lead inventories to establish variability of mass sedimentation rates (Figure 3.4).

DFO escapement records for tributaries to the study nursery lakes were retrieved from the sockeye escapement database system (NuSEDS V.1.0 2004), while sockeye catch data was supplied by the Pacific Salmon Commission.



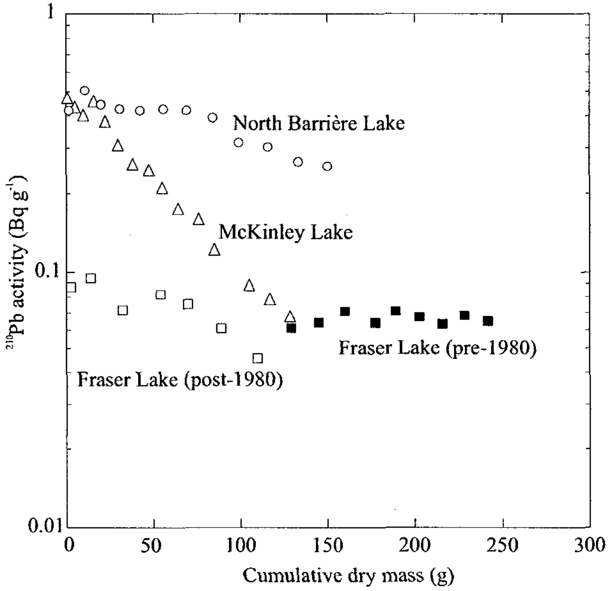


Fig. 3.3 (upper) Profiles of ^{210}Pb activities for Fraser (A), McKinley (B), and N. Barrière (C) lakes. CRS age models (circles with error bars) and sedimentation rates (squares) for Fraser (D), McKinley (E), and N. Barrière Lake (F), where the dashed line indicates 1913 (beginning of Hells Gate slides). Pre-1980 samples used for CRS age extrapolation in Fraser Lake are solid black circles

Fig. 3.4 (left) ^{210}Pb activities for Fraser (squares), McKinley (triangles), and N. Barrière (circles) lakes plotted against cumulative dry mass. Pre-1980 solid black squares in Fraser Lake represent the portion of constant sediment accumulation.

Sediment geochemistry

Freeze-dried samples were analyzed for $\delta^{15}N$ by a continuous flow isotope-ratio mass spectrometry with a coupled CNS analyzer (Europa Hydra 20/20). We report sediment $\delta^{15}N$ (‰) as well as %N and %C. Nitrogen stable isotopes are expressed in δ notation, where $\delta^{15}N=[1 - (^{15}N/^{14}N_{sample})/ (^{15}N/^{14}N_{reference})] \times 1000$. The analytical precision for $\delta^{15}N$ was ±0.15‰, and ±0.86% and 0.15% for C and N, respectively. Total %OM was determined by loss-on-ignition at 550°C (Heiri et al. 2001).

Diatom preparation, identification and enumeration

Aliquots of approximately 0.1g of dry sediment from intervals selected for diatom analysis were oxidized with 30% H_2O_2 to remove labile organic matter. Slide preparation and diatom enumeration followed standard protocols (Battarbee et al. 2001). Slides are permanently mounted using Naphrax®. Between 400 and 500 diatom valves were counted for each sample under oil immersion at a magnification of 1000x, using differential interference contrast optics. Taxonomic identification followed Foged (1981), Krammer and Lange-Bertalot (1986-1991), Cumming et al. (1995), Siver and Kling, 1996, and Fallu et al. (2000). Quality assurance of taxonomy was documented using digital micro-photography and scanning electron microscopy (SEM) (Figure 3.5). The distinction between Stephanodiscus minutulus and S. parvus is gradational and not resolvable in light microscopy (Figure 3.5H-I), and subsequently these two species were combined based on both morphological and ecological similarities (Stoermer and Håkansson 1984; Moser et al. 2004). Diatom counts are expressed as relative frequencies of each taxon for the total number of valves counted.

Statistical methods

Diatom stratigraphic zones were determined objectively by stratigraphically-constrained minimum variance cluster analysis (Ward's method), using Squared Euclidean distances

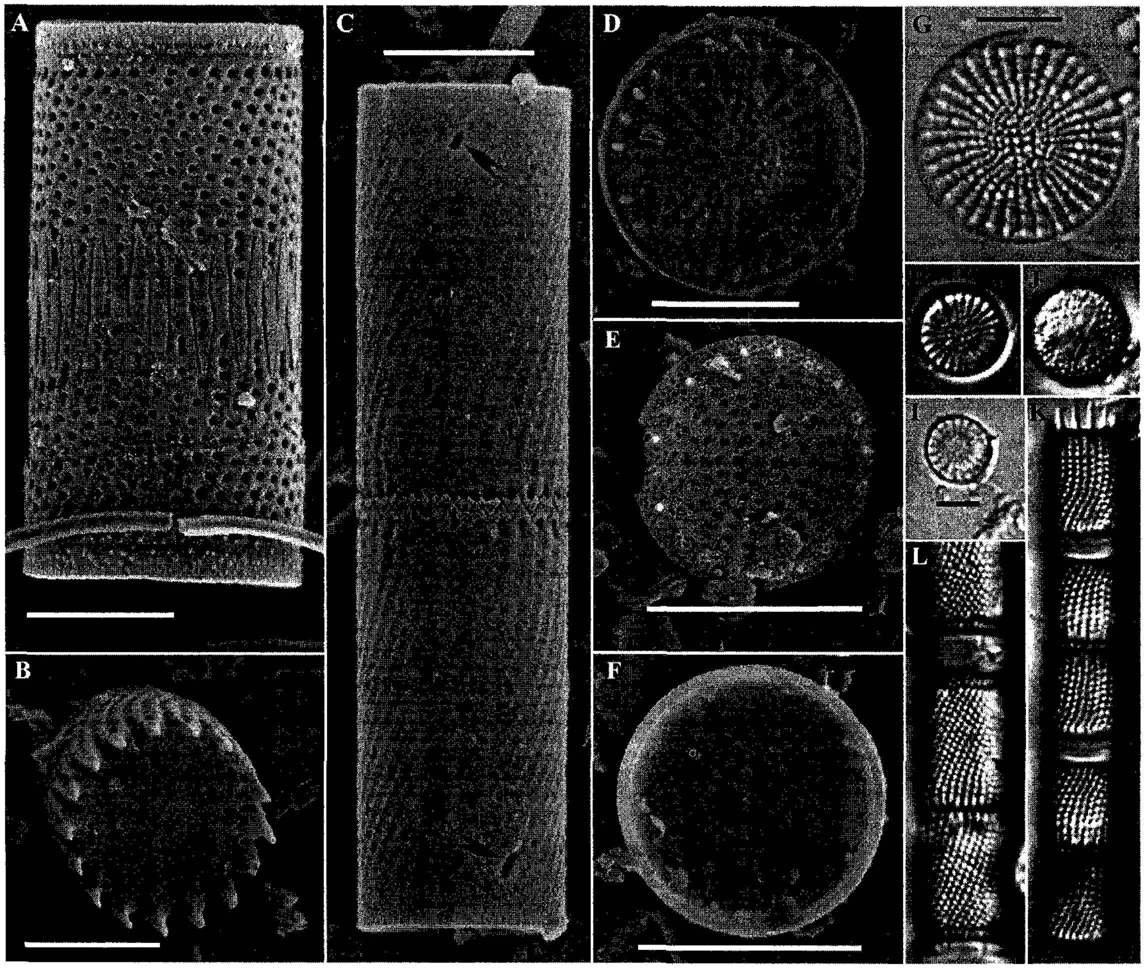


Fig. 3.5 SEM (A-F) and light (G-L) micrographs (LM) of problematic diatom taxa. (A) Mantle view of *Aulacoseira subarctica* with separation spines rising from the coalescence of costae and showing spiral arrangement of areolae, both of which can be discerned in LM (K). (B) Valve view *A. subarctica* showing a peripheral ring of areolae aligned with the base of the spines, also evident in LM (J). (C) Mantle view of *A. ambigua* with linking spines and external openings of rimoportulae (arrows) evident as perforations of the velum; comparable valve also shown in LM (L). (D) *Stephanodiscus medius* showing marginal spines at the termination of each inter-fascicular zone, and convex punctate central area; an equivalent specimen is also shown in LM (G). *S. minutulus* external (E) and internal (F) views in SEM; in LM this taxon can not be differentiated from *S. parvus*, so that forms such as those shown (H-I) are assigned to '*S. minutulus- parvus* complex'. Fultoportulae are evident on the internal valve view (F). All SEM scale bars are 5μm, and LM photos are at 1500x with a 10μm scale bar in G, and a 5μm scale in I.

as the metric (Grimm 1987). In order to assess the significance of the stratigraphic zonations, we compared the variance among the clusters against the broken-stick model using the sum-of-squares total (Bennett 1996).

Compositional changes in diatom assemblages were summarized using the first axis detrended correspondence analysis (DCA) performed with CANOCO v.4.51 (ter Braak and Šmilauer 2002). The DCA was run on relative frequencies of each taxon >1%

in any one sample in order to eliminate the influence of rare species, with detrending by segments to eliminate systematic relations between the first axis and subsequent axes (Hill and Gauch 1980). The number of taxa per sample included in the DCA ranged from 8 to 15 in Fraser Lake, 7 to 20 in North Barrière Lake, and 16 to 26 McKinley Lake. Plotted stratigraphically, DCA sample scores graphically depict down-core diatom assemblage compositional changes (Birks et al. 2000).

Results and discussion

^{210}Pb chronology

Supported ^{210}Pb activities were reached in all three sediment cores, at 18 cm in Fraser and McKinley lake, and 12 cm in N. Barrière Lake (Figure 3.3A-C). In N. Barrière Lake, supported ^{210}Pb activity increases slightly at the base of the core (Figure 3.3C), which is speculated to be due to the interference of naturally high ^{238}U-bearing bedrock and the presence of ^{226}Ra rich material at the base of the core (Brenner et al., 2004). Analysis of the sediments using alpha spectrometry precludes us from confirming variable ^{226}Ra activity. However, domestic ^{222}Rn levels in the Barrière – Clearwater region of BC, which are among the highest in the province and nationally, support the speculation of a ^{238}U – ^{226}Ra – ^{222}Rn rich environment (pers. commun. D. Morley). While variations in ^{226}Ra can suggest disequilibrium with supported ^{210}Pb activities, the interference evident in the N. Barrière core occurs below the level of supported ^{210}Pb activity (Figure 3.3C). Therefore, we feel the CRS model calculated ages presented here are reliable. Stable sediment accumulation rates are evident from primarily linear trends in log ^{210}Pb activity versus cumulative dry mass for North Barrière and McKinley lakes (Figure 3.4). Maximum ages for these cores can therefore be extrapolated somewhat beyond the unsupported ^{210}Pb inventories using the mean CRS mass accumulation rates, yielding estimated ages of ~310 and 260 years for McKinley and N. Barrière Lake, respectively (Appleby 2001).

The sedimentation rate for Fraser Lake exhibits significant variations at 6 and 10 cm in the core, corresponding to the post~1980 section of the core (Figure 3.3D). Reductions in organic content and increases in the atomic C:N in this section of the core suggest the likely cause for increases in sedimentation at the coring site is allochthonous contributions of sediment (Figure 3.7). High inlet discharges during the 1980s and 90s, coincident with land-use changes within the catchment, support this interpretation (Carmichael 1985; Environment Canada 1997). A similar sedimentological profile has been documented independently by Cumming (2001), implying that these phenomena are recorded across the basin. A stable sediment accumulation is evident prior to 1980, in the section of core containing the remaining unsupported ^{210}Pb (Figure 3.4). We therefore used this apparently reliable pre~1980 accumulation rate (0.05 gcm^{-2}yr^{-1}) to extrapolate a maximum age of ~270 years for the Fraser Lake core.

Diatom stratigraphy

There is sufficient floristic change in the study lakes to define three significant diatom zones in the Fraser and McKinley cores and two zones in the N. Barrière core (Figure 3.6). To assess whether diatom assemblages from the study lakes reacted to the Hells Gate slides, compositional changes were summarized using the diatom DCA axis scores (Figure 3.7). The amount of variance explained by the first DCA axis for Fraser, McKinley, and N. Barrière was 24.0%, 28.9%, and 15.9%, respectively. In none of the cores is there a shift corresponding to either the time of the slides, or the onset of commercial fishing. In both the Fraser and McKinley cores there are statistically-significant zones defined in the ~mid-1800s, while the N. Barrière core exhibits its only significant zonation in the mid-1900s (Figure 3.6). The upper (near surface) zone boundaries in Fraser and McKinley lakes occur within the last 30 years. No further significant diatom zones were defined by comparison to broken-stick models, implying that the period coeval to the Hells Gate slides did not result in significant diatom

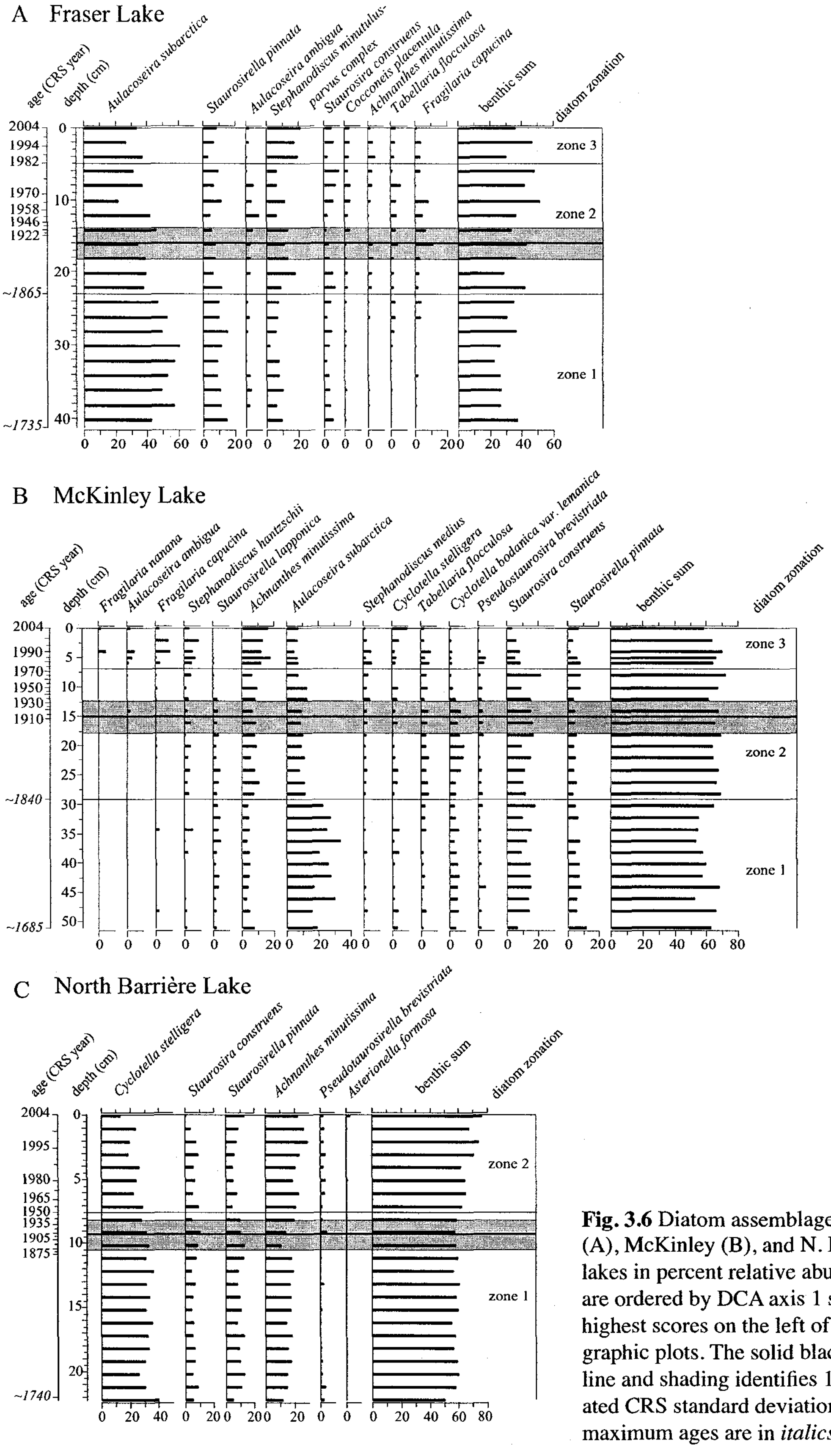
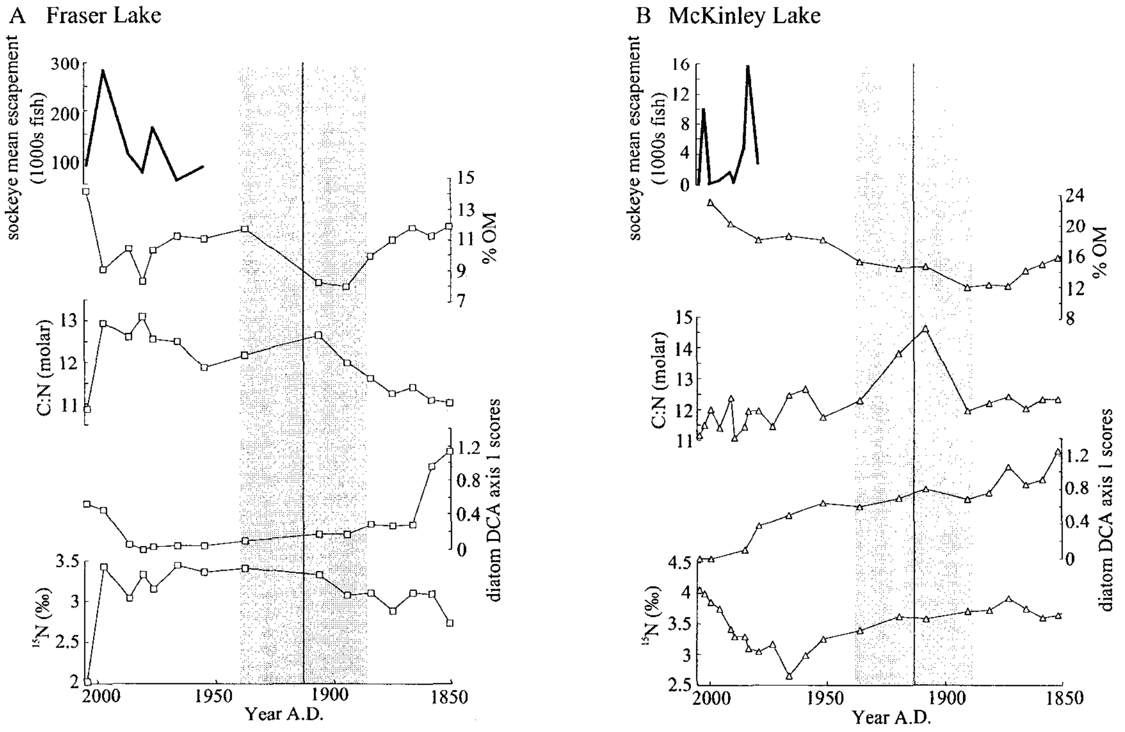


Fig. 3.6 Diatom assemblages for Fraser (A), McKinley (B), and N. Barrière (C) lakes in percent relative abundance. Taxa are ordered by DCA axis 1 scores, with the highest scores on the left of the stratigraphic plots. The solid black horizontal line and shading identifies 1913 and associated CRS standard deviation. Estimated maximum ages are in *italics*



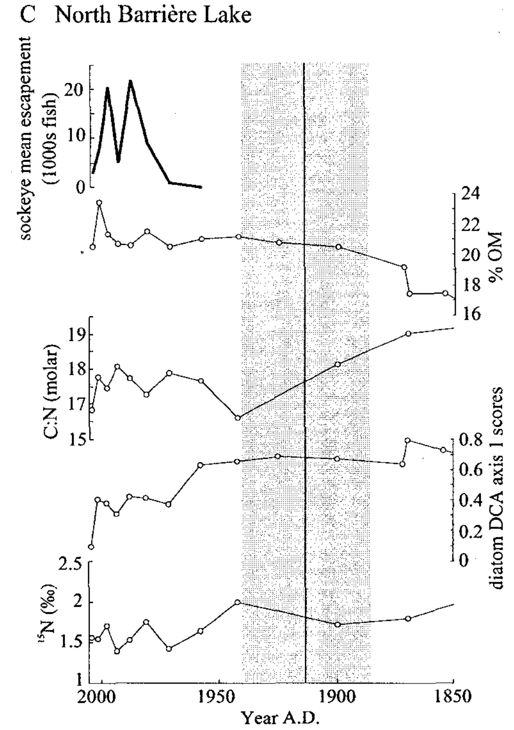


Fig. 3.7 Sediment δ^{15}N, diatom sample DCA axis 1 scores, C:N, %OM, and available sockeye escapement data for Fraser (A), McKinley (B), and N. Barrière (C) lakes. The position of 1913 is marked by a solid vertical line, with the estimated dating error for each lake shaded

community changes.

Generally, the mesotrophic-planktonic diatom *Aulacoseira subarctica* dominates the assemblages in Fraser and McKinley Lakes (Figure 3.6). In both lakes the abundance of *A. subarctica* decreases in zone 2, starting in the mid-1800s, being replaced largely by *Achnanthes minutissima* (a benthic species with wide nutrient tolerances), eutrophic-planktonic *Fragilaria capucina, Stephanodiscus sp. (S. minutulus-parvus* complex in Fraser Lake; *S. hantzschii* and *S. medius* in McKinley Lake), and mesotrophic-benthic or planktonic *Tabellaria flocculosa* (Reavie et al. 1995; Stevenson 1995; Gregory-Eaves et al. 1999). There is further indication of the eutrophication of both lakes into zone 3 (surface) of the core based on the continued increase of *S. minutulus-parvus* in Fraser and increased *S. hantzschii* and *Fragilaria capucina* in McKinley Lake. McKinley Lake experienced the most significant compositional changes of the last 300 years, in the early to mid-1970s (Figure 3.6). This zonal shift could be related to a change in the stratification and mixing of the lake due to removal of hypolimnetic waters during the late-summer salmon runs in the downstream McKinley Creek, which started in 1969-70. The coincident reduction in abundance of the tychoplanktonic *A. subarctica* following the water removals suggests that an increase in stratification has occurred, given the autecological requirements for this genus include a well mixed water column and high Si concentrations (Kilham et al., 1996). While the planktonic diatom species assemblages have all changed slightly, relative habitat preferences have remained constant (i.e. benthic sum, Figure 3.6).

North Barrière Lake is located in the drainage of the North Thompson River (the largest tributary to the Fraser River), and the observed diatom flora is slightly different from McKinley and Fraser. The stratigraphy shows the least amount of compositional change, with a single definable diatom cluster zonation occurring at ~1950 (Figure 3.6). The dominant species are *Cyclotella stelligera*, an oligotrophic-planktonic diatom, and *Achnanthes minutissima.* A very subtle progressive decrease in *C. stelligera* is evident towards the surface of the core, where the assemblage becomes dominated by *A. minutissima* and *Staurosirella pinnata*, with the presence of *Asterionella formosa. A. formosa* has a high N:P requirement, and can form impressive blooms in a range of environments (McKnight et al. 1990; Yang et al. 1996). Ultimately, the diatom assemblages of all three lakes show no evidence of changes associated with MDN variations.

Additional lakes within the Fraser River Basin were also cored at the inception of this study and analyzed for changes in the diatom communities at the top and bottom of the cores (Bowron Lake: 53° 14' N, 121° 23' W; water residence time 0.6 yrs; maximum spawning density: 3.4 10^3 km^{-2}; Momich Lake: 119° 21'N, 51° 19'W; water residence time: 0.2 yrs; maximum spawning density: 4.7 10^3 km^{-2}; Hobbs unpubl. data). Neither of these lakes showed pronounced stratigraphic changes in diatoms. Reavie et al. (2000) reported diatom stratigraphies from two ^{210}Pb-dated cores from François Lake, upstream of Fraser Lake, which also showed a minor decrease in *Aulacosiera subarctica* with an increase in *Stephanodiscus sp.* starting in the mid-1800s. The François Lake data do not preserve evidence of impacts associated with the 1913 Hells Gate landslides. Unlike the lakes we have considered, François has a water residence time of 36 years and estimated spawner density of 0.8 10^3 km^{-2}, suggesting that the low flushing rate does not enhance a lake's capacity to track changes in MDN in the Fraser River Basin.

Sediment geochemistry

The sediment $\delta^{15}N$ from the Fraser River drainage lakes ranges from 0.8‰ to 3.4‰ (McKinley 0.8-3.1‰; Fraser 2.0-3.4‰; N. Barrière 1.4-2.1‰) (Figure 3.7). The relatively enriched sediment $\delta^{15}N$ (4.7‰ to 9.8‰) found in Alaskan lakes where compelling sediment records of historical salmon abundance have been established (Finney et al. 2002; Gregory-Eaves et al. 2004; Schindler et al. 2005) suggests our study lakes are not recording variations in MDN. In an attempt to confirm this, we compare the sediment $\delta^{15}N$ as a proxy of salmon returns to well-documented variations in the salmon returns to the BC nursery lakes, namely; (1) the Hells Gate slides, (2) the onset of commercial fishing, and (3) recent sockeye escapement data. In none of the lakes does sediment $\delta^{15}N$ become depleted, as expected from loss of MDN following the Hells Gate slides (Figure 3.7). Furthermore, the predicted decline of MDN associated with commercial fishing since the 1890s does not register in the sediment $\delta^{15}N$ records of any of the lakes. This contrasts with the fishing impact to sockeye populations in Alaska, which firmly imprints the paleolimnological record (Finney et al. 2002; Schindler et al. 2005). In order to compare escapement data and ^{210}Pb-dated sediment $\delta^{15}N$ intervals, we averaged sockeye numbers over the corresponding age increments represented by each sediment interval. Given reduced age uncertainty at the top of the cores (Figure 3.3), this approach smoothes the inter-annual variability inherent in the escapement data (Figure 3.7). There is no significant statistical relation ($p>0.05$) between sediment $\delta^{15}N$ and the DFO sockeye escapement data (Figure 3.7).

The absence of MDN signatures in sediment $\delta^{15}N$ records has been documented elsewhere in coastal BC nursery lakes (Holtham et al. 2004). This has been attributed alternately to rapid flushing, dominance of allochthonous OM sources, and N-limitation. We feel the case is strongest for allochthonous nutrient inputs to Fraser River lakes, given that many fractions of terrestrial organic matter have depleted $\delta^{15}N$ signatures (Nadelhoffer and Fry 1994) and the large catchment:lake ratios (Table 3.1). Rudimentary estimates of the annual N provided by sockeye salmon to Fraser Lake, which has the greatest spawner density of the study lakes, is only ~ 3% (Carmichael 1985). It therefore appears that the proportion of MDN incorporated by the lakes in the Fraser River drainage is not sufficient to be registered by the lake sediments. We also acknowledge that water residence times are less that a year in all three study lakes, limiting the ability of aquatic production to fully assimilate MDN (Holtham et al. 2004; Hobbs and Wolfe 2007).

Sediment molar C:N can provide an effective means of inferring sediment OM source (Kaushal and Binford 1999). The sediment C:N of Fraser Lake (mean=11.8±0.8) and McKinley Lake (mean=14.5±0.7) suggest that the OM is derived from both aquatic and terrestrial sources, while N. Barrière Lake (mean=18.0±0.8) is near ratios of terrestrial sources (Meyers and Teranes 2001). Following the Hells Gate slides the C:N for each of the lakes decreases, suggesting an increasing autochthonous OM which is the opposite to what would be expected in a lake receiving diminished MDN (Figure 3.7). Furthermore, the %OM increases following the slides, which is also counter to the expected response to decreased production from less MDN.

A further component of the Fraser Lake record is the ~1.5‰ depletion of $\delta^{15}N$ in surface sediments, which is associated with minor increases of eutrophic *Stephanodiscus minutulus-parvus* diatoms (Figures 3.6 and 3.7). N-fixing cyanophytes presently bloom in Fraser Lake (Shortreed et al. 2001), potentially contributing to this light isotopic excursion. The concurrent drop in C:N, as well as the subtle diatom changes, suggest a limnological change towards increased algal production, and not diagenetic effects, as the origin of changes in surface sediments from Fraser Lake. Increased catchment agriculture and fertilizer use is also consistent with this record, all the more because it is not witnessed in the other lakes, where agriculture is limited. Once again there is no evident correlation to salmon records.

Regional context

Diatom stratigraphies have been presented from non-salmon bearing lakes in the Fraser River Basin, where minor species shifts have been attributed to human settlement (Reavie et al. 1995; 2000), deforestation, and climate (Laird and Cumming 2001). There is some regional coherence in the timing and character of diatom changes within Fraser River Basin lakes, despite often-subtle expressions. An example is the slow decline of *A. subarctica* and increase of more eutrophic *Stephanodiscus* taxa starting in the mid-1800s in both Fraser and McKinley Lake, as well as nearby Norman, Tchesinkut, and François lakes, the latter two located within the Fraser Lake drainage (Reavie et al. 1995; 2000). Tchesinkut and Norman lakes do not support any anadromous sockeye salmon.

Dendroclimatic models from BC Interior treeline sites suggest rising temperatures from the 1880s through the 1940s (Wilson and Luckman 2003). Warmer temperatures can prolong stratification during summer months, encouraging the growth of diatoms that exploit the thermocline (Bradbury 1988; Rühland and Smol, 2005), exemplified in our record by increasing abundance of *Stephanodiscus sp*. and *Cyclotella stelligera* and decreasing abundance of *Aulacoseira subarctica*. While we concede dating constraints, the climatic shifts inferred from dendroclimatology coincide reasonably with subtle and time-transgressive diatom shifts expressed in each of the study lakes, perhaps suggesting a causal linkage. More importantly to the present study, sediment records from salmon lakes regionally have comparable stratigraphic variability as non-salmon lakes, implying that regional factors including climate and land use exert greater influences than MDN.

More recent (post-1970) evidence of eutrophication is evident in Fraser and McKinley lakes, where *Stephanodiscus* spp. increase gradually, likely in response to increased anthropogenic nutrient inputs from agriculture and land development in the Fraser catchment (Carmichael 1985), coupled to effects from deforestation, construction, and hydrologic modification of the McKinley drainage. Within the Kamloops region of BC, Reavie et al. (1995) present a sediment record from Dutch Lake, a terminal lake located to the north of N. Barrière, where assemblages change from being dominated by *Cyclotella stelligera* to *Asterionella formosa* at the surface of the core in response to similar factors. A less dramatic and more recent decline in *C. stelligera* and presence of *A. formosa* in N.Barrière Lake is likely also driven by the development of cabins and septic tanks adjacent to the lake, in addition to deforestation and land development within the catchment.

Conclusion

By using the documented collapse of Fraser River sockeye salmon returns as a potential natural marker in nursery-lake sediment records, we have tested the sensitivity of paleolimnology for reconstructing sockeye population changes in the Fraser River Basin. We have searched for additional paleolimnological responses to the onset of commercial fishing in the Fraser River Delta, as well as any meaningful covariance between sediment records and sockeye escapement records. No features of the historically-documented Fraser River sockeye salmon fishery are expressed by the geochemical and biological proxies in sediments from three nursery lakes which vary in salmon density, migratory length, and catchment characteristics. Moreover, these nival-dominated catchments, which receive the majority of their hydrologic input in summer prior to spawning, show no greater capacity to record the influence of MDN than previously published sediment cores from coastal rain-dominated catchments. The sediment records thus appear more strongly shaped by twentieth-century climate warming and local catchment disturbances than by variability in MDN subsidies. Our results show that paleolimnology is incapable of tracking changes in the delivery of MDN to three Fraser River sockeye nursery lake ecosystems, suggesting this technique may not be applicable in the greater Fraser River Basin.

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CHAPTER 4: RAPID DIATOM DISSOLUTION AND ALGAL PIGMENT DIAGENESIS IN RECENT ALPINE LAKE SEDIMENTS: MECHANISMS AND PALEOECOLOGICAL IMPLICATIONS

Introduction

Diatoms use silicic acids (primarily orthosilicic acid, H_4SiO_4) to construct the solid portion of their cell walls, called frustules. It is the preservation of frustules as amorphous biogenic silica ($nH_2O{\bullet}SiO_2$, hereafter $BSiO_2$) in lake sediments which has led to their common use in freshwater paleoecology (Stoermer and Smol, 1999; Smol, 2008). However, the dissolution of diatoms within lake sediments may compromise interpretations of the sediment record (Ryves et al., 2006; Stone and Fritz, 2006), making the full understanding of conditions for dissolution imperative. A number of experimental studies have examined those conditions that promote silica hydrolysis leading to diatom dissolution revealing important roles for pH, ionic strength, temperature, silica concentration, alkalinity and alkali metals (Flower, 1996; Barker, 1994; Ryves, 2006). In general, warm, alkaline and saline lakes represent the poorest environments for long-term preservation of diatom frustules. However, the recycling of diatom silica also occurs in cold and chemically-dilute lakes, both from lake sediments into the water column or within the water column. While the Laurentian Great Lakes (Schelske et al., 1984; Conley et al., 1989) and Lake Baikal (Battarbee et al., 2005) provide the best-known examples of in-lake diatom silica recycling, it is evident that diatom dissolution occurs readily in a range of oligotrophic lakes (Cornwell and Banahan, 1992; Hoffman et al., 2002).

Prior studies of freshwater diatom dissolution have not considered the roles of

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* Co-authors: Stefan V Lalonde, Rolf D Vinebrooke, Kurt O Konhauser, R Paul Weidman, and Alexander P Wolfe (University of Alberta).

organic coatings that isolate frustules from silica-undersaturated ambient waters and may induce dissolution. Diatoms are encased in extracellular polymeric substances (EPS), which are produced during cell formation by the cytoplasm and composed mainly of amino acids and polysaccharides (Hecky et al. 1973). Although the thickness of EPS can vary between diatom taxa, its biochemical composition is fairly consistent (Duke & Reimann, 1977). Under appropriate conditions, diatom EPS also provide a suitable substrate for heterotrophic microbial communities. In the marine environment, microbial processes are directly linked to the dissolution of diatom frustules and the recycling of silica in the photic zone (Bidle & Azam, 1999). The importance of analogous processes has not previously been advanced for lakes, despite experimental results that suggest this very possibility. For example, Lewin (1961) found that the rate of freshwater diatom dissolution was greater for acid-cleaned frustules relative to either living or dead cells that retained EPS coatings.

Photoactive pigments are another important component of lake-sediment organic matter, producing a biomolecular record of primary production as well as diagenetic alteration. Chlorophylls, carotenoids, and their derivative structures can be readily identified from sediments and used to quantitatively reconstruct historical changes in community composition (Leavitt and Hodgson, 2001). The preservation of pigments in lake sediments has been explored in a range of investigations (Leavitt, 1993; Verleyen et al., 2004). The majority (>95%) of primary algal pigments photodegrade within days in the water column. In alpine lakes low dissolved organic carbon (DOC) and high ultraviolet radiation (UVR) are common (Vinebrooke and Leavitt, 2005), implying that water-column photodegredation is expected to be strong. Further post-depositional alterations occur on longer timescales (years to decades), leaving a more stable inventory of derivative compounds.

Alpine head-water lakes are considered to be sensitive ecosystems with respect to climate change and anthropogenic nutrient deposition. In many cases, paleoecological and geochemical investigations of recent sediments have proven important in demonstrating the ecological consequences of these forcings (Baron et al., 2000; Battarbee et al., 2002; Wolfe et al., 2003). For the most part, these studies have assumed that sediment proxies of algal production, including $BSiO_2$, are well-preserved due to cold water temperatures, prolonged winter ice cover, and dilute, oligotrophic water chemistries.

In this study, we investigate the mechanisms responsible for rapid diatom dissolution and pigment diagenesis in a small alpine lake. We present the first investigation into the importance of $BSiO_2$ regeneration within an alpine lake. In so doing, we evaluate the hypotheses that: (1) pore-water pH transients associated with organic matter degradation drive a range of diagenetic processes affecting diatoms and pigments; (2) microbial activity in the surface sediments degrade diatom EPS and accelerate frustule dissolution; and (3) diatom pigments can provide an indication of diatom productivity despite the loss of the frustule.

Site Description

Pipit Lake is located in Banff National Park, Alberta, Canada (2217 masl; 51°36'59"N, 115°51'42"W; Fig.4.1A; Table 1). The lake is situated just above alpine tree-line within a northeast facing cirque containing a number of perennial snow-packs that feed the lake (Fig. 4.1B). Bedrock geology of the catchment is Upper Paleozoic dark grey argillaceous limestone and dolomite with some black shales and trace lignite seams. The basin is primarily talus and bedrock, with some vegetated areas (<10% of the catchment) that include grasses, mosses, and a copse of subalpine fir immediately north of the lake. The lake waters are alkaline with a mean pH of 8.1, and high concentrations of Mg^{2+} and Ca^{2+} (Table 2). The lake is clear, oligotrophic, and currently fishless (Parker and Schindler, 2006). The water column becomes weakly stratified for a short period (~4 weeks) during summer, and the flushing rate is in the order of months. Pipit Lake was stocked from

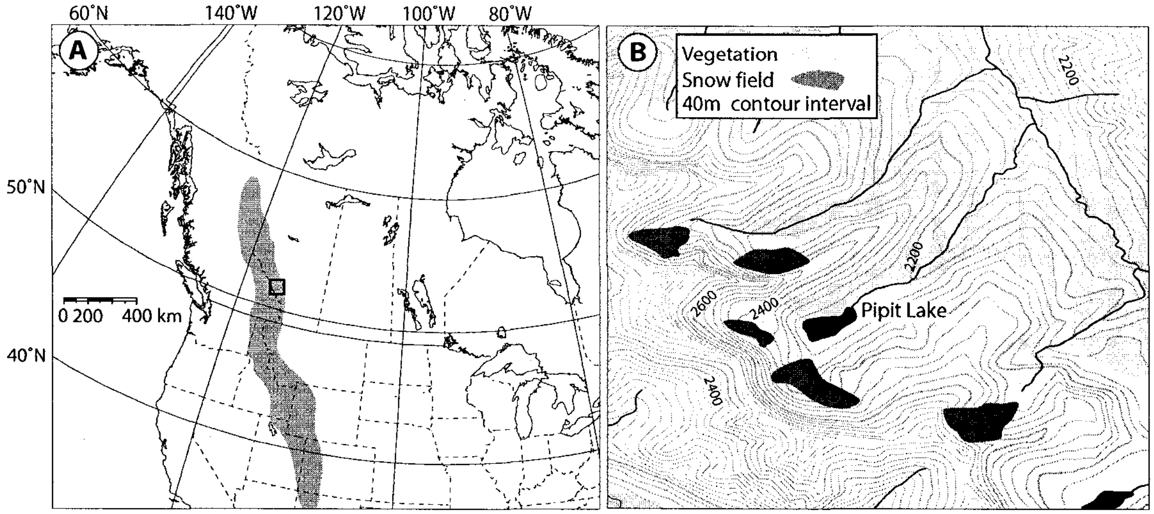


Fig 4.1 Location of study site. (A) The North American continent, where the shaded area represents the extent of the Rocky Mountains. (B) Topographic map of the Pipit Lake catchment.

1964 – 1966 with rainbow trout (*Onchorhynchus mykiss*) and brook trout (*Salvelinus fontinalis*) as part of the greater stocking program of alpine lakes in Banff (Donald, 1987). Introduced salmonids failed to reproduce and Pipit was fishless after 1977. Zooplankton typical of fishless alpine lakes (*Hesperodiaptomus arcticus* and *Daphnia middendorffiana*) are presently the top consumers in the lake's food web (Donald, 1987; Parker and Schindler, 2006).

Bi-weekly to monthly monitoring of Pipit Lake has taken place over the past 12 summers (1995-2007), as summarized in Table 2 (DW Schindler, unpublished data). The water quality data reveal no obvious temporal trends over this period. Water chemistry is representative of alpine lakes in this region: low dissolved organic carbon, total dissolved P, NO_3^-, and relatively high conductivity, alkalinity, and pH.

Table 4.1 Pipit Lake morphometry and location

Lake area (km^2)	10.6
Catchment area (ha)	254
Max depth (m)	20.6
Mean depth (m)	12.6

Methods

Sediment collection, pore-waters and geochronology

Table 4.2 Pipit Lake average summer water chemistry (1995-2007)

	Hypolimnion			Epilimnion			Inflow 1			Inflow 2			Outlfow
	mean	sd	n	mean	sd	n	mean	sd	n	mean	sd	n	
NO_3 (µg L^{-1})	55.66	23.17	83	71.66	37.84	94	131.64	49.95	40	125.89	31.43	34	127.00
NH_3 (µg L^{-1})	14.17	32.91	65	6.57	7.32	59	5.08	3.76	29	4.32	4.01	22	5.00
Total dissolved N (µg L^{-1})	157.64	168.34	81	134.61	88.06	93	180.05	93.75	40	167.39	81.65	34	171.00
Particulate N (µg L^{-1})	52.46	25.08	41	25.93	14.30	48	15.56	26.79	31	7.94	6.80	27	16.80
Total P (µg L^{-1})	9.17	4.50	83	5.19	4.39	92	6.00	4.94	40	4.32	1.47	34	5.10
Total dissolved P (µg L^{-1})	4.58	3.71	82	2.92	1.89	90	3.96	0.91	40	4.20	1.55	34	2.10
Dissolved organic C (µg L^{-1})	2.13	3.25	79	2.27	3.81	91	0.50	0.35	31	0.50	0.43	28	0.40
Particulate C	405.85	171.01	41	252.30	183.71	49	463.40	1165.68	32	120.15	51.52	28	142.23
Si (mg L^{-1})	1.90	0.50	82	1.10	0.27	96	0.68	0.19	40	1.05	0.16	34	1.04
Cl (mg L^{-1})	0.36	0.24	73	0.37	0.30	86	0.18	0.09	38	0.16	0.09	33	0.12
SO_4 (mg L^{-1})	17.55	4.74	81	12.59	4.56	94	10.69	8.81	40	5.14	1.30	34	8.91
Na (mg L^{-1})	3.07	4.83	77	1.29	0.42	90	0.19	0.09	40	0.24	0.07	34	0.86
K (mg L^{-1})	0.39	0.10	77	0.28	0.08	90	0.14	0.03	40	0.17	0.03	34	0.22
Ca (mg L^{-1})	35.54	4.93	77	27.59	2.90	90	21.73	3.55	40	21.76	1.39	34	25.20
Mg (mg L^{-1})	14.73	2.34	77	10.53	2.35	90	5.97	1.24	40	5.75	0.45	34	8.65
Conductivity (µS cm^{-1})	283.62	34.79	82	214.85	28.65	95	155.05	29.29	40	149.07	10.15	34	182.00
pH	7.98	0.22	83	8.11	0.22	96	8.05	0.14	40	8.08	0.12	34	8.16
Alkalinity (mg L^{-1} $CaCO_3$)	130.34	15.97	83	97.34	11.01	96	68.29	7.29	40	71.28	4.38	34	88.63
HCO_3 (mg L^{-1})	158.68	19.71	83	118.20	12.77	96	83.26	8.89	40	86.92	5.34	34	108.05
CO_3 (mg L^{-1})	0.11	0.72	83	0.30	1.05	96	na	na	na	na	na	na	0

na - not analyzed

sediment cores were retrieved from the deepest section of the lake (~20m) on August 16, 2007 using a modified Kajak-Brinkhurst gravity corer (Glew et al., 2001). Both cores were sealed in hypolimnetic water for transport, unsealed immediately prior to *in situ* pH and dissolved O_2 (DO) profiles being generated by microelectrode on the undisturbed cores, and analyzed within 6 hours of collection. Microelectrodes, with a tip diameter of ~50 μm, were inserted vertically into the sediment cores using a Unisense MM33-2 micromanipulator operating in 100 μm intervals. The probes included a Clark-type O_2 microelectrode (OX50, Unisense, Århus, Denmark) calibrated to atmospheric oxygen and zeroed in 0.1 M ascorbic acid, and a pH microelectrode (PH50, Unisense) calibrated using commercial pH buffers (pH 4,7,10). Microsensor data was collected using a Unisense PA2000 picoammeter, a high impedance pH meter (Radiometer Analytical SAS, Villeurbanne, France), and a PC data acquisition system. Immediately thereafter (within 8 hours of collection), both cores were sub-sampled at 0.25 cm intervals for the first 10.0 cm and 0.5 cm from then on directly into 50 ml centrifuge tubes. Pore-waters were immediately extracted on one core by centrifugation at 1500 rpm for 10 minutes. The supernatant was collected using a syringe and immediately filtered through 0.45 μm teflon syringe filters and acidified with 1M HCl. Samples were also kept out of natural light to avoid photo-degradation of fossil pigments. Both cores were frozen within 24 hours of collection and freeze-dried.

Geochronology was established through ^{210}Pb decay (measured as ^{210}Po) by alpha-spectroscopy on a single core (Fig. 4.2). The constant rate of supply (CRS) model was used to estimate ages and sedimentation rate based on the radioactive decay of excess (or unsupported) ^{210}Pb above the background (or supported) ^{210}Pb activity (Appleby and Oldfield, 1978). In order to infer estimated CRS ages within the second core, downcore % organic matter (%OM) measurements were correlated objectively, confirming consistent sedimentation between the two adjacent cores.

A sediment trap was deployed between October 2005 – July 2007 at a depth of 19.5m (0.5 m above the deepest point of the lake) and emptied approximately every 9 months. Locating the trap near the deepest point of the lake enables measurement of materials destined for the immediate region of the two cores. A length : width aspect ratio of 2:1 was used, with an active area of 100 cm^2. Sedimentation rates were calculated as mg dry sediment per unit area per year.

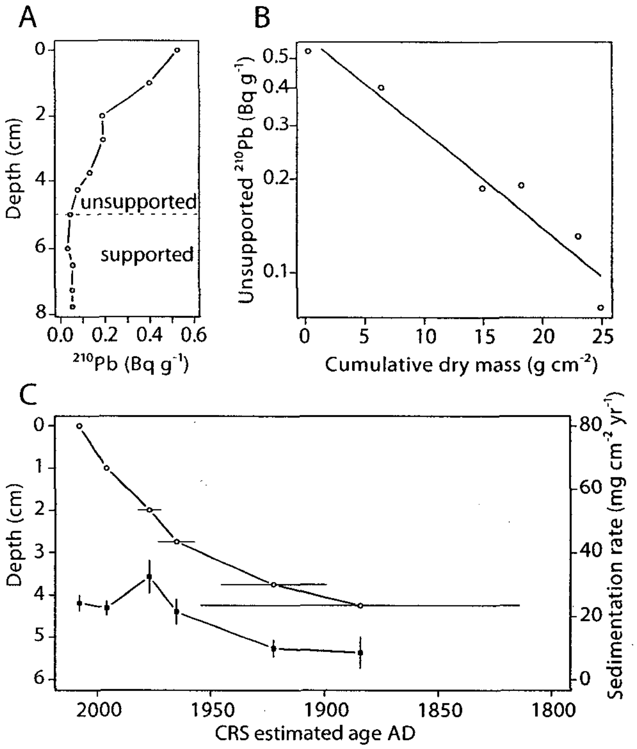


Fig 4.2 ^{210}Pb chronology of the sediment core. (A) ^{210}Pb activity (Bq g^{-1}) with depth showing the depth of background or supported amount of ^{210}Pb. (B) Linear relationship between the log of unsupported ^{210}Pb (Bq g^{-1}) and cumulative dry mass (g cm^{-2}), which establishes a constant sedimentation rate in this portion of the core. (C) CRS estimated ages with depth (cm) (open circles) and sedimentation rate (mg cm^{-2} yr^{-1}) (black squares) over the estimated dates.

Diatom analysis

Slides for diatom frustule enumeration were prepared by digesting ~100 mg of dry sediment in 30% H_2O_2 to oxidize labile organic matter. Diluted slurries were spiked with a known quantity of external markers for calculating absolute microfossil concentration (Wolfe, 1997), and permanently mounted using Naphrax® (Battarbee et al., 2001). Diatoms and chrysophyte cysts were enumerated with differential interface contrast light microscopy at 1000x and also examined by scanning electron microscopy (SEM) with a JEOL-6301F field emission system. Untreated sediment trap material was also examined under SEM.

Biogenic and pore-water silica

The analysis of biogenic silica (BSiO$_2$) in sediments provides a quantification of the total productivity of siliceous algal fossils (diatoms and chrysophyte cysts). We used a modified wet alkali digestion method from DeMaster (1991) on approximately 30 mg of freeze-dried sediment (Conley and Schelske, 2001). This method allows for the sequential digestion and separation of $BSiO_2$ and the aluminosilicate fraction. The concentration of dissolved Si (as H_4SiO_4 and abbreviated herein as DSi) in the extract and pore-water was then analyzed using the heteropoly blue method (Clescerl et al., 1999) with a Beckman DU 520 spectrophotometer operating at 815 nm.

The $BSiO_2$ method precision for triplicate digestions gave a coefficient of variation of 6.8%, while duplicate analysis on all the extracts gave relative percent differences (RPDs) <10% for those samples above the method detection limit (~0.5 wt% SiO_2 for 30 mg of sediment). Pore-water DSi samples were run in duplicate with most intervals showing < 4% RPD, those which were outside an acceptable RPD (>10%) were re-run giving a coefficient of variation (CV%) < 4% for each sample. All method blanks were below detection limits.

Metals, loss on ignition, and X-ray diffraction

Analysis of labile Fe and Mn within sediments was carried out using acid digestion and inductively-coupled plasma mass spectrometry (ICP-MS) on a Perkin Elmer Elan 6000. Sediments were digested in 10 ml of 1.6 M trace element grade HNO_3 at room temperature for 24 hrs, which targets loosely-bound elements and not those hosted within the mineral lattices. Both sediment eluates and pore-water samples were injected into the ICP-MS to attain Fe and Mn. Duplicate analyses, carried out on 10% of the samples, were < 3% RPD. Method blanks were below method detection limits.

Freeze-dried sediments were analyzed for % organic matter (% OM) and % carbonate-C (% CO_3) using the loss-on-ignition technique at 550°C and 950°C, respectively (Heiri et al., 2001). Freeze-dried sediments above and below the noted depth of complete diatom dissolution were also analyzed for X-ray diffraction using a Rigaku Geigerflex Power Diffractometer with a Co tube and a graphite monochromator.

Sedimentary pigments

Pigment concentrations were quantified using reverse-phase high pressure liquid chromatography (HPLC) (Vinebrooke et al., 2002). Pigments were first extracted from freeze-dried sediments using an acetone:methanol solution. Extracts were then filtered (0.2-μm pore nylon), dried under N_2, and reconstituted using a precise volume of injection solution. Chromatographic separation was performed with an Agilent 1100 Series HPLC equipped with a Varian Microsorb 100Å C18 column, and pigment detection using in-line diode array and fluorescence detectors. Pigment concentrations were quantified via calibration equations and an electronic spectral library constructed using standards purchased from DHI Water and Environment, Denmark. As a key reference for taxonomically diagnostic pigments Jeffrey et al. (2005) was consulted. All concentrations are expressed by mass normalized to sediment organic matter.

Sedimentary silica flux

Solute flux from sediments have been estimated and measured in a number of studies (Calvert, 1983; Hofman et al., 2002). Estimations of fluxes are based on Fick's Law of Diffusion, assuming a steady-state relationship, and the observed dissolved concentration gradient in the pore-waters. We used the following relationship to calculate flux (F) in g m^{-2} yr^{-1}:

$$F = D_e \, ø \, (\partial C / \partial z), \qquad (1)$$

where D_e is the effective solute diffusion coefficient, ø is the sediment porosity in the upper 3 cm and $\partial C/\partial z$ is the concentration gradient as calculated from pore-water analysis. The slope of the interstitial [DSi] linear model ($r = 0.9$; $p<<0.001$) is used as the concentration gradient. We adjusted the molecular diffusion coefficient (D) of silica for tortuosity, accounting for the porosity of sediment at the surface, using the formula (Ullman and Aller, 1982):

$$D_e = ø^2 D \tag{2}$$

The estimation of permanently buried silica is based on measured $BSiO_2$ concentrations and the ^{210}Pb calculated sedimentation rate (mg cm^{-2} yr^{-1}).

Results

Water chemistry

A notable feature of the long-term limnological data (Table 2) is that DSi concentrations in hypolimnetic waters (mean 1.9 mg L^{-1}) are consistently and significantly ($p<<0.001$) higher than epilimnetic (mean 1.1 mg L^{-1}) and inflowing stream waters (mean 0.7 and 1.1 mg L^{-1}). This provides a first-order indication that sediments are acting as a net source of DSi to the hypolimnion.

Lake sedimentation

Supported ^{210}Pb activities were reached at a depth of 5 cm in the Pipit Lake core (Fig 4.2A). Unsupported ^{210}Pb decays near-exponentially from surface activities of 0.53 Bq g^{-1} to a mean supported activity of 0.05 Bq g^{-1}. The stability of the sedimentation rate through the unsupported ^{210}Pb section of the core is confirmed by the linear relationship between log ^{210}Pb activity and cumulative dry mass (Fig 4.2B). The mean sedimentation rate of Pipit Lake is estimated to be 25.2 ± 3.0 mg cm^{-2} yr^{-1}. Similarly, from a core collected in 1991, Leavitt et al. (1994) found the estimated ^{210}Pb sedimentation rate in Pipit to be 29.0 ± 2.7 mg cm^{-2} yr^{-1}. Estimated CRS ages in the section of the core where dissolution is taking place are well constrained with low standard deviations (Fig 4.2C). The correlation of %OM between the two cores is strongly significant ($r = 0.7$; $p <<$

0.001; df = 32), confirming similar sediment accumulation between them.

Sedimentation rates calculated from the sediment trap material average 325 mg cm^{-2} yr^{-1} in the winter and was 1035 mg cm^{-2} yr^{-1} in the summer. These rates are orders of magnitude greater than those calculated from the sediment core. Overestimating natural sediment accumulation can be common in traps with high aspect ratios (> 5) as a result of capturing sedimenting and resuspended material (Flower, 1991), but was not expected with the low aspect ratio of our trap. However, given the position of the trap near the deepest point of the lake. Resuspension is the most likely reason for the overestimated sediment accumulation rates.

Diatom analysis

Micrographs of the uncleaned sediment collected from the sediment trap during the summer showed an abundance of littoral periphytic diatoms (*Gomphonema* sp., *Achnanthes* sp., *Cocconeis* sp.) with *Cyclotella* cf. *comensis* being the dominant planktonic form (Fig 4.3). The EPS coating is evident on a number of benthic diatoms (Fig. 4.3A,B), while many of the *C.* cf. *comensis* specimens have preserved siliceous warts on the cell face (Fig 3C), which is characteristic of this genus (Round et al, 1990).

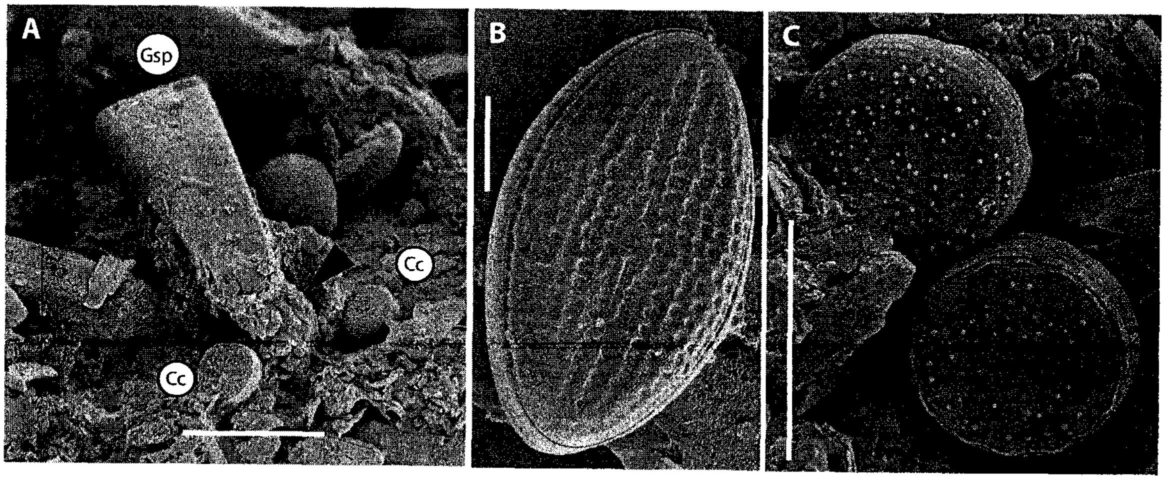


Fig 4.3 Scanning electron micrographs of sediment trap material. (A) An epiphytic diatom Gomphonema sp. (Gsp) can be seen with an EPS coating and mucilage stalk (arrow) and complete cells of Cyclotella cf. comensis (Cc). (B) EPS coated Cocconeis sp.. (C) Complete C. cf comensis cells with no EPS evident, but silica warts evident on the valve face. Scale bars are 10μm in A and 5 μm in B and C.

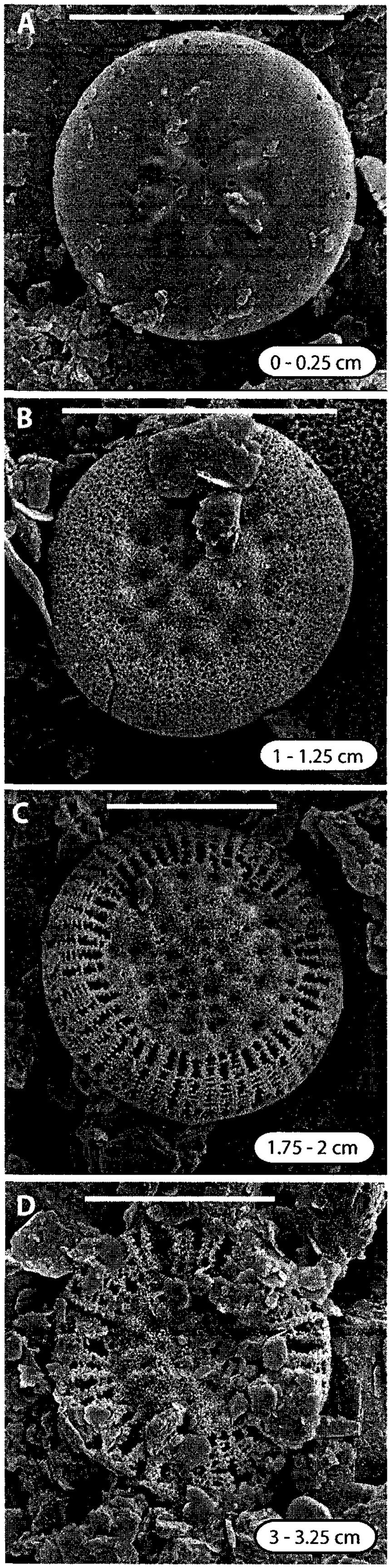


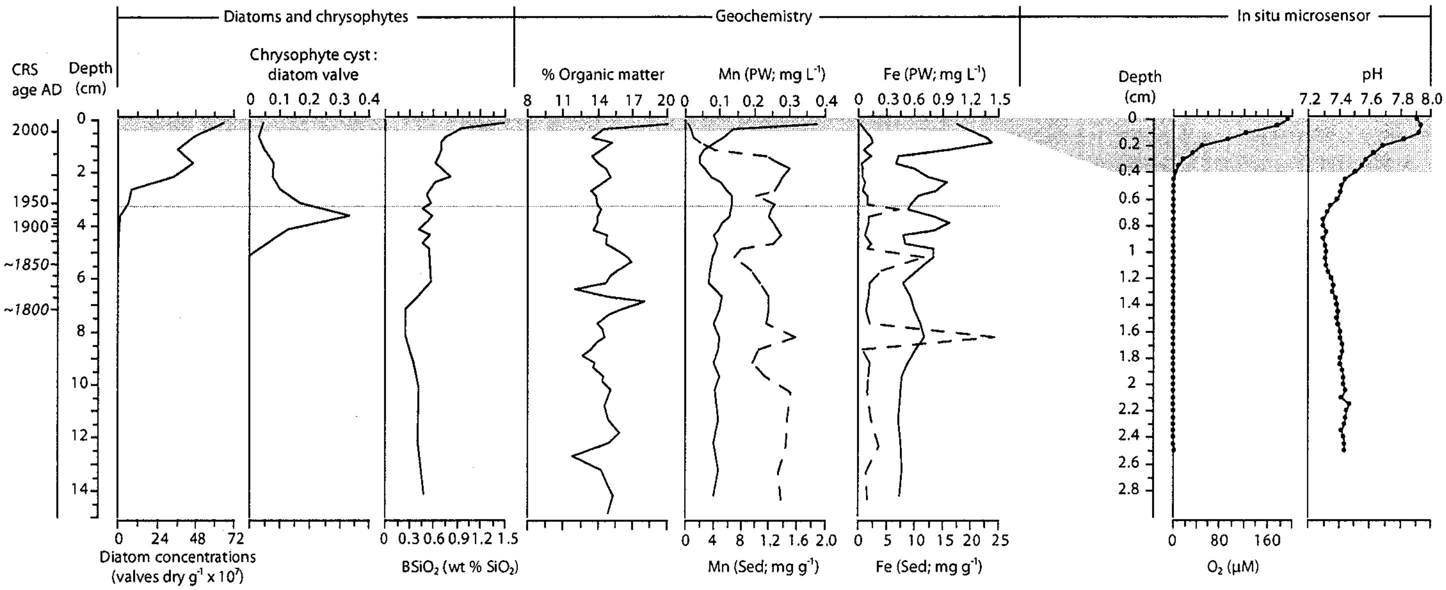
Fig 4.4 (A) A cleaned valve from the surface sediment, no pitting or warts are evident. (B) At 1 cm depth pitting and etching become more evident; (C) dissolution of puncta on the valve margins at 1.75-2 cm; (D) leaving the straie, before complete dissolution. All scale bars are 5 μm.

Cleaned (undergone peroxidation) surface sediments show signs of dissolution (pitting or etching of the cell wall) on a number of specimens, particularly on *C.* cf *comensis*. Tracking *C.* cf. *comensis* with depth in the cleaned sediment core shows the progressive loss of silica beginning at the valve margins and ending with the central area before dissolution is complete (Fig 4.4).

The absolute diatom concentrations from the Pipit lake sediments show a complete loss of frustules at a depth of 3.25 cm (Fig 4.5), corresponding to sediment accumulation of the last ~50 years. The more recalcitrant siliceous chrysophyte stomatocysts persist to ~4 cm where they too are dissolved

Biogenic silica and XRD

$BSiO_2$ within the sediment trap averaged 16.2 ± 1.7 wt% $BSiO_2$ over the period Oct. 2005 - July 2007 (Table 3). Summer abundance of $BSiO_2$ was greater than the winter collections. The loss of $BSiO_2$ from the sediment trap to the surface



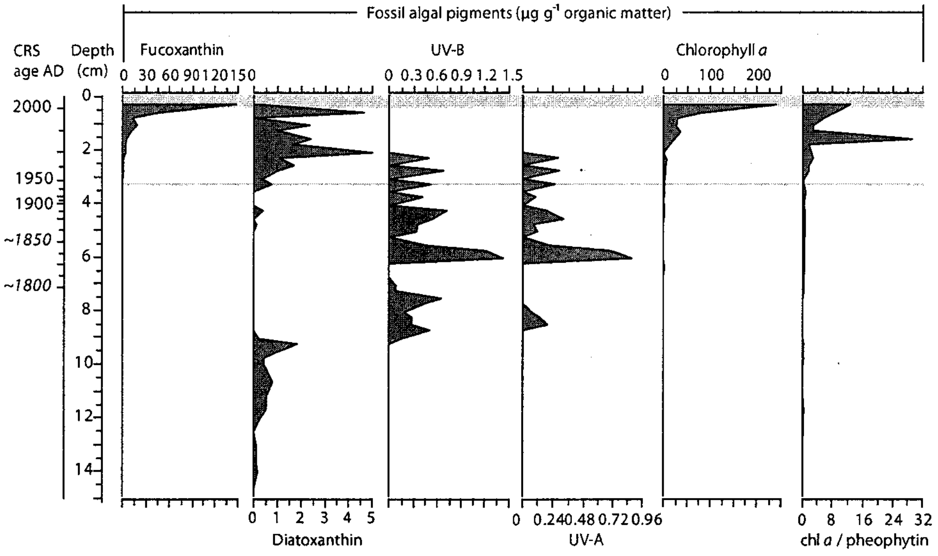


Fig 4.5 Profile of the biogenic SiO_2, geochemistry, and fossil pigments. The oxic zone of the sediments is shaded grey and the depth of complete diatom dissolution is marked by the grey line (3.25 cm). Estimated ^{210}Pb CRS age (extrapolated dates in italics) and depth on y-axis. $BSiO_2$ proxies include diatom concentrations (valves dry g^{-1}), chrysophyte cyst : diatom valve ratio, and extracted $BSiO_2$ (wt% SiO_2). Geochemical stratigraphy of OM, Mn, and Fe, where dashed lines are pore-water concentrations while solid lines are labile solid phase concentrations. In situ microprobe O_2 and pH are blown-up and shown on the right, where the maximum depth of analysis is 2.8 cm. Fossil pigments (mg pigment g^{-1} OM) include the diatom carotenoids, fucoxanthin and diatoxanthin, the UV-radiation-specific compounds A and B, and the measure of diagenesis as the labile (chl *a*) : stable (pheophytin *a*).

sediment is ~90% (16.2 % to 1.5 %). Sediment core $BSiO_2$ reflects the same profile seen in the diatom concentrations, with a 66% decrease in the upper 1.5 cm, from 1.5 % to ~0.5 % (Fig 4.5). Measurable amounts of $BSiO_2$ seem to persist beyond the depth of complete visible dissolution. We speculate two reasons for this: (1) there is a detectable amount of silica which is not evident in prepared microscope slides, and (2) a portion of the DSi is forming a colloidal silica or authigenic alumino-silicate which is undetectable through light microscopy, but would represent a relatively labile silica source during $BSiO_2$ analysis. This 'background' amount of $BSiO_2$ is roughly 0.5 wt % $BSiO_2$ and represents the approximate method detection limit. We speculate this background $BSiO_2$ to be a newly-precipitated or existing labile colloidal silica at the limit of our analytical ability. Regardless, it does not affect the dramatic drop in $BSiO_2$ in the upper 1.5 cm.

The measured $BSiO_2$ in sediments and corresponding DSi in pore-waters are inversely correlated ($r = 0.51$; $p = 0.011$; Fig. 4.6). The dissolution of biogenic Si begins to level off at ~3.5 cm depth, where the buried amount of $BSiO_2$ is approximately 0.5 % . The dissolved Si of the interstitial waters increases from the sediment water interface to a maximum concentration of 6.9 mg L^{-1} at a depth of 3.75 cm, which is just below the point of complete dissolution. Below the point of dissolution, DSi concentrations reach a relatively stable background of 5.7 ± 0.2 mg L^{-1}.

Silica flux calculations show that the vast majority (~90%) of the sedimentary

Table 4.3 Summary of sediment geochemistry and accumulation rates from Pipit Lake trap and core. Values expressed as mean ± standard deviation.

Interval	%OM	$\%CO_3^{2-}$	% $BSiO_2$	% Clastics (residual)	Sediment accumulation rate (mg cm^{-2} yr^{-1})
11-Aug-05 - 13-Jul-06	18.3 ± 4.7	19.7 ± 3.5	15.4 ± 1.1	46.6 ± 6.0	381.9
13-Jul-06 - 19-Oct-06	19.1 ± 1.9	13.5 ± 1.0	18.9	48.5 ± 2.1	1034.7
19-Oct-06 - 15-Jul-07	12.8 ± 0.5	17.2 ± 1.0	15.8	54.2 ± 1.1	269.3
Surface sediments (0-0.25 cm)	20.8	12.8	1.5	64.9	25.2 ± 3.0
Mean 0.25-3.5 cm	14.2 ± 0.6	12.9 ± 1.4	0.4 ± 0.1	72.7 ± 1.5	25.2 ± 3.0
Mean 3.5-15 cm	14.6 ± 1.2	11.9 ± 1.9	0.7 ± 0.1	73.3 ± 2.2	25.2 ± 3.0

silica pool is recycled back to the water column. It is estimated that 0.29 gSi m^{-2} yr^{-1} is diffusing from the interstitial waters to the water column, whereas only 0.04 gSi m^{-2} yr^{-1} is permanently buried in sediments. The diffusive flux results from the sediments are consistent with other estimates from oligotrophic lakes (Hofmann et al. 2002).

X-ray diffraction (XRD) analysis showed no change in sediment mineral composition above and below the depth of complete dissolution. This suggests that DSi from dissolved $BSiO_2$ is not being transformed into authigenic aluminosilicates such as illite or smectite, or to micro-crystalline quartz, but rather being recycled into the water column.

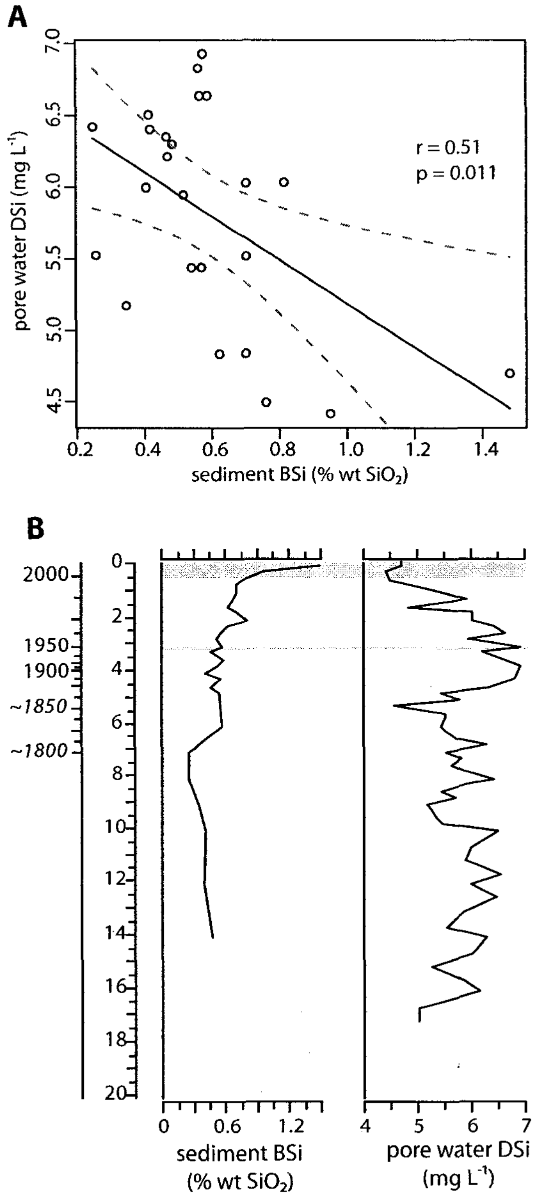


Fig 4.6 (A) The significant linear relationship between pore-water DSi and sediment $BSiO_2$; 95% confidence intervals are shown as dashed lines. (B) $BSiO_2$ in sediments and DSi in pore-water profiles; shaded area is the oxic zone of the sediment, while complete diatom dissolution is delineated by the grey line.

Organic matter and redox sensitive metals

The organic content of the sediment trap material averaged 16.5 % ± 4.0 %, while CO_3 content is 17.1 ± 3.3 %. The summer sediment trap sample has higher OM content and greater sediment accumulation when compared with the winter sediments (Table 4.3). Surface sediment % OM from the core is 20.8, while % CO_3 is 12.8. The organic content of the sediment decreases extremely rapidly and remains relatively stable for the remainder of the core (mean 14.5 ± 0.3 %)

(Fig 4.5).

Solid-phase [Mn], most likely present as oxihydroxides, decline rapidly in near-surface sediments (0-1 cm), while pore-water [Mn] increase proportionally (Fig 4.5). Below the depth of Mn mobilization, solid-phase [Fe], similarly presumed to reflect oxihydroxides decrease at 1-2 cm, however pore-water [Fe] does not increase possibly due to diffusion into the lake water. Oxic remineralization of organic matter in the surface sediments is evident by the loss of %OM and O_2. Oxygen is consumed within the upper 4 mm of the sediment and is positively correlated with a drop in pH of 0.8 units (Fig 4.5).

Sedimentary pigments

Diatoms produce chlorophylls *a* and *c*, as well as the carotenoids fucoxanthin and diatoxanthin. Fucoxanthin is an easily degradable compound and subsequently forms diatoxanthin (Leavitt and Hodgson, 2001). This transition is evident in the upper oxic zone of the core, where microbial activity is highest. The loss of both fucoxanthin and diatoxanthin is complete by 3.25 cm, consistent with the depth where diatoms are completely dissolved (Fig 4.5). Trace amounts of diatoxanthin are evident in the core from a depth of 9-15 cm, however no diatoms are present at this depth suggesting that residual amounts of this carotenoid are being preserved from dissolved diatom communities. Coincident with the loss of diatom pigments is the presence of UV-radiation-specific pigments resembling compounds A and B of Leavitt et al. (1997). These compounds are suggested to be produced by benthic algae when exposed to ultraviolet radiation. They are similar carotenoid-like structures to scytonemin, which is produced in cyanobacterial sheaths to protect against UVR (Leavitt et al., 1997). The ratio of primary chlorophyll *a* (chl *a*) to its derivative pheophytin *a* (labile : stable) can be used as a means to assess the post-depositional diagenesis of fossil pigments (Leavitt, 1993). The loss of all the chl *a* and subsequent drop in the chl *a* : pheophytin in the upper 3.25 cm confirms the importance of diagenetic processes in Pipit Lake sediments (Fig 4.5).

Discussion

Diatom dissolution and organic matter remineralization

SEM images of sediment-trap material reveal intact diatom cells with organic coatings and attached epiphytic species (Fig 4.3A). Loss of EPS and the first signs of dissolution, including pitting and etching, become immediately evident on surface-sediment frustules, and progress rapidly down-core (Fig 4.4). Diatom frustules disappear below 3.5 cm, and chrysophyte cysts at 5 cm (Fig. 4.5). The latter are slightly less susceptible to dissolution due to their spherical and inaperturate morphology. These observations suggest that loss of EPS coatings occurs very soon after deposition and potentially during sedimentation. Experimental study has shown that exposed frustules are more susceptible to chemical dissolution than counterparts with intact EPS (Lewin, 1961). Heterotrophic microbial processes are predicted to accelerate diatom EPS removal and hence accelerate frustule dissolution (Bidle and Azam, 1999). The microelectrode profiles reveal the surface-sediment organic matter respiration, where pore-water DO declines markedly in the upper few millimeters of the core and anoxia is encountered at 4.0 mm (Fig. 4.5). A concurrent decrease in pH reflects the heterotrophic production of CO_2 and hence of carbonic acid (H_2CO_3) through hydrolysis. At pH = 8, comparable to lake waters and surface sediment pore-waters, all dissolved inorganic carbon (DIC) is predicted to occur as HCO_3^-, whereas the drop in pore-water pH in the upper 1 cm indicates up to ~20% of DIC as free CO_2 and H_2CO_3 (Kalff, 2002). These observations show that an alkaline pH within the pore-waters is not driving the rapid dissolution of diatom frustules.

Coeval losses of sediment $BSiO_2$ and organic matter are equally striking (Fig 4.5), and we propose that common processes are responsible. During and after sedimentation, organic matter including diatom EPS is rapidly consumed, promoting dissolution of $BSiO_2$ surfaces in waters undersaturated with respect to DSi. Carbonic and silicic acids are by-products of organic matter respiration and diatom solubilization, respectively, providing the potential for addition protonation, as evidenced by pore-water pH trends.

Diagenetic loss of organic matter from the upper 4 mm in Pipit Lake sediments represents ~30% of the hypolimnetic seston. This is slightly greater than the estimates of Gälman et al. (2008), who showed that up to 20% of new organic matter is lost from lake sediments within 5 years of deposition. The theoretical sequence of microbial remineralization of organic matter generally follows the order of decreasing energy production (O_2>Mn oxides, NO_3^->Fe oxides) in sediments (Froelich, 1979; Konhauser, 2007). This model is confirmed by the *in situ* pore-water DO, Mn, and Fe concentrations from Pipit Lake sediments, and the associated solid-phase Mn and Fe profiles that indicate preferential loss of Mn-oxyhydroxides with depth relative to those of Fe (Fig 4.5).

Alpine lakes and silica recycling

Although the theoretical solubility of amorphous silica occurs at a pH of ~10 (Langmuir, 1997), the dissolution of $BSiO_2$ can clearly be sustained at lower pH values, given results from Pipit and other lakes (Battarbee et al., 2005; Ryves et al., 2006). Therefore solution of $BSiO_2$ driven solely by pH, is not a prominent mechanism in such lakes. The disequilibrium of DSi in natural waters becomes a more likely mechanism for dissolution, as highlighted by Lewin (1961). DSi saturation in natural waters is 122 mg L^{-1} at pH 8 (Langmuir, 1997), while lake water DSi concentrations across the Canadian Rocky Mountain lakes range from 0.5-5.5 mg L-1 (Anderson, 1969; Anderson & Donald, 1976; Anderson & Donald, 1978). This degree of undersaturation is driven by the combination of low catchment DSi production, which results from slow weathering of quartz-poor lithologies, and rapid biological uptake by diatoms and chrysophytes. The natural tendancy towards hydrolysis of $BSiO_2$ is augmented in absence of protective organic coatings that are oxidized soon after deposition.

These observations are not isolated. We have observed the complete loss of diatom microfossils from recent alpine lake sediments in 8 of 12 lakes sampled in the Rocky Mountains of Alberta (spanning 51.6 °N to 53.6 °N), suggesting that reliable diatom preservation is the exception rather than the rule in this region. However, rapid dissolution has not been documented in other Canadian alpine lakes, which instead present discrete intervals of diatom dissolution during the Holocene (Hickman and Reasoner, 1994, 1998; Karst-Riddoch et al. 2005). The inference being that conditions which obliterate the diatom record are potentially episodic.

The regeneration of silica from the sediments of Pipit Lake thus appears to be both biologically and chemically mediated. $BSiO_2$ recycling is initiated between hypolimnetic waters and surface sediment. The $BSiO_2$ content of the sediment trap material is 16.2% compared to 1.5% at the sediment surface, meaning only an estimated 10% arrives at the sediment surface or is rapidly dissolved at the sediment surface (Fig 4.7). In addition, the flux of DSi from the sediments represents a further return of ~90% of the sedimentary silica pool from the interstitial waters back to the water column, where it can be re-utilized or exported in outflow. Therefore, only ~1% of the original $BSiO_2$ standing crop is buried permanently within the sediments. Comparatively, Conley and Schelske (1989) reported that only 5% of the $BSiO_2$ produced in Lake Michigan accumulates in sediments. We are unable to close the net DSi budget for Pipit Lake because groundwater DSi contributions are not constrained. However, the magnitude of recycled DSi from the sediments suggests this is a greater source for siliceous algae than DSi derived from the sum of catchment

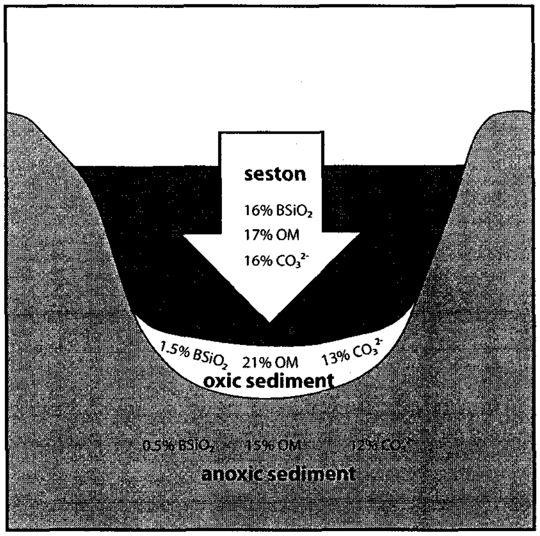


Fig 4.7 Movement of sedimentary biogenic silica, organic matter, and carbonates. All values are expressed as % sediment dry weight. Values are from sediment trap, surface, and mean core.

inputs (Table 2).

Sedimentary pigments

As a component of the sediment organic matrix, fossil pigments are predicted to be affected by the processes outlined above. Indeed, the zone of diatom dissolution is matched by diagenetic alteration of sedimentary pigments (Fig 4.5). We investigated the individual diode-array spectra for chl *a*, fucoxanthin, diatoxanthin, and the UV-B compound at selected intervals. Although there is some indication of isomerization of structures, wavelengths of maximum absorption remained consistent among samples for each pigment. Only the intensity, and not the shape, of absorption spectra between samples varied, indicating that structures remained intact until the pigment was no longer present.

Fucoxanthin is present only in the upper 3 cm of sediment, and is rapidly converted to the more stable diatom carotenoid diatoxanthin. The abundance of the UV-shielding compounds A and B of Leavitt et al. (1997) coincides with the loss of diatoxanthin at ~3.5 cm. Diatoxanthin appears again between 9-15 cm, at depths where both UV pigments disappear (Fig 4.5). Given limits on the present characterization of these compounds we offer two possible reasons for this stratigraphic pattern: (1) they represent intervals of increased UVR penetration from lower dissolved organic carbon (DOC) in the water column; or (2) the UV compounds are actually derivative or degraded structures from other pigments, potentially originating from diatoms. The chlorophyll *a*/ pheophytin *a* profile demonstrates that rapid diagenesis shapes the recent sedimentary pigment record of Pipit Lake. Although this degree of post-depositional alteration is pronounced, it is in no way unique (Carpenter et al., 1986; Leavitt and Findlay, 1994).

Comparison of our results with the pigment stratigraphy from a core recovered from Pipit Lake in 1991 (Leavitt et al., 1994) confirms that pigment diagenesis is highly dynamic. Down-core profiles of chlorophyll *a*, diatoxanthin, fucoxanthin, and

UV-sensitive pigments are all very similar on their respective depth scales, despite 15 years of difference in sediment accumulation. This comparison suggests that the Pipit Lake pigment record is largely the product of post-depositional diagenesis rather than ecological changes among algal communities. On the other hand, diatoxanthin is preserved at depth in both the 1991 and 2007 cores, which indicates that diatom-specific pigments have the potential to survive despite complete dissolution of their microfossil record. We caution that the highly-variable preservation regimes of individual pigments mandates the utmost care in their paleoecological interpretation.

Implications for paleoecology

The results from Pipit Lake challenge the assumption that sediments from cold oligotrophic lakes faithfully archive trends of primary production. For example, the use of $BSiO_2$ as a proxy for siliceous algal production assumes *a priori* that the preservation of $BSiO_2$ in sediments is proportional to diatom production. Given the importance of recycled silica in Pipit Lake, caution should be exercised when interpreting this proxy, especially if microfossils are not examined in parallel. This is particularly important on longer timescales (i.e. Holocene records) where diatom microfossils can intermittently disappear from stratigraphic records (e.g. Hickman & Reasoner, 1998; Karst-Riddoch et al., 2004). It is possible that episodes of pervasive dissolution are being recorded, analogous to conditions in Pipit Lake, rather than the absence of diatom communities from algal standing crops.

Variable states of pigment preservation are present in the Pipit Lake sediment core. While the labile chlorophyll *a* and fucoxanthin are being diagenetically lost in the surface sediments, the more recalcitrant diatom carotenoid, diatoxanthin, appears to persist through this zone. This suggests sedimentary pigments can be a reliable proxy of algal production despite active diagenesis in the upper sediments. In support of this, sediment records from additional lakes in the Canadian Rocky Mountains where complete diatom dissolution is occurring retain sedimentary pigments and do not appear to be affected by diagenesis (R.D. Vinebrooke unpubl. data).

Conclusion

Despite the importance of diatom taphonomy in freshwater paleoecology, few studies seem to acknowledge or discuss the extent of early diagensis. Our work shows that the degredation of diatom cells and fossil pigments in alpine lake sediments, can occur rapidly and as a result of a number of factors acting in concert. In Pipit Lake, microbial activity in a very shallow (~4 mm) oxic layer is the locus for organic matter remineralization, affecting both diatom EPS and photoactive pigments. Decreases in pore-water pH and DO result from this metabolism, ultimately freeing cells of EPS and facilitating the chemical dissolution of unprotected frustules. The hydrolysis of $BSiO_2$ then proceeds rapidly in the upper 3 cm of sediments, likely from DSi undersaturation. The vast majority (~90%) of $BSiO_2$ is lost during sedimentation, with an additional ~9% recycled back to the water column from the sediments through the diffusion of DSi. Pigment diagenesis occurs equally rapidly, with major transformations in the upper 3.5 cm, before a more stable inventory of recalcitrant carotenoids is reached. The results from Pipit Lake highlight how important diagenetic processes can be in shaping the lake-sediment record, even in cold, low-nutrient, and undisturbed environments.

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CHAPTER 5: QUANTIFYING LIMNOLOGICAL CHANGE IN THE ANTHROPOCENE: A COMPARISON OF HIGH-ALTITUDE AND HIGH-LATITUDE ECOSYSTEMS *

Introduction

The evidence for recent biogeochemical changes in both arctic and alpine lakes implies that these environments can no longer be considered pristine. These ecosystems are recognized as highly-sensitive to changes in climate (Battarbee *et al.*, 2002; Smol *et al.*, 2005) as well as atmospheric deposition of pollutants such as nitrogen (Wolfe *et al.*, 2006; Bergström & Jansson, 2006). The sensitivity of arctic and alpine lakes derives from their geographical settings that produce a number of limnological characteristics, such as dilute water chemistry, low primary production, and high flushing rates. The polar amplification of 20th century climate warming, mainly through positive feedbacks associated with changes in the albedo from loss of sea-ice and snow (Moritz *et al.* 2002), has led to major ecological changes in arctic lakes since 1850 AD (Smol *et al.*, 2005). Similarly, an altitudinal amplification has been observed in alpine surface air temperatures (Beniston *et al.*, 1997). Alpine and arctic climates are spatially heterogeneous, owing to the variable interplay between synoptic and localized orographic influences (Diaz & Bradley, 1997; New *et al.*, 2000). Regional syntheses of both instrumental data and paleoclimate proxies have smoothed the spatial variability somewhat, revealing coherent temperature increases since the mid-19th century in both arctic and alpine regions (Overpeck *et al.*, 1997; Luckman & Wilson, 2005). Anthropogenic disruption of the global N cycle, through fossil fuel combustion and fertilizer production, is an additional and important dimension to the concept of global change (Galloway & Cowling, 2002). The increased atmospheric load of nitrogen has led to the fertilization of unproductive lakes around the world

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* Co-authors: Alexander P Wolfe (University of Alberta), Richard J Telford and H John B Birks (University of Bergen & Bjerknes Centre for Climate Research), Jasmine E Saros (University of Maine), Roderick R O Hazewinkel (Alberta Environment), Bianca B Perren (University of Toronto), and Émilie Saulnier-Talbot (Université Laval).

(Bergström & Jansson, 2006).

The lack of long-term climatic and environmental monitoring data in alpine and arctic regions can be alleviated by the use of proxy data from high-resolution sedimentary records. Geochemical signatures and biological remains are continuously archived in the sediments accumulating at the bottoms of lakes. Diatoms (Bacillariophyceae) are unicellular aquatic photoautotrophs that respond rapidly to changes in water chemistry mediated by environmental change. The siliceous component of their cell walls is often preserved in lake sediments, recording the limnological history of a given lake. In the last few decades diatom records from lake sediments have highlighted global environmental issues such as lake acidification (Battarbee & Renberg, 1990; Charles & Whitehead, 1990), eutrophication (Bennion *et al.*, 1996), and climate change (Smol & Douglas, 2007). These data have augmented the evidence that the planet has entered the Anthropocene (Crutzen, 2002; Zalasiewicz *et al.*, 2008), the era of human dominance over all key biogeochemical cycles, with direct evidence of climatic and biological repercussions (IPCC, 2007).

Paleoclimatic reconstructions from arctic and alpine regions consistently reveal the Little Ice Age (LIA, ~1450-1850 AD) as one of the coldest intervals of the Holocene, when glacial advances were widespread and low summer temperatures prevailed (Bradley *et al.*, 2003). The onset of the LIA was gradual, and maximum glacier expansions occurred asynchronously between the late 17th and 19th centuries. The LIA terminated by the end by the 19th century, and temperatures have increased since, although not monotonically. Subsequently, the latter part of the 20th and the first decade of the 21st century have probably witnessed the highest temperatures of at least the last millennium (Jones *et al.*, 2001).

Climate-driven biological turnover since 1850 AD in arctic lakes has been shown to be greater at higher latitudes (Smol et al., 2005). In this study we analyze the amount of diatom compositional turnover in 52 North American and west Greenland lakes during three time periods, defined by large-scale climatic change, (1) the onset of the LIA, ~1550-1800, (2) warming following the LIA maximum, 1800-1900, and (3) the 20th century. Examining biological responses over the large climatic variations of the last ~450 years, through lake sediment records, gives us an opportunity to explicitly show the effects of climate change on diatom assemblage structure. Our aim is to test the biological sensitivity of selected lakes over a temporal (~450 years) and spatial gradient (~40°N to 80°N; ~10 m asl to 3400 m asl). We find that turnover during the 20th century is significantly greater than in the last ~350 years for arctic and alpine lakes. Individual physical or environmental lake characteristics do not explain the changes in diatom compositional turnover. We therefore consider the combined influence of climatic change and atmospheric nutrient deposition on diatom compositional turnover in our 52 lakes.

Materials and methods

Core collection, dating, and diatom preparation

Fifty-two diatom stratigraphies were compiled from lakes situated in North America and western Greenland (Figure 5.1). Latitudes of the lakes range from 38°N to 79°N, while altitudes range from 12 m asl to 3389 m asl (Table 5.1). Sites can be roughly categorized into arctic lakes (> 60°N; *n*=20), alpine lakes (above tree-line; *n*=15), and montane-boreal lakes (< 60°N; *n*=17) (Table 5.1). The montane-boreal sites can be viewed as 'reference lakes', as they are not implicit in our hypothesis to test biological sensitivity in relation to altitude, nor are they situated at northern latitudes where biological turnover might be greater (Smol *et al.*, 2005). All the lakes in our analysis have not been affected by any direct anthropogenic activities (e.g. shoreline development, effluent discharge, acidification).

Lake-sediment cores were collected using a modified Kajak-Brinkhurst gravity corer to collect a continuous sediment record with an intact sediment-water interface

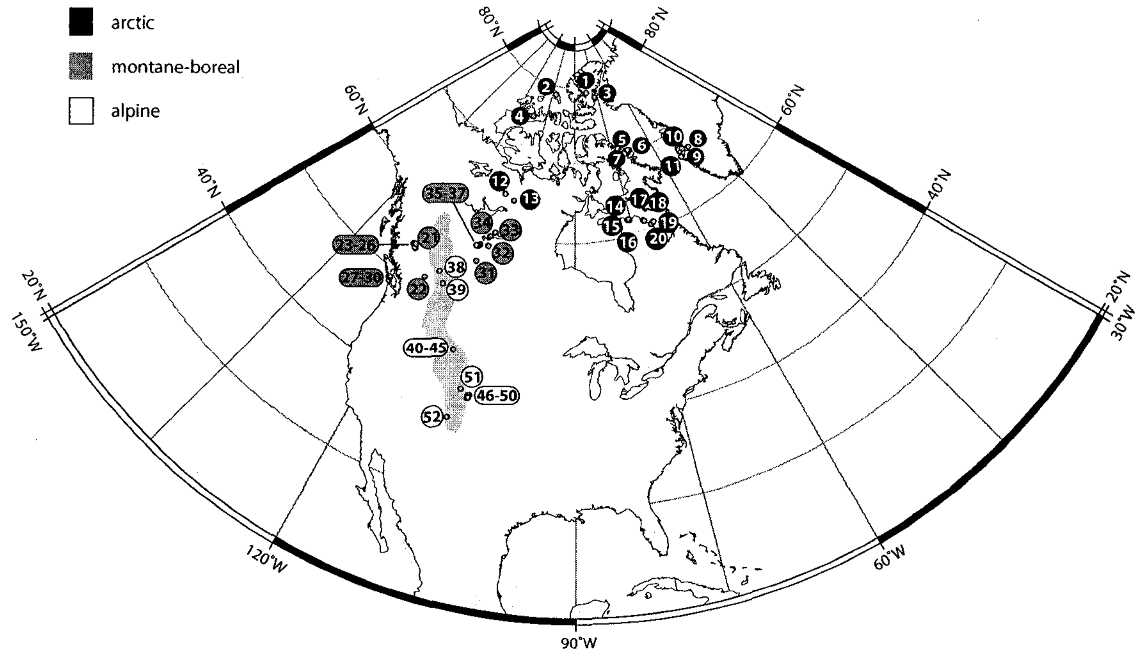

Fig 5.1 Map locating the study sites in North America and Greenland. Numbers correspond to the lake descriptions in Table 1. Shaded area represents the extent of the Rocky Mountains.

(Glew *et al.* 2001). Cores were sampled either every 0.25 cm or 0.5 cm intervals. Chronostratigraphy of the cores was established through analysis of ^{210}Pb by alpha or gamma spectroscopy (Appleby *et al.*, 2001). Sedimentation rates from the lower portions of the cores were extrapolated to give an estimated age for the base of each core. Preparation of sediment samples for diatom enumeration followed standard protocols (Battarbee *et al.*, 2001). We have used species 'complexes' on two occasions to refer to ecologically compatible, small (< 15μm) *Cyclotella* spp., where species cannot be resolved by light microscopy. We refer to the *Cyclotella stelligera* complex (*C. stelligera* and *C. pseudostelligera*) and the *Cyclotella comensis* complex (*C. comensis*, *C. rossii*, and *C. tripartita).*

Numerical analyses

In order to estimate the compositional turnover of the fossil diatom assemblages over time, the relative abundances were analyzed using detrended canonical correspondence analysis (DCCA) constrained by time (ter Braak, 1986; Birks, 2007). DCCA statistically

Table 5.1 Locations, physical characteristics, pH, and conductivity of the lakes used in this study. References: 1-Perren et al., (2003); 2-Antoniades et al., (2005); 3-Michelutti et al., (2006); 4-Keatley et al., (2006); 5-Wolfe et al., (2006); 6-Michelutti et al., (2007); 7-BBP unpubl. data; 8-Rüland & Smol (2005); 9-Rüland (2001); 10-ÉS-T unpubl. data; 11-Hobbs & Wolfe (2007); 12-Laird & Cumming (2001); 13-Laird et al. (2001); 14-Hazewinkel et al. (2008); 15-WOH unpubl. data; 16-Saros et al. (2003); 17-Saros et al. (2005); 18-Wolfe et al. (2003).

	Region	Lake	Latitude (°N)	Longitude (°W)	Altitude (masl)	Lake area (km^2)	Catchment area (km^2)	Max depth (m)	pH	Conductivity ($\mu S\ cm^{-1}$)	Reference
1	Ellesmere Island	Sawtooth Lake	79.33	81.85	275	2.60	50.0	90.0	8.0	119.4	1
2	Ellef Ringnes Island	Isachsen I-F	78.79	103.42	12	0.00	0.04	0.3	5.9	158.0	2
3	Ellesmere Island	Rock Basin	78.50	76.73	295	0.02	0.2	15.0	6.0	12.3	3
4	Melville Island	Pond MV-AT	75.32	111.42	120	0.10	0.4	0.4	8.1	39.0	4
5	Baffin Island	Lake CF-11	70.47	68.67	96	0.11	0.6	11.0	6.9	42.7	5
6	Baffin Island	Lake CF-10	70.43	69.12	435	0.09	2.7	9.6	6.4	23.9	5
7	Baffin Island	Lake CF-3	70.53	68.37	27	0.20	0.6	7.2	5.9	68.9	6
8	W. Greenland	Lake B	67.27	51.58	671	1.10	4.1	unk	unk	unk	7
9	W. Greenland	Nunutak Lake	66.97	49.80	470	0.16	2.2	21.0	7.3	unk	7
10	W. Greenland	Lake ss16	66.91	50.46	477	3.30	0.2	12.2	7.2	unk	7
11	W. Greenland	Lake ss53	66.49	53.53	50	7.30	23.1	8.3	6.9	unk	7
12	NW Territories	Slipper Lake	64.62	110.83	460	1.90	unk	17.0	6.6	31.2	8
13	NW Territories	TK-20	64.15	107.82	390	0.10	unk	8.8	7.2	8.7	9
14	N Québec	Airport Lake	62.18	75.66	225	0.04	0.1	8.6	6.8	72.0	10
15	N Québec	Tasikutaaq	62.16	75.72	50	0.31	8.6	13.6	6.5	23.0	10
16	N Québec	Qaanganiittuq	62.12	75.59	342	0.06	0.4	13.9	unk	unk	10
17	N Québec	Nipingngajulik	61.57	71.77	84	0.79	14.3	24.5	6.1	230.0	10
18	N Québec	Allagiap Tasinga	61.54	72.01	156	0.21	3.8	9.0	6.0	21.0	10
19	N Québec	Tasing	61.07	69.56	61	0.03	0.5	3.5	6.6	78.0	10
20	N Québec	Lake X	60.86	70.13	128	0.31	20.4	6.5	7.2	80.0	10
21	BC Interior	Fraser Lake	54.08	124.75	670	54.60	6707.1	30.5	7.5	unk	11
22	BC Interior	North Barrière Lake	51.33	119.83	634	4.50	517.7	52.6	6.6	unk	11
23	BC Interior	Boomerang Lake	53.68	124.58	1140	0.52	3.9	11.0	7.1	50.0	12
24	BC Interior	Secord Lake	53.63	124.34	1220	0.40	2.2	8.0	7.0	55.0	12

25	BC Interior	Justine Lake	53.85	125.09	820	2.48	43.7	10.0	7.1	59.0	12
26	BC Interior	Unnamed Lake	53.85	125.09	1100	0.79	2.1	19.5	7.5	68.0	12
27	Vancouver Island, BC	Little Toquart	49.06	125.35	75	0.55	9.9	16.0	6.5	22.5	13
28	Vancouver Island, BC	Toquart	49.08	125.35	75	1.15	66.8	37.5	6.7	28.6	13
29	Vancouver Island, BC	Blue	48.73	124.90	90	0.47	5.3	11.0	7.0	24.3	13
30	Vancouver Island, BC	Angora	49.09	125.53	245	0.31	2.1	46.5	7.8	42.8	13
31	N. Alberta	Lake A86	55.68	111.83	678	75.00	197.0	2.7	6.6	25.7	14
32	N. Alberta	Lake L39	57.96	110.38	356	1.12	18.1	1.5	6.8	108.0	14
33	N. Alberta	Lake L107	59.72	110.01	366	3.73	12.2	7.8	7.3	59.7	14
34	N. Alberta	Lake L109	59.12	110.82	274	1.29	111.7	13.7	7.1	49.9	14
35	N. Alberta	Legend Lake	57.41	112.93	787	16.80	93.1	10.2	6.9	29.7	14
36	N. Alberta	Namur Lake	57.44	112.62	731	43.39	224.0	24.0	7.3	63.6	14
37	N. Alberta	Otosan Lake	57.71	112.39	750	3.44	23.4	7.6	6.8	24.7	14
38	CDN Rockies (Jasper)	Curator	52.80	117.87	2232	0.05	0.8	25.0	8.4	220.0	15
39	CDN Rockies (Banff)	McConnell	51.63	115.97	2300	0.08	2.7	31.0	unk	unk	15
40	US Rockies (Beartooths)	Beartooth	44.95	109.60	2713	0.45	61.1	26.2	7.6	30.0	16
41	US Rockies (Beartooths)	Beauty	44.97	109.57	2874	0.36	15.0	35.1	6.9	7.0	16
42	US Rockies (Beartooths)	Emerald	45.00	109.53	3292	0.16	0.7	unk	6.0	unk	16
43	US Rockies (Beartooths)	Fossil	45.00	110.00	3018	0.67	unk	45.7	6.7	6.0	17
44	US Rockies (Beartooths)	Heart	44.98	109.54	3162	0.16	0.9	45.7	7.3	6.4	17
45	US Rockies (Beartooths)	Island	44.95	109.54	2901	0.59	18.8	30.5	7.1	7.0	17
46	US Rockies (RMNP)	Sky Pond	40.28	105.67	3322	0.03	2.0	7.0	6.5	12.5	18
47	US Rockies (RMNP)	Snowdrift	40.34	105.73	3389	0.03	0.4	14.0	6.6	14.7	18
48	US Rockies (RMNP)	Husted	40.58	105.68	3350	0.04	1.5	11.0	6.9	13.4	18
49	US Rockies (RMNP)	Louise	40.55	105.62	3360	0.03	0.7	8.0	6.9	19.9	18
50	US Rockies (RMNP)	Nokoni	40.25	105.73	3292	0.08	0.8	38.0	6.4	10.4	18
51	US Rockies (Zirkels)	Pristine	40.69	106.68	3366	0.01	0.2	unk	7.0	15.9	17
52	US Rockies (San Juans)	Crater	37.67	107.71	3546	0.03	0.4	13.4	7.0	39.0	15

unk = unknown or not sampled

models assemblage compositions in relation to one or more environmental variable (only time in our analysis). This approach is a constrained or canonical version of a detrended correspondence analysis (DCA) (Hill & Gauch, 1980). Both DCA and DCCA enable compositional changes in biotic assemblages to be summarized as compositional turnover (β-diversity) in standard deviation units. By constraining the DCCA to time (as inferred through ^{210}Pb modeled ages) we maintain the biostratigraphic integrity of the diatom sedimentary records. The larger the β-diversity estimate over the time-period of analysis, the greater the biological or assemblage turnover. We selected a minimum of three time intervals over which to estimate compositional turnover in order to test explicitly the biological response to known climate shifts (Bradley *et al.*, 2003). Our rationale allows for the comparison of any modern shifts during the 20th century to the previous ~350 years and thereby tests whether changes are within the range of turnover experienced during the onset of the Little Ice Age (1550-1800) and warming following the LIA maximum (1800-1900). Owing to the variable sediment recovery from site to site, the number of diatom records used in the analysis decreases towards the 1550-1800 time interval. It should be noted that we found no evidence that the number of sediment intervals included in the DCCA influenced the estimates of β-diversity. Our DCCA protocol included square-root transformation of species percentage data in order to stabilize variance among species, no down-weighting of rare species, the inclusion of all species with >1% relative abundance, detrending by segments, and non-linear rescaling. DCCA was implemented using CANOCO 4.51 (ter Braak & Šmilauer, 2002)

We used linear modeling to assess whether selected environmental variables (lake water [NO_3^-], modeled atmospheric NO_3^-, winter air temperature, summer air temperature, pH, conductivity) and physical catchment characteristics (lake area, catchment area, maximum lake depth) influenced the 20th century β-diversity. β-diversity results were analyzed using non-parametric Wilcoxon rank sum tests to assess the statistical significance between lake categories within each time period and between time periods for each lake category. Levels of statistical significance were evaluated using adjusted p-values through Bonferroni tests. Finally, in order to evaluate collective environmental influences on β-diversity lake-by-lake, ordination by principal components analysis (PCA) was undertaken on the following variables: latitude, altitude, Δ N deposition, lake:catchment ratio, and pH. PCA was applied to a correlation matrix of these variables, centered, and standardized. Statistical analyses (other than DCCA) were made using the open-source software R (R Development Core Team, 2008).

Results

Selected diatom stratigraphies

The changes in diatom β-diversity during a given time period are a summary of the shifts observed in the lake diatom assemblages. We present abbreviated examples of sedimentary diatom records from four of our study lakes representing different diatom assemblage change and a range of lake characteristics (Figure 5.2). In the alpine and arctic lakes (Figure 5.2A-C) the success of planktonic *Cyclotella* spp. in the 20th century is evident. It has been demonstrated that *Cyclotella* spp. are competitive in stratified water columns, which can be a result of a longer open-water period in the summer (Bradbury, 1988; Lotter & Bigler, 2000; Rühland & Smol, 2005). During periods of low planktonic diatom abundance, small benthic and generally alkaliphilous fragilarioid taxa (*Pseudostaurosira brevistriata, Staurosirella pinnata, Staurosira construens*) predominate. The benthic diatoms are successful in terms of relative abundance when light transmission is low, ice-free growing seasons are short, and only littoral areas of lakes can be colonized (Smol & Douglas, 2007). It is the offsetting success of planktonic and benthic forms which results in the β-diversity changes observed (Figure 5.2). An exception to this within our dataset is Emerald Lake in the Beartooth Mountain Range of the US Rocky Mountains where dramatic shifts in the planktonic flora alone are evident

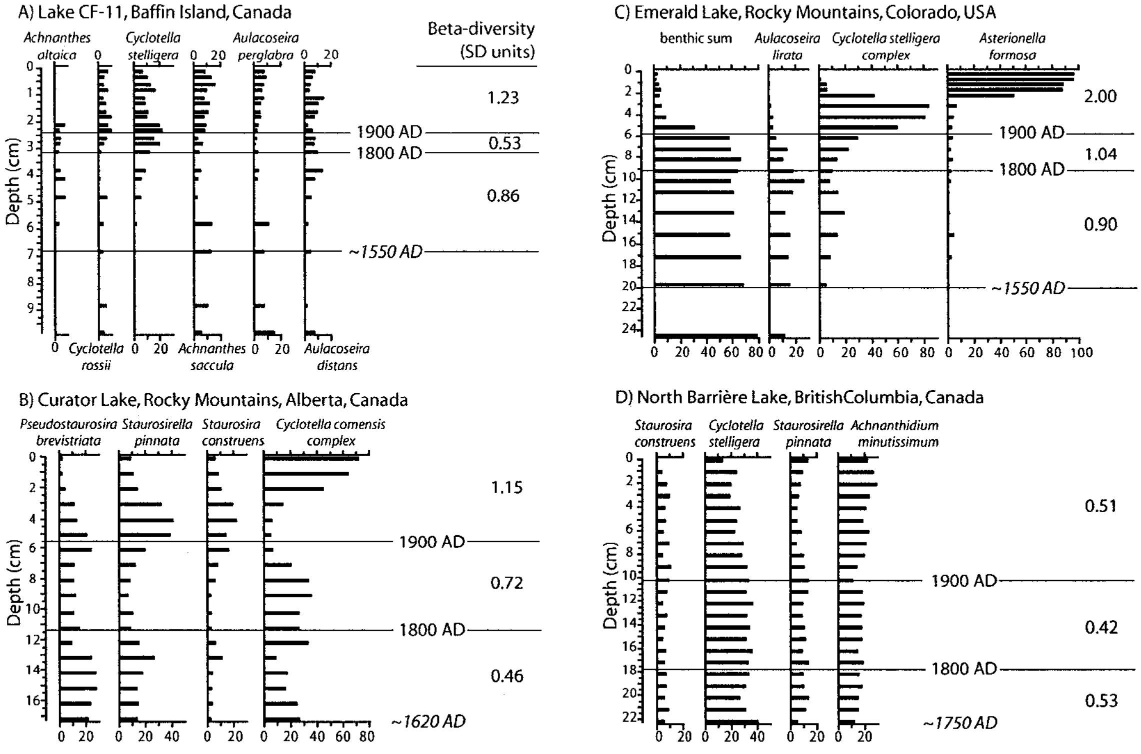

Fig 5.2 Example relative abundance diatom stratigraphies from an arctic lake (A), two alpine lakes (B and C), and a montane-boreal lake (D). All diatom species are ordered by descending DCCA axis 1 scores from left to right. The corresponding beta-diversity estimates for each stratigraphic time period are shown to the right of the figure. Only the major taxa for each core are shown, however all taxa >1% are included in the numerical analyses. The time periods for the analysis of β-diversity are indicated.

over the last 450 years (Figure 5.2C). The most obvious of these shifts is complete dominance by the taxon *Asterionella formosa* starting at ~1970, replacing the *Cyclotella stelligera* complex. The growth of *A. formosa* in alpine lakes is strongly stimulated by nitrogen enrichment, suggesting an increase in N-deposition within this lake system (McKnight *et al.*, 1990, Saros *et al.*, 2005). Prior to the rise of the *C. stelligera* complex during the 19th century and early 20th century, the tychoplanktonic taxon *Aulacoseira lirata* is a dominant feature of the diatom record. The autecology of *Aulacoseira* spp. requires a well-mixed water column and high available Si (Kilham *et al.*, 1996), suggesting it is favored by a more turbid and perhaps shorter open-water season. At the opposite end of the spectrum to Emerald Lake is North Barrière Lake, BC where the diatom assemblage has changed very little over the past 450 years, resulting in low, near constant β-diversity over the length of the core (Figure 5.2D).

Diatom β-diversity

The β-diversities of both arctic and alpine diatom lake-sediment records during the 20th century are significantly higher than the montane-boreal lake records (Figure 5.3). The alpine sites range from 0.52 - 2.00 SD (mean 1.01 ± 0.43), the arctic sites range from 0.44 - 1.34 SD (mean 0.84 ± 0.22), and the montane-boreal sites range from 0.24 - 1.17 SD (mean 0.65 ± 0.27). During the 19th century and the time period 1550-1800, β-diversities for the arctic and alpine sites do not differ

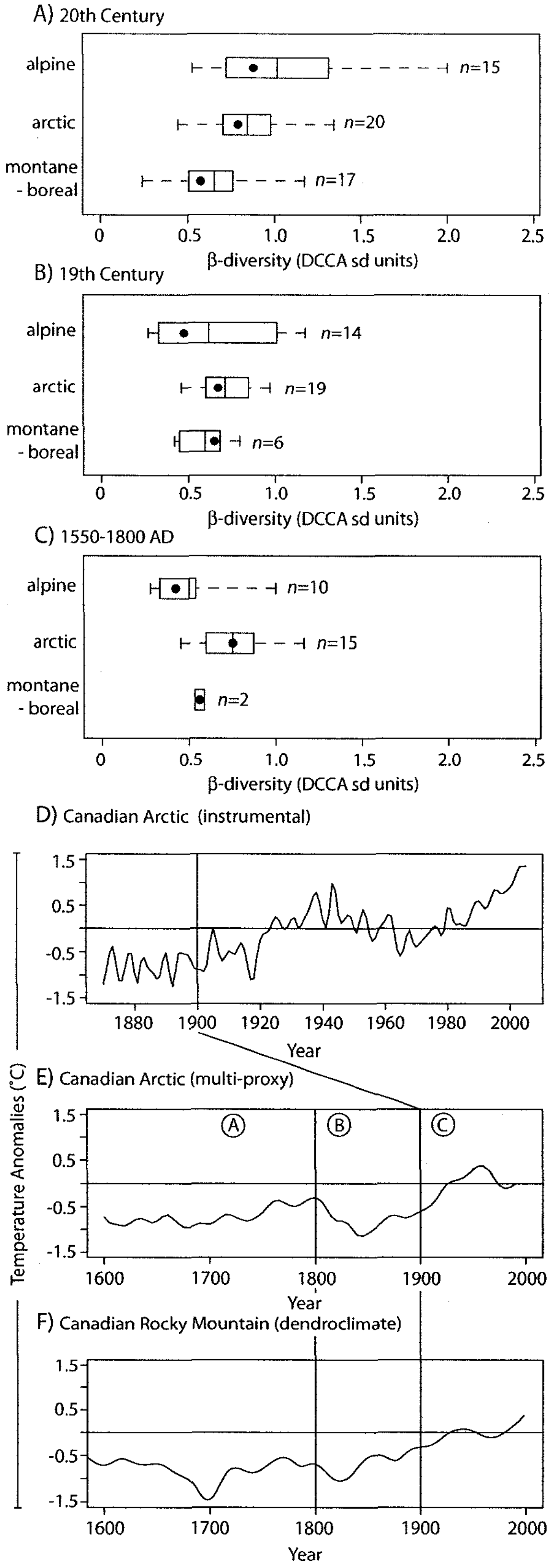

Fig 5.3 Box plot of diatom compositional turnover results from DCCA categorized into Alpine, Montane-Boreal (shaded), and Arctic sites. Black dots represent the median value, while the vertical lines within the 25th percentile box shows the mean value. (A) 20th century results, statistical significance between the alpine and montane-boreal ($p = 0.003$) and the arctic and montane-boreal sites ($p = 0.004$). (B) and (C) results of the 19th century and cold LIA phase (1550-1800), respectively. Note that a statistically significant difference between compositional turnover of the lake groups exists only in the 20th century. (D) regional compilation of arctic (> 60 °N) instrumental temperature data for the period 1870-2005 (data from HadCRUTv2 relative to the period 1961-1990; http://www.cru.uea.ac.uk/). (E) arctic multi-proxy paleoclimatic reconstructions and (F) an alpine dendroclimatic reconstruction, showing the temperature deviations over the last 400 years. The three time periods of the DCCA detailed in box-plots A-C are marked on (E) and (F). Both reconstructions are calculated relative to the mean period 1901-1960 (Overpeck et al., 1997; Luckman & Wilson, 2005).

significantly from the montane-boreal sites (Figure 5.3).

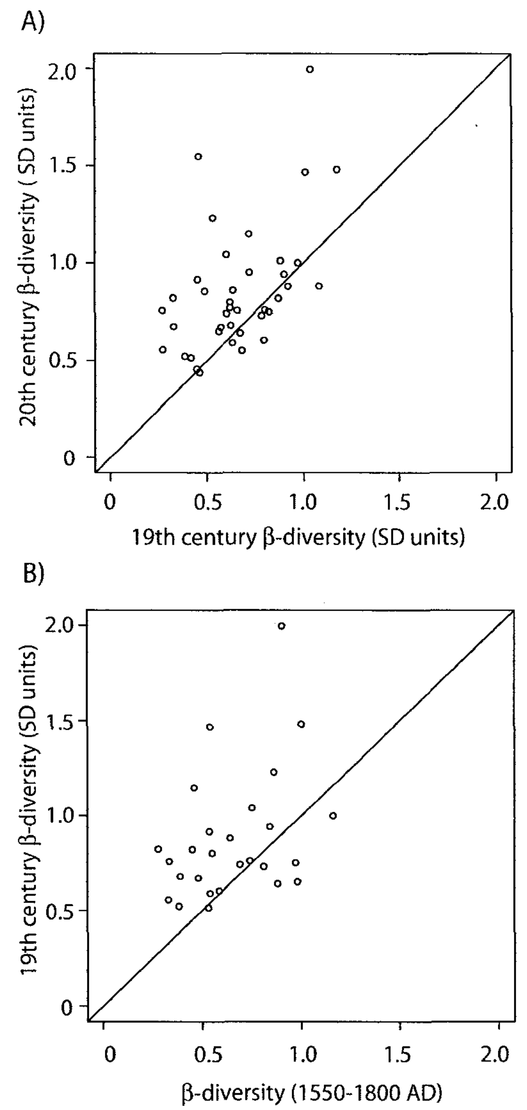

Fig 5.4 Scatterplots showing the distribution of 20th century β-diversity relative to the 19th century (A), and the 19th century relative to the LIA period (1550-1800) (B). 1:1 lines are drawn to highlight the greater β-diversity present in the more recent time periods.

The diatom β-diversity for all 52 lakes during the 20th century is significantly greater than the 19th century ($p = 0.03$; Figure 5.4A), while there is only a small and non-significant difference in turnover between the 19th century and 1550-1800 ($p = 0.86$; Figure 5.4B). The turnover of diatoms in alpine lakes during the 20th century is significantly greater than the previous 350 years ($p = 0.01$). Alpine-lake β-diversities increase from a mean value of 0.52 SD during the onset of the LIA (1550-1800) to 0.61 SD during the warming following the LIA maximum and to 1.01 SD in the 20th century. The significance of the increase in 20th century turnover is less in the arctic lakes ($p = 0.05$), where β-diversity changes from 0.71 SD (1550-1800 AD) to 0.75 SD (19th century) to 0.84 SD (20th century). The montane-boreal lakes showed no significant change in diatom assemblage turnover in the last 450 years (Figure 5.3). We can confidently say that alpine and arctic lakes show a greater diatom assemblage turnover in the 20th century when compared to the previous 350 years at the same sites and when compared to a number of reference sites.

Drivers of β-diversity

As a means to investigate those factors influencing the biological turnover, we tested the relationships between β-diversity and a number of environmental and physical characteristics of the lakes. We normalized the 20th century β-diversity estimates relative to the 19th century estimates as a means of accounting for those lakes where local β-diversity is high and to highlight the magnitude of 20th century change within a regional context. Physical parameters include lake and catchment area, catchment:lake ratio (a surrogate for water residence time), maximum depth, and January and July ambient air temperatures (New *et al.*, 2002). Environmental variables include modern lake water pH, specific conductance, NO_3^-+NO_2^-, and modeled atmospheric NO_3^- deposition (Δ 1993-1860; Galloway *et al.*, 2004). We found no statistically significant relationships between normalized 20th century β-diversity and any of the physical or environmental variables.

Discussion

Diatom biodiversity and altitude

There are two regions within our dataset where β-diversity within the 20th century is the highest: low altitude, high latitude sites (arctic) and low latitude, high altitude sites (US Rocky Mountains). Smol *et al.* (2005) have previously demonstrated recent shifts in diatom communities since 1850 AD in arctic lakes. Our results confirm these findings, and furthermore place them in a longer temporal context: the last ~450 years (Figure 5.3 A-C). In addition, the new data compilation shows that diatom shifts of similar or greater magnitude to those recorded in the Arctic have occurred in high altitude lakes. To investigate β-diversity and altitude we removed the low elevation, high β-diversity arctic sites and found a strong linear relationship between 20th century β-diversity and altitude (Figure 5.5A). Lakes at higher elevation appear to have a greater range of diatom assemblage shifts. Comparable to our findings, Heegaard *et al.* (2006) found that over an

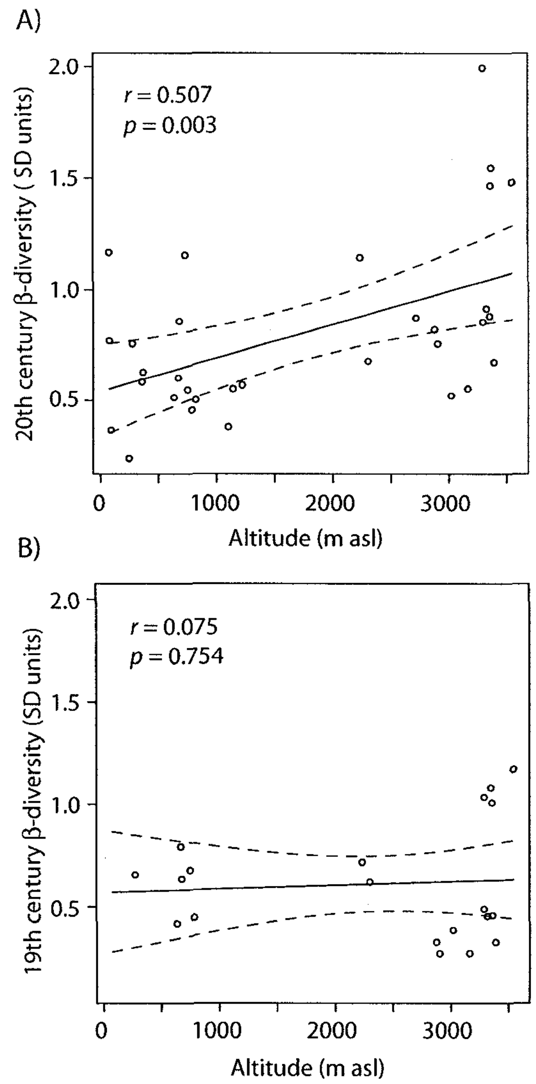

Fig 5.5 Relationships of β-diversity against altitude for the alpine and montane-boreal sites. A significant linear relationship exists in the 20th century (A), while no relationship is evident in the 19th century (B).

altitudinal gradient in the European Alps, modern diatom β-diversity increased at higher altitudes defining a distinct ecotone above tree-line. This response could be due to the different thermal regime of alpine lakes found in the Alps (Livingstone *et al.*, 2005). The apparent influence of the tree-line on diatom assemblages and thermal regimes raises the question of whether our higher 20th century β-diversity is a result of shifting tree-lines. Dendroclimatic and palynological studies from the Rocky Mountains show fluctuations in tree-line throughout the Holocene, but not on the temporal scale or at compatible elevations to affect the lakes within our dataset (Luckman & Kearney, 1986; Reasoner & Hickman, 1989; Carrara *et al.*, 1991; Vierling, 1998).

In our dataset, assemblage shifts frequently result from the success of planktonic versus benthic diatoms (Figure 5.2). Total species richness (α-diversity) has become progressively reduced over time in many alpine lakes where β-diversity has increased and as planktonic taxa become increasingly dominant (Saros *et al.*, 2005).sdoes While, in many arctic lakes recent increases in β-diversity are matched by greater species richness (Smol *et al.*, 2005). In modern diatom assemblages, species richness has been shown not to influence the β-diversity with altitude (Heegaard *et al.*, 2006). Similarly in our dataset we find no evidence that α-diversity (averaged over time) is influencing the observed 20th century β-diversity.

In contrast to the 20th century, do sno relationship between β-diversity and altitude is evident during the 19th century (Figure 5.5). Given that there is a significant difference between the 20th and 19th century β-diversities in relation to altitude (p=0.02), it appears that it is not an altitudinal effect alone that has driven increased diatom compositional turnover.

Synthesis of β*-diversity, N-deposition, and climate change*

There are strong *a priori* reasons to suspect that N deposition and climate warming are driving 20th century β-diversity increases, dominating the limnological regimes of alpine and arctic sites, respectively. These suspicions, however, are not supported by simple correlations between β-diversities and surrogates for either climate or N deposition. Furthermore, these drivers are clearly not independent from one another, and thus should be considered together. A multivariate consideration of available environmental variables reveals that climate and N deposition are indeed synergistic, and together exert a dominant influence on diatom assemblage turnover (Figure 5.6A). The first axis of PCA extracted from this matrix illustrates this elegantly (Figure 5.6B): gradients of latitude, altitude, and modeled ΔN deposition each align closely with this axis. Axis 1 is the only significant principal component in this analysis, when compared to the broken-stick model for a matrix of identical proportions and total explanatory power. Thus axis 2, which reflects water chemistry and catchment morphology, indicates that these variables do not influence the amount of biotic turnover in any given lake, and accordingly that lake chemistry and physiography do not provide any insight concerning lake resilience or vulnerability. When 20th century diatom β-diversity is superimposed on this PCA as a passive variable, and subsequently contoured, values increase concentrically away from the origin, implying greater diatom change towards the extremes on axis 1, and relative complacency in between (Figure 5.6A). Accordingly, the ordering of sample (lake) scores on axis 1 differentiates clearly the arctic from the alpine sites, with montane-boreal systems in between (Figure 5.6B). This result is not a statistical artefact, because the gradient defined by axis 1 is continuous, with slight degrees of overlap between regions.

We now consider in detail these two main drivers of 20th century diatom species turnover, namely increased atmospheric N deposition and rising ambient temperatures associated with anthropogenic climate change. We considerassemblage -ssThe β-diversity over the latitudinal range of the lakes (40°N to 80°N) reflects the sensitivity of high and low latitude sites (Figure 5.7A). Over the last century the release of reactive or bio-available N into the atmosphere by

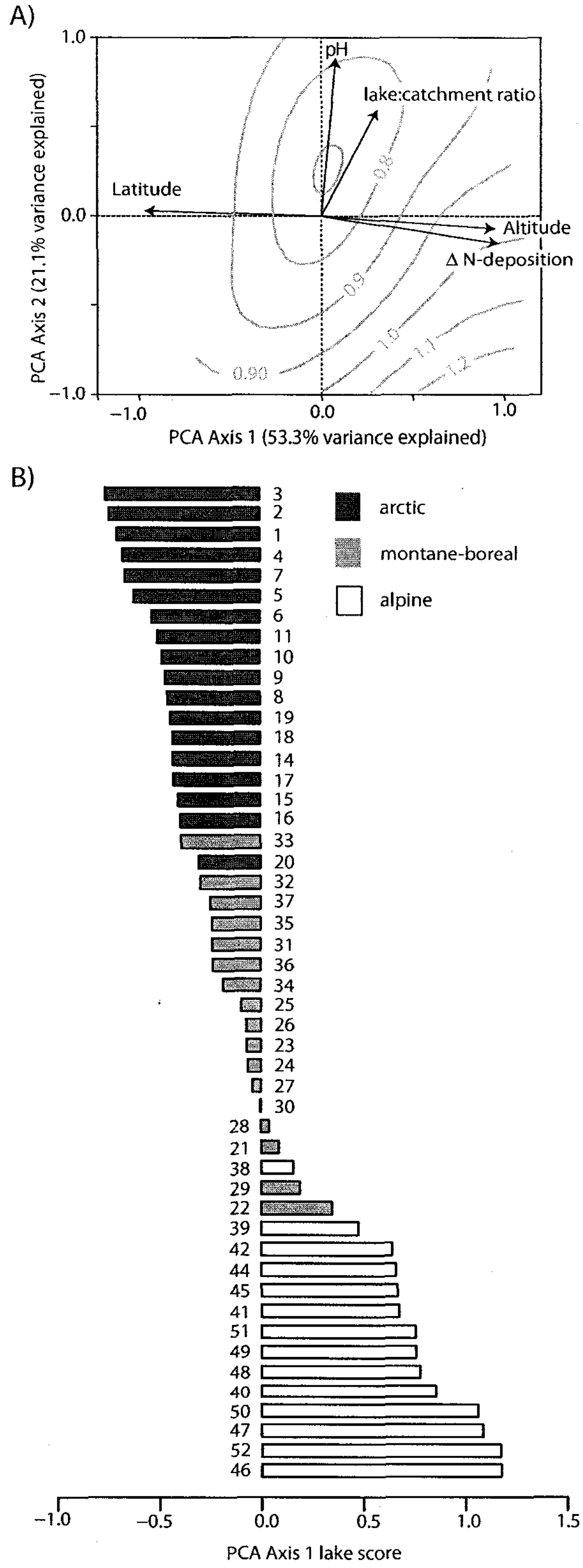

Fig 5.6 Principal components analysis (PCA) for 20th century period using latitude (climate surrogate), altitude, ΔNO_3^- deposition, pH and lake:catchment area (water residence time surrogate) (A). β-diversity is plotted passively as smoothed contours (0.10 interval) using thinplate splines over the ordination space. Testing axes against a broken-stick model, shows only axis 1 to be significant. Lakes are ordered according to axis 1 score (B), with corresponding lake number from Table 1 and shading which corresponds to region (alpine, arctic, or montane-boreal).

human activities has increased 9-fold to ~140 Tg N yr^{1} (Galloway & Cowling, 2002). Both arctic and alpine lakes are dilute and contain low and/or limiting concentrations of nutrients (N and P) (Morales-Baquero *et al.*, 1999; Antoniades *et al.*, 2003; Sickman *et al.*, 2003). An increase in atmospherically deposited nutrients has been shown to increase aquatic primary production and lead to shifts in diatom assemblages in alpine lakes (Baron *et al.*, 2000; Saros *et al.*, 2005) and has been suggested for some low-arctic lakes (Wolfe *et al.*, 2006). The sensitivity of arctic and alpine aquatic ecosystems to N deposition is largely derived from the alleviation of N limitation.

The atmospheric N deposition rates of Galloway *et al.* (2004), show that the change in N deposition from 1860 to 1993 is greatest over the low-latitude, high-altitude lakes (Figure 5.7B). This trend relates to the pattern of greater human settlement and activity at lower latitudes. Monitoring of atmospheric nutrient deposition and paleolimnological evidence of anthropogenically-derived N provides direct evidence of increased N in the alpine regions of the United States (Williams *et al.*, 1996; Baron *et al.*, 2000; Wolfe *et al.* 2003). The influence of atmospheric nutrient deposition is inconclusive for the Canadian High Arctic, and in some cases can be deemed minimal (Douglas et al., 1994). While there is no direct linear relationship between the β-diversity and change in N-deposition in our dataset, it is appropriate to acknowledge that the high β-diversity seen at these low-latitude lakes is likely influenced by the increased N-deposition over the 20th century.

The second potential driver of β-diversity is the well-documented change in climate experienced in arctic and alpine regions over the last century (Luckman & Wilson, 2005; Overpeck *et al.* 1997). A feature of recent arctic climate change is polar amplification of surface temperature warming during the last ~50 years (Figure 5.7C) (Moritz *et al.*, 2002). This phenomenon has been previously cited as a driver of greater biological turnover in arctic lakes (Smol *et al.*, 2005). Indeed, the arctic temperature increase is threefold greater than the increase over the alpine latitudes (Figure 5.7C). This

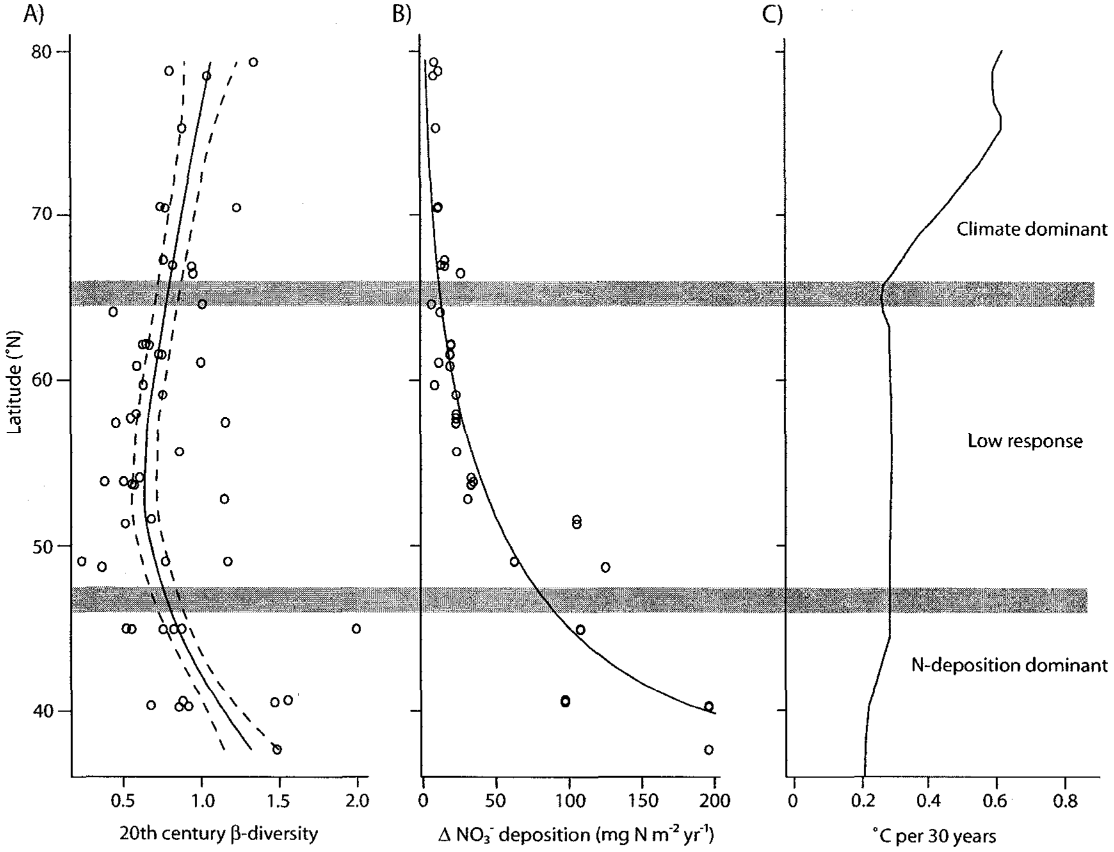

Fig 5.7 (A) latitudinal distribution of the 20th century β-diversity for all the lakes. For comparison over the latitudinal gradient the estimated change in NO3 deposition over the study sites is shown in (B), and the measured change in temperature over the period 1948-2002 is shown in (C). Nitrate data are extracted from Galloway et al. (2004), while the zonal trends of surface air temperature are compiled from NCEP/NCAR reanalysis data, adapted from Moritz et al. (2002). Approximate latitudinal zonation of β-diversity forcings are delineated by shaded lines.

feature is also evident in paleoclimatic reconstructions for the arctic and alpine regions over the last 400 years (Figures 5.3B and C). Given this amplification, it is reasonable to suggest that diatom compositional turnover in the Canadian-west Greenland arctic lakes is forced by climate change to a greater degree than in alpine lakes.

A regional compilation of instrumental data from the Arctic shows a climatically variable 20th century (Figure 5.3A), which may have resulted in high diatom β-diversity as assemblages respond to changes in ice cover and growing season length. In addition, temperatures since ~1970 have been increasing beyond that experienced over the last 400 years in both arctic and alpine regions, where paleoclimatic reconstructions reveal similar patterns of temperature anomalies (Figs 5.3B and C). The cold period of the LIA (1550-

1800) is clearly shown in both records, as is the warming during the transition following the LIA maximum (1800-1900). The 20th century clearly represents a period of warming above that of the last 400 years, where we start to see positive temperature anomalies. The 20th century temperature deviations in both arctic and alpine regions are leading to greater diatom compositional turnover.

The impact of climate change on alpine aquatic ecosystems has been observed and projected for some time (Bradley *et al.*, 2004; Battarbee *et al.*, 2002; Schindler & Donahue, 2006). A number of studies on European alpine lakes have shown direct responses of aquatic biota to recent changes in climate (e.g. winter precipitation, length of growing season) (Lotter & Bigler, 2000; Catalan *et al.*, 2002). It is important to note that local surface temperature trends in mountainous regions can run contra to regional patterns (Pepin & Losleben, 2002; Agustí-Panareda & Thompson, 2002). The lack of coherency in alpine temperature reconstructions or instrumental data is due to the inherent variability of local topography and continentality, which can affect local climate (e.g. cloud cover) (Beniston *et al.*, 1997). Despite possible differences in the changes of local climate on alpine lakes, our results show a clear regional and direct positive relationship between the amount of diatom compositional turnover and altitude. The significance of this result confirms the view that these ecosystems are sensitive to impacts associated with human activity and truly represent sentinels of change during the Anthropocene.

Finally, we note that some alpine areas have documented increased precipitation during the later half of the 20th century (Watson & Luckman, 2001; Williams *et al.*, 1996), while warmer summers and winters have led to the shrinking of alpine glaciers and loss of perennial snow (Schindler & Donahue, 2006). Therefore, the contribution of both glacially stored and modern freshwater into the lakes of these regions only stands to increase the amount of N they receive (Williams *et al.*, 1996). The same can be said for arctic regions where the loss of local ice caps has been directly observed (Anderson *et al.*, 2007). Also of note in the arctic is the potential contribution of nutrients to lakes in watersheds underlain by permafrost (Jones *et al.*, 2005). Given forecasts of amplified future warming along the American Cordillera (Bradley *et al.*, 2004) and the Arctic (IPCC, 2007), and projected increases in N-deposition (Galloway *et al.*, 2004), it seems unlikely that lakes spanning these vast regions will return to the more stable diatom community structures characteristic of pre-20th century limnological regimes. As diatoms are frequently a dominant component of primary production in arctic and alpine lakes, these changes may be viewed as harbingers of biological changes that are likely to be propagated to higher trophic levels.

Conclusion

During the 20th century, diatom assemblages in both arctic and alpine lakes of North America and west Greenland changed at faster rates that at any time in the previous 350 years. Elevated 20th century β-diversity is attributable primarily to climate change and N-deposition with strong regional variations in the degree of influence of either forcing factor. Future climate scenarios predict further loss of glacial ice and attendant reduction of hydrologic inputs to both arctic and alpine ecosystems (IPCC, 2007). Coupled to prolonged open-water growing seasons and deeper light penetration in both arctic and alpine lakes, we speculate that the primary production of these ecosystems will continue to increase. N-deposition scenarios also predict future increases over the spatial range of the lakes considered here, with greater fertilization of the low-latitude, high-altitude lakes (Galloway *et al.*, 2004). The future response of diatom assemblage composition to these scenarios is unclear, as no prior analogues exist for the coupled influences of anthropogenic climate change and N deposition.

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CHAPTER 6: CONCLUSION

Summary of work

This body of work highlights some of the limitations in paleolimnology, but also shows how effective the discipline can be in explicitly testing questions over variable temporal and spatial scales. To reiterate from chapter 1, the objectives of this work are to: (1) ascertain whether paleolimnology is meaningful in the discussion of historical salmon abundance within the Fraser River Basin, British Columbia, Canada, (2) determine if diatom microfossils can be used in recent alpine paleolimnology within the Canadian Rocky Mountains, and (3) quantitatively assess the amount of biological change in alpine and arctic regions of North America through sedimentary diatom records.

Marine-derived nutrients and paleolimnology in British Columbia

It appears that paleolimnology is not capable of providing meaningful insight into the historical abundance of MDN from sockeye salmon within the Fraser River Basin, British Columbia, Canada. The study lakes seem to be influenced mainly by allochthonous organic material and the catchment drainage or flushing rate of the lake. Efforts to utilize additional sedimentary proxies of salmon abundance, $\delta^{15}N$ of physically separated light (autochtonous) organic matter and fossil pigments (namely astaxanthin, the reddish carotenoid found in salmon flesh), provided no further clarity to the investigations. In those systems where MDN reconstructions from sediments have been successful, the salmon nutrients represent a significant annual proportion of the lake nutrient budget and the water residence time is sufficient for the freshwater aquatic ecosystem to take advantage of this subsidy. These results do not suggest that MDN are not important to the BC aquatic and riparian systems, rather they are not readily disentangled from other aquatic and terrestrial sources.

Diatom dissolution in alpine lakes, Canadian Rocky Mountains

Complete dissolution of diatom frustules within recent sediments was observed in eight out of twelve lakes sampled from the mountain parks, within the Canadian Rocky Mountains, suggesting that reliable diatom preservation is the exception not the rule in this region. Analysis of sediment trap material from Pipit Lake, Banff National Park, showed that ~90 % of the biogenic silica ($BSiO_2$) is lost during sedimentation within the hypolimnetic waters prior to burial. Silica flux calculations, based on dissolved silica (as H_4SiO_4) in pore waters, show a further ~9% of $BSiO_2$ is returned to the water column from the upper sediments (~ 4 cm), meaning only ~1% of the total $BSiO_2$ is permanently buried in the lake sediments. Scanning electron micrographs of sediment trap material confirms the loss of extracellular polymeric substances (EPS) coating the diatoms.

It is our conclusion that, similar to the marine environment, the loss of EPS exposes the diatom to chemical dissolution. This work is the first to quantify and highlight the importance of internal silica cycling in an alpine lake. It also has implications for the interpretation of biogeochemical proxies in alpine paleolimnology.

Quantifying limnological change in the Anthropocene

Fifty-two diatom-based paleolimnological records from North America and west Greenland, including alpine (*n*=15) and arctic (*n*=20) ecosystems, as well as a range of boreal-montane sites (*n*=17) as 'controls', are synthesized. For all of these sites, diatom compositional turnover (β-diversity) was quantified over the last ~450 years. For both arctic and alpine lakes, β-diversity during the 20th century is significantly greater than the previous 350 years. Species turnover increases with both latitude north and altitude. A multivariate consideration of available environmental variables reveals that climate and N deposition are acting synergistically and exert a dominant influence on diatom assemblage turnover. Regional temperature increases and polar amplification during the

20th century suggest a climate-driven trend of greater diatom β-diversity in arctic lakes. Whereas, the increase of anthropogenic N deposition at mid-latitudes suggests nutrient changes are of greater influence on β-diversity in alpine lakes. It is our prediction from this work that these lakes will continue to shift towards new ecological states in the Anthropocene, as these two dominant forcings begin to intersect geographically.

Broader implications for paleolimnology

The use of paleolimnology to reconstruct the historical abundance and cycles of Pacific salmon, has been successful over centennial (Finney et al., 2002) to mid-Holocene timescales (D Selbie pers.comm.). The need for fisheries managers to understand the forcing mechanisms behind natural cycles has led to an active research community in paleo-salmon records. Further analysis of numerous sediment cores (22 lakes) from southern BC and Vancouver Island has shown no evidence of MDN subsidies (PR Leavitt pers. comm.). However, it remains the contention of some researchers that paleolimnology can be used in southern BC if isotopic ratios are adjusted using the sediment C:N and $\delta^{15}N$ of chitinous zooplankton remains (Brahney et al., 2006). The consideration of nutrient subsidies to lake ecosystems, must include an acknowledgement of the annual nutrient budget, and water residence time. While paleolimnology has proven its utility in Alaskan salmon nursery lakes, the inability to recognize historical nutrient subsidies in southern BC lakes should be accepted and further research efforts should be directed to other aspects of the salmon – freshwater ecosystem.

The chapters discussing MDN demonstrate the importance of publishing null results. The necessity to accept the null hypothesis following a long and detailed study is not the most desirable outcome, and I would speculate that it has lead to a large amount of data remaining unpublished. Whether there are experimental flaws, or simply a negative result to the question asked, it remains part of the scientific method and should be reported on.

Large regional paleolimnological studies have successfully highlighted global environmental issues such as lake acidification, eutrophication, and climate change. Paleolimnology is currently being applied in Europe as a means of establishing background water quality conditions under the Water Framework Directive, which requires quality improvement to a certain status or conservation of all water within member countries by 2015 (Bennion & Battarbee, 2007). Therefore the applied use of quantitative paleolimnological studies can be a valuable asset in environmental legislation and protection. Large regional studies, such as that presented within this dissertation (Chapter 5), provide insights into the mechanisms of coherent regional change. Further understanding of the mechanisms behind large biological shifts, by documenting ecosystem response, will allow for future protection of lake ecosystems in an environment increasingly dominated by humans.

As in early paleolimnology (*sensu* Deevey, 1969), this work recognizes that regional coherence of sediment records suggests a common historical process (Chapter 5). However, this work also shows that the methodology of conducting 'experiments' through lake sediments has its limitations. The inability of southern BC lake sediments to record the presence of MDN would suggest that these nutrient subsidies are not important to the freshwater ecosystems. However, it can and has been argued that in oligotrophic lakes of southern BC, MDN are used rapidly by both aquatic and terrestrial ecosystems (Naiman et al. 2002, Hocking and Reimchen, 2007). It is simply not possible to disentangle this use through the sediment record. The poor preservation of biogeochemical proxies (Chapter 4) is also an unrecognized limitation in paleolimnology, as described by Deevey, however while I feel it is under-reported it is recognized in today's literature.

Future Work

Marine-derived nutrients in BC lakes

The study of MDN subsidies to the modern limnology of BC lakes deserves further consideration. One of the current limitations is the knowledge gap on the movement of MDN through the freshwater ecosystem and the proportion within the annual nutrient budget. Further work should focus on estimating the annual nutrient budget to a selection of salmon nursery lakes, including MDN contributions during peak and off-peak run years (4-year cycle in the case of sockeye salmon). Quantification of the C:N:P pool within the freshwater system would also allow for the investigation of allochthonous nutrient sources. Analyzing for C and N stable isotopes throughout this system (in water and particulate organics) would provide insight into the potential for MDN contributions and movement.

Diatom dissolution

This work has shown that the microbial consumption of EPS coatings on diatoms is occurring prior to the chemical dissolution of the diatom frustule in an alpine lake. This is the first such observation in freshwater environments and needs further research attention. There are two lines of investigation which I see appropriate: (1) determine how widespread the issue of dissolution is within Canadian Rocky Mountain alpine lakes and further characterize the water conditions of the lakes, and (2) apply the same approach detailed in this study to a lake where preservation is good and determine if EPS coatings are aiding in preservation of the frustule. The usefulness of the first recommendation is simply to expand our understanding of those lakes where paleolimnology can be applied in the Canadian Rockies and possibly constrain the variables, in a predictive manner, which are important to dissolution in this region (*sensu* Ryves et al., 2006). The second recommendation is a more specific investigation into the mechanisms of diatom preservation within lake sediments. In addition to SEM work on the frustules, the stain ruthenium red has proven to be effective at staining live diatom cell walls (Duke and Reimann, 1977) and might have applications for testing the presence of EPS coatings on surface sediment diatoms.

Alpine diatom shifts during the Anthropocene

Several aspects of this dissertation have dealt with recent biogeochemical changes in lake ecosystems in response to anthropogenic forcing. It is somewhat unsatisfying to not see these changes over the temporal variability of the lake's entire history. There are very few Holocene mountain lake records of climate change (e.g. Stone and Fritz, 2006). If we are to consider these systems as 'sentinels' of ecosystem change, as they have been periodically referred to (Williamson et al., 2008), we should look at the documented changes over the entire history of these lakes. Expanding both the temporal and spatial scale of alpine paleolimnology will contribute to defining the current era, namely the Anthropocene.

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APPENDIX A: DIATOM SPECIES NAMES AND AUTHORITIES

Diatom genus-level nomenclatural revision, authorities, and references are listed according to:

Fourtanier E, Kociolek JP. Catalogue of diatom names, California Academy of Sciences, on-line version. http://www.calacademy.org/research/diatoms/names/index.asp. Updated 12 December 2007

Round FE, Crawford RM, Mann DG (1990) The diatoms: biology & morphology of the genera. Cambridge University Press, Cambridge

Biogeographical information is included prior to each species, where: a = BC Interior, b = Canadian Rocky Mountains, and c = US Rocky Mountains.

a	*Achnanthes acares* Hohn & Hellerman 1963
a	*Achnanthes amoena* Hustedt 1952
a b c	*Achnanthes biasolettiana* Grunow in Van Heurck 1880
a b c	*Achnanthes curtissima* Carter 1963
a b	*Achnanthes flexella* (Kützing) Mann 1937
a	*Achnanthes frigida* Cleve-Euler 1939
a b	*Achnanthes holsatica* Hustedt in Schmidt et al. 1936
a b c	*Achnanthes ingratiformis* Lange-Bertalot in Lange-Bertalot & Krammer 1989
a	*Achnanthes kolbei* Hustedt 1930
a b c	*Achnanthes laevis* Østrup 1910
a	*Achnanthes minuscula* Hustedt 1945
a b c	*Achnanthes minutissima* Kützing 1833
a b	*Achnanthes nitidiformis* Lange-Bertalot in Lange-Bertalot & Krammer 1989
a b	*Achnanthes nodosa* A. Cleve 1900
a	*Achnanthes oblongella* Østrup 1902
a b	*Achnanthes petersenii* Hustedt 1937
a	*Achnanthes rupestoides* Hohn 1961
a	*Achnanthes stolida* (Krasske) Krasske 1949
a	*Achnanthes silvahercynia* Lange-Bertalot in Lange-Bertalot & Krammer 1989
a	*Achnanthes ziegleri* Lange-Bertalot 1993
b	*Achnanthidium altergracillima* (Lange-Bertalot) Round & Bukhtiyarova 1996
a b	*Achnanthidium exiguum* (Grunow) Czarnecki
a	*Achnanthidium kranzii* (Lange-Bertalot) Round & Bukhtiyarova 1996

		c	*Achnanthidium helveticum* (Hustedt) O. Monnier, H. Lange-Bertalot & L. Ector in Monnier et al. 2007
a	b		*Achnanthidium pusillum* (Grunow in Cleve & Grunow) Czarnecki in Czarnecki & Edlund 1995
a	b	c	*Adlafia bryophila* (J.B. Petersen) G. Moser, H. Lange-Bertalot & D. Metzeltin 1998
	b	c	*Adlafia minuscula* (Grunow) H. Lange-Bertalot in H. Lange-Bertalot & S.I. Genkal 1999
a			*Amphipleura pellucida* (Kützing) Kützing 1844
a			*Amphora aequalis* Krammer 1980
	b		*Amphora commutata* Grunow in Van Heurck 1880
a	b	c	*Amphora fogediana* Krammer in Krammer & Lange-Bertalot 1985
a	b		*Amphora inariensis* Krammer 1980
a	b	c	*Amphora ovalis* (Kützing) Kützing 1844
a	b	c	*Amphora pediculus* (Kützing) Grunow in Schmidt et al. 1875
a			*Amphora subcapitata* (Kisselev) Hustedt 1959
a	b		*Amphora thumensis* (A. Mayer) Cleve-Euler 1932
a	b		*Aneumastus tusculum* (Ehrenberg) Mann & Stickle in Round, Crawford & Mann 1990
a		c	*Asterionella formosa* Hassall 1850
a		c	*Aulacoseira alpigena* (Grunow) Krammer 1991
a			*Aulacoseira ambigua* (Grunow) Simonsen 1979
a	b		*Aulacoseira distans* (Ehrenberg) Simonsen 1979
a			*Aulacoseira granulata* (Ehrenberg) Simonsen 1979
a		c	*Aulacoseira lirata* (Ehrenberg) R. Ross in Hartley 1986
a		c	*Aulacoseira perglabra* (Østrup) Haworth 1990
a			*Aulacoseira subarctica* (Otto Müller) Haworth 1990
a		c	*Brachysira brebissonii* R. Ross in Hartley 1986
a	b	c	*Brachysira vitrea* (Grunow) R. Ross in Hartley 1986
a			*Brevisira arentii* (R.W. Kolbe) K. Krammer 2001
a			*Caloneis aerophila* Bock 1963
a	b		*Caloneis alpestris* (Grunow) Cleve 1894
a	b		*Caloneis bacillum* (Grunow) Cleve 1894
	b		*Caloneis branderii* (Hustedt) Krammer in Krammer & Lange-Bertalot 1985
a			*Caloneis macedonia* Hustedt 1945
a			*Caloneis schumanniana* (Grunow in Van Heurck) Cleve 1894
a			*Caloneis silicula* (Ehrenberg) Cleve 1894
a	b		*Caloneis undulata* (Gregory) Krammer in Krammer & Lange-Bertalot 1985
a	b		*Campylodiscus noricus* Ehrenberg 1840
a	b	c	*Cavinula cocconeiformis* (Gregory ex Greville) Mann & Stickle in Round, Crawford & Mann 1990
a	b	c	*Cavinula jaernefeltii* (Hustedt) D.G. Mann & A.J. Stickle 1990
a	b	c	*Cavinula pseudoscutiformis* (Hustedt) Mann & Stickle in Round, Crawford & Mann 1990

		c	*Cavinula pusio* (Cleve) H. Lange-Bertalot in Werum & Lange-Bertalot 2004
a	b	c	*Cavinula scutiformis* (Grunow ex A. Schmidt) Mann & Stickle in Round, Crawford & Mann 1990
	b		*Cavinula variostriata* (Krasske) Mann in Round, Crawford & Mann 1990
a			*Cavinula weinzierlii* (Schimanski) Czarnecki 1994
a			*Cocconeis neodiminuta* Krammer 1990
a			*Cocconeis neothumensis* Krammer 1990
a	b	c	*Cocconeis placentula* (Héribaud) Kolbe 1927
a	b		*Craticula halophila* (Grunow ex Van Heurck) Mann in Round, Crawford & Mann 1990
a	b		*Craticula molestiformis* (Hustedt) H. Lange-Bertalot in U. Rumrich, H. Lange-Bertalot & M. Rumrich 2000
a	b		*Cyclotella comensis* Grunow in Van Heurck 1882
	b		*Cyclotella cyclopuncta* Hakansson & Carter 1990
a			*Cyclotella meneghiniana* Kützing 1844
a			*Cyclotella michiganiana* Skvortzow 1937
a	b		*Cyclotella ocellata* Pantocsek 1902
a	b		*Cyclotella rossii* Håkansson 1990
a			*Cymatopleura solea* Van Heurck 1881
a			*Cymbella affinis* Kützing 1844
a	b	c	*Cymbella amphicephala* Naegeli in Kutzing 1849
a	b		*Cymbella caespitosa* (Kützing) Schutt 1896
a	b	c	*Cymbella cistula* (Hemprich in Hemprich & Ehrenberg) Kirchner 1878
a		c	*Cymbella cuspidata* Kützing 1844
a		c	*Cymbella cymbiformis* Pantocsek 1892
a			*Cymbella ehrenbergii* Kützing 1844
a			*Cymbella falaisensis* (Grunow) Krammer & Lange-Bertalot 1985
		c	*Cymbella gracilis* (Rabenhorst) Cleve 1894
a	b		*Cymbella helvetica* Kützing 1844
a		c	*Cymbella laevis var. rupicola* (Grunow in Schmidt et al.) Van Heurck 1896
a			*Cymbella leptoceras* (Ehrenberg) Kützing 1844
a	b	c	*Cymbella microcephela* Grunow in Van Heurck 1885
a			*Cymbella subcuspidata* Krammer 1982
a			*Cymbella tumidula* (Brébisson in Kützing) Van Heurck 1882-1885
a			*Cymbopleura naviculiformis* (Auerswald ex Heiberg) Krammer 2003
a	b	c	*Delicata delicatula* (Kützing) K. Krammer 2003
	b		*Denticula kuetzingii* Grunow 1862
a		c	*Diatoma mesodon* Kützing 1844
a			*Diatoma tenuis* Agardh
a			*Diatoma vulgaris* Bory 1831

a			*Didymosphenia geminata* (Lyngbye) M. Schmidt emend Antoine & Benson-Evans 1984
a			*Diploneis oculata* (Brébisson in Desmazières) Cleve 1894
a			*Diploneis marginestriata* Hustedt 1922
a			*Diploneis minuta var. peterseni* (Hustedt) Cleve-Euler 1953
a			*Diploneis modica* Hustedt 1945
	b	c	*Diploneis oblongella* (Naegeli ex Kuetzing) Ross 1947
a			*Diploneis oblongella var. ovalis* (Hilse in Rabenhorst) Ross 1947
a	b	c	*Diploneis parma* Cleve 1891
a		c	*Discostella stelligera* (Cleve et Grunow) Houk & Klee 2004
a			*Ellerbeckia arenaria* (Moore ex Ralfs) Crawford 1988
a			*Encyonema brehmii* (Hustedt) Mann in Round, Crawford & Mann 1990
a			*Encyonema caespitosa* Kützing 1849
	b		*Encyonema latens* (Krasske) Mann in Round, Crawford & Mann 1990
a	b	c	*Encyonema minuta* Hilse
a			*Encyonema perpusillum* (A. Cleve) Mann in Round, Crawford & Mann 1990
a	b	c	*Encyonema silesiacum* (Bleisch in Rabenhorst) Mann in Round, Crawford & Mann 1990
	b		*Encyonopsis cesatii* (Rabenhorst) Krammer 1997
a			*Encyonopsis descripta* (Hustedt) Krammer 1997
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a			*Eolimna subminuscula* (Manguin) G. Moser, H. Lange-Bertalot & D. Metzeltin 1998
a		c	*Epithemia adnata* (Kützing) Brébisson 1838
a		c	*Epithemia argus* (Ehrenberg) Kützing 1844
a			*Epithemia cistula* (Ehrenberg) Ralfs in Pritchard 1861
a			*Epithemia sorex* (Kützing) Rabenhorst 1853
a			*Epithemia turgida* (Ehrenberg) Kützing 1844
a			*Eunotia arculus* Lange-Bertalot & M. Nörpel in Krammer & Lange-Bertalot 1991
		c	*Eunotia arcus* Ehrenberg 1838
a		c	*Eunotia bilunaris* Ehrenberg
a			*Eunotia delicatula* (Tscheremissinova) Ceremissinova 1955
a			*Eunotia denticulata* (Brébisson in Kutzing) Rabenhorst 1864
a			*Eunotia diodon* Ehrenberg 1837
a			*Eunotia exigua* (Brébisson in Kutzing) Rabenhorst 1864
a			*Eunotia faba* (Ehrenberg) Kützing 1844
a			*Eunotia fallax* A. Cleve 1895
a			*Eunotia implicata* Norpel, Alles et Lange-Bertalot in Alles, Norpel & Lange-Bertalot 1991
a		c	*Eunotia incisa* Gregory 1854
a			*Eunotia intermedia* (Krasske ex Hustedt) Nörpel & Lange-Bertalot in Lange-Bertalot 1993

a			*Eunotia minor* Fusey 1964
a			*Eunotia monodon* Ehrenberg 1843
a			*Eunotia muscicola* Krasske 1939
a			*Eunotia nymanniana* (Grunow emend) Berg 1939
a		c	*Eunotia paludosa* Grunow 1862
a		c	*Eunotia praerupta* Ehrenberg 1843
a			*Eunotia rhomboidea* Hustedt 1950
a			*Eunotia rhynchocephala var. satelles* M. Nörpel & Lange-Bertalot in Lange-Bertalot in Krammer & Lange-Bertalot 1991
a			*Eunotia robusta var. serra* (Ehrenberg; Ehrenberg) Meister 1912
a			*Eunotia soleirolii* (Kützing) Rabenhorst 1864
a			*Eunotia veneris* (Kützing) A. Berg 1939
	b		*Fallacia fracta* (Hustedt ex Simonsen) Mann in Round, Crawford & Mann 1990
a			*Fallacia indifferens* (Hustedt) Mann in Round, Crawford & Mann 1990
a			*Fragilaria biceps* (Kützing) Lange-Bertalot 1993
a		c	*Fragilaria capucina* Desmazieres 1825
a			*Fragilaria crotonensis* Kitton 1869
a			*Fragilaria cyclopum* (Brutschy) Lange-Bertalot 1980
a			*Fragilaria delicatissima* (W. Smith) Lange-Bertalot 1980
a	b	c	*Fragilaria exigua* (W. Smith) Lemmermann 1908
a			*Fragilaria mazamaensis* (Sovereign) Lange-Bertalot 1980
a			*Fragilaria montana* (Krasske) Lange-Bertalot 1980
a			*Fragilaria nanana* Lange-Bertalot 1993
a	b		*Fragilaria nitzschoides* Grunow in Van Heurck 1881
		c	*Fragilaria tenera* (W. Smith) Lange-Bertalot 1980
a	b	c	*Fragilariforma virescens* (Ralfs) Williams & Round 1988
a	b	c	*Frustulia rhomboides var. crassinervia* (Brébisson in W. Smith) Ross 1947
	b	c	*Frustulia subtilissima* (Cleve) Steinecke 1916
a			*Gomphoneis heterominuta* S. Mayama & Kawashima in Mayama, S., Idei, M., Osada, K. & T. Nagumo 2002
a			*Gomphoneis rhombica* (Fricke) Merino, García, Hernández-Mariné & Fernández 1994
a		c	*Gomphonema acuminatum* Ehrenberg 1832
a		c	*Gomphonema angustatum* (Kützing) Rabenhorst 1864
a	b	c	*Gomphonema angustum* Kützing 1844
a			*Gomphonema constrictum f. ventricosa* (Gregory) Mayer 1928
a			*Gomphonema exiguum* Kützing 1844
a	b	c	*Gomphonema gracile* Ehrenberg 1854
a			*Gomphonema olivaceum* (Hornemann) Kützing 1844
a	b	c	*Gomphonema parvulum* (Kützing) Van Heurck 1880

a			*Gomphonema pumilum* (Grunow) Reichardt & Lange-Bertalot 1991
a	b		*Gomphonema subramosum var. clavatum* (Ehrenberg) Rabenhorst 1864
a			*Gomphonema tergestinum* (Grunow in Van Heurck) Fricke in Schmidt et al. 1902
a			*Gomphonema truncatum* Ehrenberg 1832
a	b	c	*Gomphosphenia grovei* (M. Schmidt) Lange-Bertalot 1995
a	b		*Gyrosigma acuminatum* (Kützing) Rabenhorst 1853
a		c	*Gyrosigma attenuatum* (Kützing) Cleve 1894
a			*Gyrosigma strigilis* (W. Smith) Cleve 1894
a			*Hannaea arcus* (Ehrenberg) Patrick 1961
a	b	c	*Hippodonta capitata* (Ehrenberg) Lange-Bertalot, Metzeltin & Witkowski 1996
a	b		*Hippodonta costulata* (Grunow) Lange-Bertalot, Metzeltin & Witkowski 1996
a			*Hippodonta hungarica* (Grunow) Lange-Bertalot, Metzeltin & Witkowski 1996
a			*Hippodonta lueneburgensis* (Grunow) Lange-Bertalot, Metzeltin & Witkowski 1996
a	b	c	*Karayevia clevei* (Grunow in Cleve & Grunow) Round et Bukhtiyarova 1996
a	b	c	*Karayevia laterostrata* (Hustedt) F.E. Round & L. Bukhtiyarova 1996
a			*Kolbesia ploenensis* (Hustedt) Round et Bukhtiyarova 1996
a	b	c	*Kolbesia suchlandtii* (Hustedt) Kingston
a			*Luticola mutica* (Kützing) Mann in Round, Crawford & Mann 1990
		c	*Luticola saxophila* (Bock ex Hustedt) Mann in Round, Crawford & Mann in Round, Crawford & Mann 1990
a			*Martyana martyi* (Héribaud) Round in Round, Crawford & Mann 1990
a			*Mayamaea fossalis* (Krasske) Lange-Bertalot 1997
a			*Melosira undulata* (Ehrenberg) Kützing 1844
a		c	*Meridion anceps* (Ehrenberg) D. M. Williams 1985
a	b	c	*Meridion circulare* (Greville) Agardh 1831
a	b	c	*Microcostatus kuelbsii* (Lange-Bertalot in Krammer & Lange-Bertalot) H. Lange-Bertalot 1999
a			*Navicula aboensis* (Cleve) Cleve-Euler 1953
a		c	*Navicula absoluta* Hustedt 1950
	b	c	*Navicula arvensis* Hustedt 1937
a			*Navicula bituminosa var. cincta* (Pantocsek) Cleve 1895
a			*Navicula cari* Ehrenberg 1836
a	b		*Navicula concentrica* J.W. Bailey 1844
a	b	c	*Navicula cryptocephala* Kützing 1844
a	b	c	*Navicula cryptotenella* Lange-Bertalot in Krammer & Lange-Bertalot 1985
	b		*Navicula delicatula* Cleve 1894
a			*Navicula detenta* Hustedt 1943
a			*Navicula difficillima* Hustedt 1950
a	b		*Navicula digitulus* Hustedt 1943

a			*Navicula elginensis* (Gregory) Ralfs in Pritchard 1861
a			*Navicula farta* Hustedt in Schmidt et al. 1934
a	b		*Navicula gallica* (W. Smith) Lagerstedt 1873
a	b		*Navicula gerloffii* Schimanski 1978
		c	*Navicula goeppertiana* (Bleich ex Rabenhorst) H.L. Smith 1876-1888
a			*Navicula ignota* Krasske 1932
a			*Navicula jaernefeltii* Hustedt in Schmidt et al. 1936
		c	*Navicula kriegeri* Krasske 1943
a			*Navicula lapidosa* Krasske 1929
a			*Navicula libonensis* Schoeman 1970
	b	c	*Navicula mediocris* Krasske 1932
	b		*Navicula menisculus var. menisculus* (Schumann) Cleve-Euler in Backman & Cleve-Euler 1922
	b		*Navicula micropunctata* (Germain) Kobayasi & Nagumo 1988
a	b	c	*Navicula modica* Hustedt 1945
a			*Navicula oppugnata* Hustedt 1945
a			*Navicula porifera* Hustedt 1944
a		c	*Navicula porifera v. opportuna* (Hustedt) Lange-Bertalot in Krammer & Lange-Bertalot 1985
	b		*Navicula praeterita* Hustedt 1945
a			*Navicula pseudoventralis* Hustedt in Schmidt et al. 1936
a			*Navicula radiosa* Kützing 1844
a			*Navicula reinhardtii* (Grunow) Grunow 1880
	b	c	*Navicula rhyncocephala* Kützing 1844
a		c	*Navicula schadei* Krasske 1929
a			*Navicula schoenfeldii* Hustedt 1930
a		c	*Navicula seminuloides* Hustedt 1937
		c	*Navicula soehrensis* Krasske 1923
a	b	c	*Navicula submuralis* Hustedt 1945
a			*Navicula subplacentula* Hustedt in Schmidt et al. 1930
a			*Navicula subrotundata* Schumann 1867
a	b	c	*Navicula utermoehlii* Hustedt 1943
a	b		*Navicula ventralis* Krasske 1923
a			*Navicula viridula* (Kützing) Kützing 1844
a			*Navicula viridula f. linearis* (Hustedt) H. Kobayasi in Mayama, S., Idei, M., Osada, K. & T. Nagumo 2002
a	b		*Navicula vitiosa* Schimanski 1978
	b		*Naviculadicta circumborealis* Lange-Bertalot in Lange-Bertalot & Moser 1994
a	b	c	*Naviculadicta schmassmannii* (Hustedt) M. Werum & H. Lange-Bertalot 2004
a		c	*Neidium ampliatum* (Ehrenberg) Krammer in Krammer & Lange-Bertalot 1985

a			*Neidium bisulcatum* (Lagerstedt) Cleve 1894
a			*Neidium hercynicum* Mayer 1915
a			*Neidium temperei* Reimer 1959
	b		*Nitzschia aequorea* Hustedt 1939
	b		*Nitzschia alpina* Hustedt 1943
a			*Nitzschia bacillum* Hustedt 1921
	b		*Nitzschia commutata* Grunow in Cleve & Grunow 1880
a			*Nitzschia commutatoides* Lange-Bertalot in Lange-Bertalot & Krammer 1987
a			*Nitzschia dissipata* (Kützing) Rabenhorst 1860
a			*Nitzschia dissipata v. media* (Hantzsch) Grunow in Van Heurck 1881
a	b	c	*Nitzschia fonticola* (Grunow) Grunow in Van Heurck 1881
a	b	c	*Nitzschia frustulum* (Kützing) Grunow in Cleve & Grunow 1880
a			*Nitzschia frustulum var. inconspicua* (Grunow) Grunow 1882
	b	c	*Nitzschia gracilis* Hantzsch 1860
		c	*Nitzschia intermedia* Hantzsch ex Cleve & Grunow 1880
a	b		*Nitzschia palea* (Kützing) W. Smith 1856
a	b	c	*Nitzschia perminuta* (Grunow in Van Heurck) M. Peragallo 1903
a			*Nitzschia pura* Hustedt 1954
a			*Nitzschia pusilla* (Kützing) Grunow emend Lange-Bertalot 1976
	b	c	*Nitzschia rosenstockii* Lange-Bertalot 1980
a			*Nitzschia subacicularis* Hustedt in Schmidt et al. 1922
a			*Nitzschia sublinearis* Hustedt in Schmidt et al. 1921
a	b	c	*Nupela impexiformis* (Lange-Bertalot in Lange-Bertalot & Krammer) H. Lange-Bertalot 1999
a	b	c	*Pinnularia biceps* Gregory 1856
a	b		*Pinnularia mesolepta* (Ehrenberg) W. Smith 1853
a		c	*Pinnularia microstauron* (Ehrenberg) Cleve 1891
a			*Pinnularia subcapitata* Gregory 1856
a			*Pinnularia subrostrata* Lohman et Andrews 1968
a	b		*Pinnularia viridis* Ehrenberg 1845
a	b	c	*Placoneis clementis* (Grunow) Cox 1987
a			*Placoneis explanata* (Hustedt) H. Lange-Bertalot in U. Rumrich, H. Lange-Bertalot, & M. Rumrich 2000
a			*Placoneis placentula* (Ehrenberg) Mereschkowsky 1903
a			*Placoneis protracta* (Grunow in Cleve & Grunow) Mereschkowsky 1903
a			*Placoneis symmetrica* (Hustedt) H. Lange-Bertalot in D. Metzeltin, H. Lange-Bertalot & F. García-Rodríguez 2005
a			*Planothidium calcar* (Cleve) M.B. Edlund in M.B. Edlund, N. Soninkhishig, R.M. Williams, & E.F. Stoermer 2001
a	b	c	*Planothidium conspicuum* (Mayer) E.A. Morales 2006
a			*Planothidium delicatulum* (Kützing) Round et Bukhtiyarova 1996

a			*Planothidium dispar* (Cleve) A. Witkowski, H. Lange-Bertalot & D. Metzeltin 2000
a			*Planothidium distinctum* (Messikommer) H. Lange-Bertalot 1999
a	b		*Planothidium granum* (Hohn & Hellerman) H. Lange-Bertalot 1999
a		c	*Planothidium joursacense* (Héribaud) H. Lange-Bertalot 1999
a	b	c	*Planothidium lanceolatum* (Brébisson ex Kützing) H. Lange-Bertalot 1999
a		c	*Planothidium oestrupii* (Cleve-Euler) Round et Bukhtiyarova 1996
a	b	c	*Planothidium peragalli* (Brun & Héribaud) Round et Bukhtiyarova 1996
a			*Planothidium polaris* (Østrup) A. Witkowski, H. Lange-Bertalot & D. Metzeltin 2000
a			*Pleurosigma angulatum* W. Smith 1852
a	b	c	*Pleurostauron smithii* (Grunow) Grunow in Cleve & Moller 1879
a			*Psammothidium bioretii* (Germain) Bukhtiyarova et Round 1996
a			*Psammothidium chlidanos* (Hohn et Hellermann) Lange-Bertalot 1999
a			*Psammothidium daonense* (Lange-Bertalot in Lange-Bertalot & Krammer) H. Lange-Bertalot 1999
a		c	*Psammothidium didymum* (Hustedt) Bukhtiyarova et Round 1996
a			*Psammothidium kryophilum* (Petersen) E. Reichardt 2004
a			*Psammothidium lacus-vulcani* (Lange-Bertalot et Krammer) Bukhtiyarova in Bukhtiyarova & Round 1996
a	b	c	*Psammothidium levanderi* (Hustedt) Bukhtiyarova et Round 1996
a	b	c	*Psammothidium marginulatum* (Grunow) Bukhtiyarova et Round 1996
a			*Psammothidium montanum* (Krasske) Mayama in Mayama, S., Idei, M., Osada, K. & T. Nagumo 2002
a			*Psammothidium rechtensis* (Leclercq) H. Lange-Bertalot 1999
a			*Psammothidium rosenstockii* (Lange-Bertalot in Lange-Bertalot & Krammer) H. Lange-Bertalot 1999
		c	*Psammothidium rossii* (Hustedt) Bukhtiyarova et Round 1996
a			*Psammothidium sacculum* (Carter) Bukhtiyarova in Bukhtiyarova & Round 1996
a	b	c	*Psammothidium subatomoides* (Hustedt) Bukhtiyarova et Round 1996
a			*Psammothidium scoticum* (Flower et Jones) Bukhtiyarova et Round 1996
a			*Psammothidium ventralis* (Krasske) Bukhtiyarova et Round 1996
a	b	c	*Pseudostaurosira brevistriata* (Grunow in Van Heurck) Williams & Round 1987
a	b	c	*Pseudostaurosira pseudoconstruens* (Marciniak) Williams & Round 1987
a			*Pseudostaurosira robusta* (Fusey) Williams & Round 1987
a		c	*Puncticulata radiosa* (Lemmermann) Håkansson 2002
a	b	c	*Reimeria sinuata* (Gregory) Kociolek & Stoermer emend Sala, Guerrero & Ferrario 1993
a		c	*Rhopalodia gibba* (Ehrenberg) Otto Müller 1895
a			*Schizonema gibbum* (Ehrenberg) Kuntze 1898
a	b	c	*Sellaphora pupula* (Kützing) Mereschkowsky 1902
a			*Sellaphora mutata* (Krasske) J.R. Johansen in J.R. Johansen et al. 2004
a	b	c	*Sellaphora seminulum* (Grunow) Mann 1989

a			*Sellaphora stroemii* (Hustedt) H. Kobayasi in Mayama, S., Idei, M., Osada, K. & T. Nagumo 2002
a	b	c	*Sellaphora vitabunda* (Hustedt) Mann 1989
a		c	*Stauroneis anceps* Ehrenberg 1843
	b		*Stauroneis kriegerii* Patrick 1945
a		c	*Stauroneis phoenicenteron* Ehrenberg 1843
a	b		*Stauroneis producta* Grunow in Van Heurck 1880
a			*Stauroptera divergens* (Smith) Kirchner 1878
a			*Staurosira bidens* (Heiberg) Grunow 1882
a	b	c	*Staurosira construens* Ehrenberg 1843
a	b	c	*Staurosira parasitica* (W. Smith) Pelletan 1889
a	b		*Staurosirella lapponica* (Grunow in Van Heurck) Williams & Round 1987
a	b	c	*Staurosirella leptostauron* (Ehrenberg) Williams & Round 1987
a	b	c	*Staurosirella pinnata* (Ehrenberg) Williams & Round 1987
a			*Stephanodiscus hantzschii* Grunow in Cleve & Grunow 1880
a			*Stephanodiscus medius* Håkansson 1986
a			*Stephanodiscus minutulus* (Kützing) Cleve & Möller 1882
a			*Stephanodiscus niagare* Ehrenberg 1845
a			*Stephanodiscus parvus* Stoermer & Hakansson 1984
a			*Surirella angusta* Kützing 1844
a	b		*Surirella bifrons* Ehrenberg 1843
a			*Surirella elegans* Ehrenberg 1843
	b		*Surirella lapponica* A. Cleve 1895
a			*Surirella linearis* W. Smith 1853
a			*Surirella robusta* Ehrenberg 1840
	b		*Surirella subsalsa* W. Smith 1853
	b		*Surirella turgida* W. Smith 1853
a			*Tabellaria fenestrata* (Lyngbye) Kützing 1844
a		c	*Tabellaria flocculosa* (Roth) Kützing 1844
a		c	*Tabellaria flocculosa var. ventricosa* (Kützing) Grunow 1862
a	b		*Tabularia fasciculata* (Agardh) Williams & Round 1986
a		c	*Ulnaria ulna* (C.L. Nitzsch) Compère 2001

APPENDIX B: R CODE USED IN DATA EXTRACTION AND MULTIVARIATE STATISTICAL ANALYSIS IN CHAPTER 5

Nitrate deposition over N. America

 # data are extracted from Galloway et al. (2004) Biogeochemistry 70: 153-226. Downloadable as: Dentener, F. J. 2006. Global Maps of Atmospheric Nitrogen Deposition, 1860, 1993, and 2050. Data set. Available on-line [http://daac.ornl.gov/] from Oak Ridge National Laboratory Distributed Active Archive Center, Oak Ridge, Tennessee, USA

#plot of N-deposition map

```
NOx.1860<-read.table(“Metadata/N deposition/N-deposition1860.txt”, header=F, sep=”\t”)
NOx.1860<-scan(“Metadata/N deposition/N-deposition1860.txt”,skip=1)
NOx.1860<-matrix(data=NOx.1860, nrow=48, ncol=72, byrow=T)
image(t(NOx.1860))
seq(-90,90,3.75)
seq(-180,180,5)
```

#txt file ‘metadata’ is a list of lake names used in Chapter 5

```
NO3.1860<-sapply(rownames(metadata), function(N){
        lat<-which.min(abs(seq(-88.875,88.875,3.75)-metadata[N,”Lat”]))
        long<-which.min(abs(seq(-177.5,177.5,5)-metadata[N,”Long”]))
        NOx.1860[lat,long]
        })

NO3.1993<-sapply(rownames(metadata), function(N){
        lat<-which.min(abs(seq(-88.875,88.875,3.75)-metadata[N,”Lat”]))
        long<-which.min(abs(seq(-177.5,177.5,5)-metadata[N,”Long”]))
        NOx.1993[lat,long]
        })

NO3.2050<-sapply(rownames(metadata), function(N){
        lat<-which.min(abs(seq(-88.875,88.875,3.75)-metadata[N,”Lat”]))
        long<-which.min(abs(seq(-177.5,177.5,5)-metadata[N,”Long”]))
        NOx.2050[lat,long]
        })

delta.NO3<-NO3.1993-NO3.1860

NO3<-data.frame(delta.NO3, NO3.1860, NO3.1993)
write.table(NO3, file=”NO3.txt”)
```

PCA (Figure 6)

#’meta.pca’ is a dataframe containing lake variables; and ‘metadata’ is a dataframe listing lakes

```
rownames(meta.pca)=metadata$Filename
NA.pca<-rda(meta.pca, scale=TRUE)
summary(NA.pca, scaling = 2)
screeplot(NA.pca, bstick=T, type=”lines”,xlab=”PCA axis”, ylab=”Variance”)
```

```
plot(NA.pca, type=”n”, choices=c(1,2))
points(NA.pca, display=”sites”)
text(NA.pca, display=”sites”, labels=rownames(meta.pca))
text(NA.pca, display=”species”, cex=1.2, col=”red”)
env<-scores(NA.pca)$species
arrows(0,0, env[,1]*0.85,env[,2]*0.85,col=”red”, length=0,05)
ordisurf(NA.pca, betaD, add=TRUE,)

#expresses the axis variance (eigen) as a percentage of total variance
NA.pca$CA$eig/NA.pca$tot.chi

#barplot in Figure 6
lakes<-scores(NA.pca)$sites
lakes<-rev(sort(lakes[,1]))
barplot(lakes, horiz=TRUE, xlim=c(-1,1.5), width=0.05, space=0.6)
```