Historic Reconstruction of Watershed Land-use Impacts on Water Quality in Freshwater Systems

by

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B. Sc. (Hons.) University of Chittagong, 1996
M. Sc. University of Chittagong, 1998
M. Sc. University of Alberta, 2004

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Abstract

Watershed land use has a pervasive influence on a variety of properties within aquatic ecosystems including productivity and community composition. Long-term data, which are rare or absent for many lakes are crucial for taking or making management decisions. Paleolimnological approaches can provide long-term data. In this study, emphasis was placed on exploring how the traditional proxies can be applied in alternative ways as well as to evaluate novel tools to reconstruct water quality with contrasting watershed land uses. I examined Sooke Lake Reservoir (SOL) and Shawnigan Lake (SHL), located on Vancouver Island, British Columbia, Canada. SOL is an impounded lake that is used as a drinking water reservoir, and has a watershed with restricted public access and development. SHL has a similar limnological regime, but the surrounding watershed has been developed extensively for residential uses. In recent years elevated primary production was observed in SHL as compared to SOL. Results also suggest increased variability for most phytoplankton groups in SHL during post-disturbance periods compared to SOL. I

also investigated how the history of local disturbance in a watershed can influence the regional coherence of ecosystem properties in lakes, by measuring sedimentary $\delta^{13}C$, $\delta^{15}N$, C:N and $\%BSiO_2$ (SOL and SHL). Data suggest that local disturbances can influence the $\%BSiO_2$ (proxy for lake productivity) and C:N ratio of lake sediments, but is less likely to alter the regional coherence of %C, %N and $\delta^{13}C$ between lakes. Fossil pigment records along with other geochemical indicators ($\delta^{13}C$, $\delta^{15}N$, C:N and $\%BSiO_{2)}$ in lake sediments can provide information on changes in aquatic productivity, temporal coherence and variability due to either natural or anthropogenic disturbances and thus can be used to guide and manage lake water quality.

The relationship between phytoplankton community composition (as inferred from diatoms and fossil pigments) and trophic status was different with contrasting watershed land uses. My results suggest that the hump-shaped (or unimodal) relationship between diatom species richness and production may be limited to high productive systems with maximum richness and diversity in intermediate states. In addition, fossil pigment records as proxies for algal functional groups reveal that in a mid to high productive system with intense watershed scale disturbances, community composition of algal functional groups declined favoring certain diatoms. These findings have broader implications for aquatic ecosystem management.

Given that continuing pressure on land and subsequent land-use changes is a threat to freshwater resources, it is critical to trace watershed disturbances and subsequent

alterations in accumulation of organic matter and impacts on aquatic ecosystems. An alternative approach to reconstruct organic matter accumulation using stable isotopes from lake sediments was explored. Stable isotope signatures from defined organic matter sources from the catchment and surface water of Shawnigan Lake (SHL) and Elk Lake (ELL), were compared with sedimentary proxy records. Results from this study reveal that terrestrial inputs and catchment soil coinciding with the watershed disturbance history probably contributed to the recent trophic enrichment in SHL. In contrast, cultural eutrophication in ELL was partially the result of input from catchment soil (agricultural activities) with significant input from lake primary production as well. The organic matter source detection technique that I have developed in this study can be applied to limit the effects of land use change in the vicinity.

Bacterial production in the water column is positively correlated with algal primary production and therefore, may be responsive to watershed land-use changes. Bacteria release extracellular enzymes to hydrolyze high molecular weight organic compounds and are sensitive to the amount and type of organic matter in the aquatic environment. Aminopeptidase activity (a protease enzyme) in sediment core was strongly related to the watershed land-use history and subsequent changes in organic matter in the aquatic environment. The enzymatic activity changed with the degree of watershed disturbances, and therefore, suggests that enzymatic activity in lake sediments could be a proxy to infer historical productivity.

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List of abbreviations

CD = Chlorophyll derivatives

TC = Total carotenoids

%C = Percent carbon

%N = Percent nitrogen

C:N = Carbon to nitrogen molar ratio

$\delta^{13}C$ = Carbon isotope

$\delta^{15}N$ = Nitrogen isotope

$\%BiSO_2$ = Percent biogenic silica

Z_{max} = Maximum depth

DOC = Dissolved organic carbon

OM = Organic matter

POM = Particulate organic matter

TN = Total nitrogen

TP = Total phosphorus

Leu-MCA = L-Leucine-4-methylcoumarinyl-7-amide

c.f.u. = Colony forming unit

TSA = Trypticase soy agar

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Chapter 1: General Introduction

Introduction

Watershed land use is known to influence the geochemical properties of lakes, rivers and streams (Flintrop et al. 1996; Gergel et al. 2002) resulting in nutrient enrichment, or eutrophication, and is associated with deterioration of water quality (Hall and Smol 1995), along with alteration of aquatic community composition (Schindler 2000). There have been numerous attempts to determine the relationship between land use and water chemistry at the watershed level. However, long-term monitoring data, which are rare or absent for most lakes, are essential in assessing the rate and magnitude of nutrient enrichment, to provide a context for proper water quality management.

Paleolimnological approaches can provide long-term data sets, and have been used to examine a variety of environmental issues relating to freshwater quality (Smol, 2002). Many paleolimnological indicators such as, siliceous microfossils (diatoms and chrysophytes), invertebrates, pigments, and geochemistry (Leavitt 1989; Quinlan et al. 2002; Itoh et al. 2003; Das et al. 2005), have been used to infer nutrient enrichment in the sediment record. Fossil remains in lake sediments have been used in reconstructing paleoproductivity along with changes in historic algal communities (Leavitt and Hodgson 2001; Das et al. 2005) and temporal coherence and variability (Cottingham et al. 2000; Patoine and Leavitt 2006).

Increased nutrient loading from water- and land-use has detrimental impacts on aquatic biodiversity and ecological integrity. Among the aquatic inhabitants, phytoplankton (primary producer) and bacteria (secondary consumer) are the key communities affecting aquatic ecosystem processes and hence, the water quality. In this study I demonstrated how these communities can be affected by increased nutrient inputs as a function of different water- and land-use activities. This project focused on several watersheds on Vancouver Island. These watersheds are influenced by forest fires, reservoir formation, agriculture, and urbanization (CRD 1994). There is a close relationship between land-use type and the quality and quantity of water (Gburek and Folmer 1999). Runoff from different land uses may be enriched with different contaminants. For example, runoff from agricultural watersheds may be enriched with nutrients and sediments. In addition, other processes including evapotranspiration, infiltration, absorption, and types of vegetative surfaces can also modify watershed surface characteristics along with the hydrologic cycle and water temperature (LeBlank et al. 1997). Taken all together, among the on-going anthropogenic pressures placed on ecosystems, increased nutrient input from these land-use activities are a major concern for freshwater quality.

Water quality in lakes is a function of internal and external processes. Water residence time and watershed disturbance are the major factors controlling these processes in aquatic systems. The present study builds upon the assumptions that regulated water level and land-use changes may alter primary production and can affect bacterial communities in lakes and reservoirs. Creating new reservoirs or

raising water level in reservoirs can enhance nutrient loading following impoundment. In turn, this will change aquatic productivity and community composition (Ostrofsky and Duthie 1978; Hall et al., 1999). The trophic upsurge period may vary depending on reservoir-specific morphological features, terrestrial inputs and other factors related to aquatic communities including depth of water column and water residence time (Ostrofsky and Duthie 1978; Thornton et al. 1990). Following this trophic upsurge, a trophic depression is often evident due to a decreased supply of nutrients with a deeper water column (Schallenberg, 1993) and be traced by using fossil pigment records in lake sediments (Leavitt and Hodgson 2001).

Watershed disturbance could also influence the stable isotope signatures in aquatic systems. Ecological studies, specifically those using carbon ($\delta^{13}C$) and nitrogen ($\delta^{15}N$), have allowed for the interpretation of stable isotope stratigraphies from lake sediments with respect to variations in internal and external nutrient cycles (Hodell and Schelske 1998). The fractionation of carbon and nitrogen isotopes during and following primary production is a result of algal physiology, source concentrations and post-depositional diagenesis (Goericke et al. 1994). Water level changes in reservoirs and human settlement in watershed can directly and indirectly alter nutrient inputs into a lake from plant decomposition, soil erosion and nutrients from diffusive sources (Larmola et al. 2004; Bunting et al. 2007). Autochthonous dissolved organic carbon from littoral wetlands has been suggested to be the largest continuous nutrient load to reservoir ecosystems (Glazebrook and Robertson 1999). In addition, land-use

changes within a watershed can also impact – mostly in negative pattern – the quality of runoff and, in turn, anthropogenic nutrient loadings can deteriorate water quality (Bradbury and Van Metre 1997; Douglas et al. 2002; Rosenmeier et al. 2004). The alteration of nutrient loading from different sources (autochthonous or allochthonous) can be traced using stable isotope signatures. Temporal coherence and variability could also be affected by watershed land-use in addition to influence on productivity and nutrient supply in aquatic ecosystems (Underwood 199; Carpenter et al. 1998; Heathwaite et al. 2000; Berka et al. 2001). Increased variability of environmental indicators (e.g., $\delta^{13}C$ and $\delta^{15}N$), which is an undesirable feature of managed ecosystems, is associated with high nutrient loads and productivity (Carpenter et al. 1998), rapid changes in species richness and community structure (Lehman and Tilman 2000), and reduced predictability (Cottingham et al. 2000). In addition, temporal coherence and variability could also differ in disturbance type (Bender et al. 1984). However, little is known about how divergent watershed management practices affect ecosystem-level temporal variability and temporal coherence of productivity among lakes.

Watershed disturbance and subsequent habitat destruction is a major threat to biodiversity in aquatic systems. Biodiversity could also be affected by varying trophic status. In an experimental study Proulx and Mazumder (1998) demonstrated that the disturbance level that maximizes species richness is influenced by the level of productivity. Vinbrooke et al. (2004) developed a conceptual model describing the effects of multiple stressors on aquatic diversity. Previous studies concentrated on

contemporary ecological regimes to relate the effect of multiple stressors on aquatic diversity. In this research, I tested the applicability of disturbance-productivity-diversity hypotheses in paleolimnological analysis based on the fossil pigment records responding to different anthropogenic events. Results from recent paleolimnological studies, suggest that contrasting land-use activities may alter nutrient accumulation resulting in increased primary production. Fossil algal remains, specifically diatoms and pigments can be used in reconstructing paleoproductivity and changes in historic algal communities in lentic systems (Leavitt and Hodgson 2001). The current study was based on the above-mentioned diversity-production-disturbance theories, to see whether similar responses can be detected from fossil remains in lake sediments in a historical perspective responding to different anthropogenic events.

In the previous sections, a brief description was given on tracing organic matter sources and reconstructing paleoproductivity using a number of proxies, including stable isotopes (e.g., $\delta^{13}C$ and $\delta^{15}N$). In addition, how these environmental indicators can be altered by watershed disturbance was also illustrated. However, one of the limitations of using C:N ratio, $\delta^{13}C$ and $\delta^{15}N$ in a traditional way in organic matter source detection studies is these proxies cannot clearly discriminate specific sources. The goal of this study was also to understand sedimentary organic matter dynamics as a function of land-use changes. The assumptions behind this are: (1) differentiate end member sources clearly, and (2) minimal post-depositional changes of the end member signatures. There is also the potential complexity of variable sources and

diagenetic alteration of source signals, including ammonification, nitrification and denitrification (Matson and Brinson 1990; Thornton and McManus 1994; Cifuentes et al. 1996; Andrews et al. 1998; Yamamuro 2000; Graham et al 2001). I hypothesized that if sediment organic matter (OM) composition can be explained by mixing known and well defined OM end member sources and OM diagenesis will not significantly change the isotopic composition. However, determination of OM source in the sediment will only reflect the component of the OM that is preserved and not the original flux to the sediment. Thus, it is only possible to determine the source of the residual refractory OM in the sediment.

Watershed land-use can also alter the accumulation of organic matter in aquatic systems. Organic matter that is being transported to aquatic systems is composed of relatively high molecular weight compounds. Prior to use by bacteria, these high molecular weight compounds need to be hydrolyzed by extracellular enzymes. Bacterial biomass is dynamic and quite sensitive to elevated nutrient loading, which in turn can change the extracellular enzymatic activities (Morgan and Pickup 1993; Burns and Ryder 2001; Prenger and Reddy 2004). In addition, Bacterial communities in lake sediments are important both for the decomposition of organic material and remobilization and cycling of nutrients. Previous studies documenting enzyme assays in surface water (Danovaro et al. 2000; Karrasch et al. 2003; Obayashi and Suzuki 2005) and surface sediments in marine environments (Fabiano and Danovaro 1998; Coolen and Overmann 2000) and none of them looked at the activities in sediment samples with the objective to relate with the anthropogenic input of organic matter.

Research Objectives

The principal objectives of this research were three fold. The first was to examine the responses and temporal coherence and variability of different paleoindicators (i.e., pigments, stable isotopes, etc.) to contrasting watershed land-use histories. The second was to examine the efficacy of an alternative approach to reconstruct historical organic matter sources. Third was to apply the microbial ecological technique (bacterial exo-enzyme) to reconstruct paleoproductivity. Overall, the goal was to evaluate novel tools to see what the accuracy and power of these techniques are in assessing land-use changes on lake geochemistry and, therefore, to assess watershed management options using paeloindicators for water quality protection.

Outline of this Dissertation

This dissertation comprises seven chapters. Background information and specific objectives are summarized briefly in Chapter 1. Chapters 2, 3, 4, 5 and 6 contain the primary data and are presented as separate, but related, manuscripts submitted or published in the peer-reviewed literature. General conclusions and suggestions for future research are proposed in Chapter 7.

Chapter 2 examines the effects of two types of watershed disturbances (water level changes and human settlements) on a whole-lake scale and potentially identifies some

causes of these changes. Anthropogenic perturbations may alter lake productivity and variability and, therefore, can be traced from fossil pigment records in lake sediments (Cottingham et al. 2000). Establishing a dam on a lake, accompanied by watershed flooding due to increasing water levels, leads to a transformation in aquatic productivity and a new equilibrium. Several factors, including flushing rate changes, seasonal succession of algal communities, decomposition of plant litter and the release of nutrients from submerged soil, changes in water column depth, and turbidity are responsible for this change in productivity (Ostrofsky and Duthie 1978; Grobbelaar 1989). In addition, increased export of nutrients from forest harvesting and road building, in addition to minor organic matter input from wildfire incidents and inputs from diffuse sources may affect lake primary production (Carignan et al. 2000; Patoine et al. 2000; Charette and Prepas 2003). Two study lakes with contrasting watershed disturbance histories, water-level changes in Sooke Reservoir, and land-use changes on the shoreline of Shawnigan Lake, both located within close proximity on Vancouver Island, British Columbia, Canada were selected. This study, which has been submitted in the *Journal of Lake and Reservoir Management*, suggests that fossil pigments in lake sediments, can be applied to compare lake productivity in lakes with contrasting histories of watershed land use.

Chapter 3, I hypothesized that watershed disturbances not only affect overall ecosystem-level productivity and nutrient supply (Carpenter et al. 1998; Heathwaite et al. 2000; Berka et al. 2001), but also the temporal variability of these processes (Underwood 1991). Increased temporal or spatial variation may be viewed as an

undesirable feature of managed ecosystems. High variability of environmental indicators (e.g., phytoplankton) are associated with high nutrient loads and productivity (Carpenter et al. 1998), rapid changes in species richness and community structure (Lehman and Tilman, 2000), and reduced predictability (Cottingham et al. 2000). The analysis of variability in ecosystem properties over space and time can help ecologists understand the factors that influence ecosystem dynamics and stability. Comparisons of variability across spatially separated systems allow the identification of ecosystem regulators acting over distinct spatial scales (Patoine and Leavitt 2006). Alternatively, comparisons of variability over time allow the identification of regulators that cause shifts in ecosystem dynamics within a given location (Cottingham et al. 2000). Results from this study, which has been published in the *Journal of Paleolimnology* (DOI 10.1007/s10933-008-9269-4), reveal that variability in the paleoindicators was uniquely affected by local disturbances.

Chapter 4, I explored how ecosystem-level disturbances could affect species and community structure with contrasting watershed land-use and trophic status. Species composition can be influenced by both natural factors (Shurin 2001; Bruno et al 2003) and human activities (Proulx et al. 1996; Dodson and Lillie 2001). Accordingly, lake production and species richness is often used as a measure of aquatic environmental health. In the literature, two different approaches have been used to determine the relationship between productivity and species richness. One approach has examined how contrasting ecosystem processes affect species numbers and community composition (Tillman and Pacala 1993; Huston 1994). The other

approach focused on the affect of community composition on ecosystem functioning (Tillman et al. 1992; Lawton 1994; Naeem et al. 1996; Huston 1997). Diatom and pigment records in lake sediments can be used to track changes in species richness and functional group structures, respectively, by responding to contrasting watershed scale land use changes (Quinlan et al. 2002; Itoh et al. 2003; Saros et al. 2003). Results from this study have been published in *Aquatic Ecosystem Health and Management 11: 78-90* and suggest that both watershed land use and trophic status affect the phytoplankton community composition.

Chapter 5, I demonstrated an alternative approach to reconstructing organic matter accumulation using stable isotopes from lake sediments. Organic matter (OM) preserved in lake sediments can provide key information on lacustrine nutrient dynamics as a function of historical watershed scale land-use change (Meyers 1994; Meyers et al. 2001). Changes in land-use within watersheds, commonly involving the conversion of forest cover to agricultural land or urban areas, results in increased input of nutrients (Peterjohn and Correll 1984; Rhodes et al. 2001), which may lead to changes in community structure in aquatic ecosystems (Harding et al. 1998; Gergel et al. 1999; Ometo et al. 2000). Despite the potential complexity of variable sources and diagenetic alteration of source signals, including ammonification, nitrification and denitrification (Matson and Brisnon 1990; Thornton and McManus 1994; Cifuentes et al. 1996; Yamamuro 2000; Graham et al. 2001), stable isotopes ($\delta^{13}C$ and $\delta^{15}N$) can provide information on paleoproductivity, trophic structure and food web dynamics associated with land use changes (Brenner et al. 1999; Alin et al. 2002; Lawson et al.

2004; Andrews et al. 1998). Recently, it has been demonstrated that the IsoSource mixing model could be an alternative source detection technique and it has been applied in contemporary (Philips and Gregg 2003; Hall-Aspland et al. 2005) and paleo-human dietary analyses (Philips et al. 2005) using stable isotopes ($\delta^{13}C$ and $\delta^{15}N$). I used the IsoSource mixing model technique to reconstruct changes in OM accumulation pertinent to contrasting disturbance histories from lake sediments. Results from this study have been published in *Environmental Pollution 155:117-124* and suggest that the OM source detection approach that I have developed in this paper could be a robust tool in defining dominant OM accumulating sources with contrasting watershed-scale disturbance histories when combined with the IsoSource source separation program.

Bacterial production in the water column is positively correlated with algal primary production (Bird and Kalff 1984; Porter et al. 2004) and the relationship could change with contrasting histories of watershed land use. In the last data chapter (chapter 6) I explore how bacterial enzymatic activity in lake sediment correlates with existing traditional indicator variables to infer lake productivity. Much of the useable organic matter in aquatic ecosystems is comprised of relatively high molecular weight compounds. Prior to use by bacteria, high molecular weight compounds need to be hydrolyzed by extracellular enzymes (Misic et al. 1998; Ogawa et al. 2001). Bacterial biomass in the water column is dynamic and quite sensitive to elevated nutrient loading, which in turn can alter extracellular enzymatic activities (Morgan and Pickup 1993; Burns and Ryder 2001; Prenger and Reddy 2004). Most studies documenting

enzyme assays have been conducted in surface water (Karrasch et al. 2003; Obayashi and Suzuki 2005) and surface sediments, mostly in marine environments (Fabiano and Danovaro 1998; Coolen and Overmann 2000). Results from this research, which has been published in the *Verhandlungen Internationale Vereinigung für theoretische und angewandte Limnologie 30: 117-121*, suggest that enzymatic activity in lake sediments could be used as a proxy to infer historical productivity.

Chapter 2: The influence of anthropogenic disturbance history on the paleoproductivity and nutrient status of two lakes

Abstract

Sedimentary pigment profiles were used as proxies for paleo-production and historical algal community composition in Sooke Reservoir (SOL) and Shawnigan Lake (SHL), located on Vancouver Island, British Columbia, Canada. SOL is an impounded lake that is used as a drinking water reservoir, and has a watershed with restricted public access and development. SHL has a similar limnological regime, but the surrounding watershed has been developed for human residential and recreational purposes. The reconstructed pigment stratigraphies indicated that lake productivity changed over time with contrasting watershed disturbance histories in the two study lakes. Elevated primary production in recent years was observed in SHL compared to SOL, where lake productivity was subtly changed. A median-log Levene's test suggests enhanced variability for most phytoplankton groups in SHL during post-disturbance periods compared to SOL. Additionally, temporal coherence analysis indicated that sedimentary pigment profiles in the two study watersheds were different from each other. This approach can be used to evaluate watershed management options for water-quality protection.

Introduction

Watershed disturbances (e.g., elevated water level, deforestation, human settlement) can alter external nutrient inputs and runoff (Cooke and Prepas 1998) resulting in nutrient enrichment, or eutrophication, and associated deterioration of water quality (Hall and Smol 1995), and alternation of aquatic community composition (Schindler 2000). Watershed inundation may also increase nutrient, carbon and sediment loading, which in turn affect aquatic productivity and community composition (Ostrofsky and Duthie 1978; Hall et al. 1999). The resulting trophic enrichment may last for several years depending on reservoir specific morphological features, terrestrial inputs and other factors related to aquatic communities including water residence time (Ostrofsky and Duthie 1978; Thornton et al. 1990). Following an increase in primary production, a decrease in production is often evident in the longer term due to a decreased supply of nutrients with a deeper water column (Pannard et al. 2006). Developments in the watersheds typically increase lake productivity by elevating nutrient export from the catchments to the lake (Bennett et al. 1999; Knoll et al. 2003).

Watershed disturbances not only affect overall ecosystem-level productivity and nutrient supply (Carpenter et al. 1998; Heathwaite et al. 2000; Berka et al. 2001), but also the temporal variability of these processes (Underwood 1991). Increased temporal or spatial variation may be viewed as an undesirable feature of managed ecosystems. High variability of environmental indicators (e.g., phytoplankton) is associated with high nutrient loads and productivity (Carpenter et al. 1998), rapid

changes in species richness and community structure (Lehman and Tilman 2000), and reduced predictability (Cottingham et al. 2000). Additionally, ecosystem variability could also differ with disturbance types (Bender et al. 1984).

Many paleolimnological indicators have been used to infer nutrient enrichment using the sediment record, including siliceous microfossils (diatoms and chrysophytes), invertebrates, pigments, and geochemistry (Leavitt 1989; Quinlan et al. 2002; Itoh et al. 2003; Das et al. 2005). Fossil algal remains, specifically pigments (i.e., chlorophylls and carotenoids) are preserved in lake sediments and can be used in reconstructing paleoproductivity along with changes in historic algal communities in lakes (Leavitt and Hodgson 2001; Das et al. 2005) and temporal coherence and variability (Cottingham et al. 2000; Patoine and Leavitt 2006). For the study lakes on Vancouver Island I report here that, forest fires, reservoir formation and watershed land-use change (urbanization) are the main threats to surface water quality (CRD 1994). These anthropogenic perturbations may alter the lake productivity and variability and, therefore, can be traced from fossil pigment records in lake sediments (Cottingham et al. 2000). Although fossil pigments in lake sediments are well preserved, the effect of diagenetic processes has to be considered. Changes in the ratio between primary (chlorophyll) and degraded chlorophyll (pheopigments) are commonly used to address diagenesis issues (Vinebrooke et al. 2002). Additionally, chlorophyll derivatives (CD) to total carotenoids (TC) ratio (CD/TC) in sediment can be used as a proxy for relative abundance of cyanobacterial communities (Waters et al. 2004).

This study concentrated on predicting the effects of two types of watershed disturbances (water level changes and human settlements) at a whole-lake scale and potentially identifying some causes of these changes. Additionally, I hypothesized that watershed disturbances not only affect overall ecosystem-level production and nutrient supply (Carpenter et al. 1998), but also the temporal variability of these processes (Underwood 1991). To address these queries two study lakes with contrasting watershed disturbance histories, water-level changes in Sooke Reservoir, and land use changes on the shoreline of Shawnigan Lake both located within close proximity on Vancouver Island, British Columbia, Canada) were selected. Afield study was conducted in two lakes (a) to reconstruct the temporal pigment profiles from lake sediments, (b) to trace changes in phytoplankton community structure reconstructed from fossil pigment records, and (c) to compare temporal coherence and variability affecting the pigments with contrasting watershed disturbance histories. Chronological event similarities of the two study watersheds have been compiled in Table 2.1.

Materials and methods

Study locations

Both Sooke Lake (48°33′N latitude and 123°42′W longitude) and Shawnigan Lake (48°37′N latitude and 123°27′W longitude) are located within 5 km of each other on southern Vancouver Island, British Columbia, Canada (Figure 2.1). These study lakes lie within the Insular and Coastal Mountain Limnological region of south-eastern

Vancouver Island, and are classified as warm monomictic lakes. Both lakes have two basins with subtle changes in surface water chemistry.

Sooke Lake is a typical oligotrophic coastal lake. The seasonal and vertical differences in oxygen content are not significant. Among 18 catchment streams, only eight contribute significant quantity of water and water residence time of the lake is 1.4 yr (Nowlin et al. 2004).. The Devonian and Carboniferous bedrock of the Sooke watershed is principally comprised of Metchosin volcanic materials including basalt flows, tuffs and agglomerates (CRD 1994; Barraclough 1995). The catchments are characterized by Western Hemlock stands interspersed with Coastal Douglas Fir and Western Red Cedar. The lake water is characterized by slightly dilute (specific-conductivity of ~ 45 $\mu S \cdot cm^{-1}$), and with low nutrient concentrations.

Shawnigan Lake is also classified as oligotrophic. It is fed through the major inflow of Shawnigan Creek and has a short residence time (~ 1 yr) (Nowlin et al. 2004). The bedrock for most of the watershed is of Devonian origin with part of the Wark and Coquitz Gneiss Complexes (Barraclough 1995; CRD 1994). Catchment vegetation types are similar to Sooke.

The first dam on Sooke Lake (hereafter, Sooke Reservoir) was constructed in 1910 to supply drinking water to the city of Victoria. Since initial dam construction, the water level in Sooke Reservoir has been raised twice, once in 1970 by 5 meters and once in 2002 by 6 meters. The Sooke Reservoir watershed is without human settlement. In

comparison, the first human settlement began on the shoreline of Shawnigan Lake around 1910 and since then the population has been increasing steadily. Inundation records for Sooke Reservoir and comparison of physicochemical variables and parameters of the two study lakes have been compiled in Table 2.2 and 2.3 respectively.

Sampling and sediment chronology

One sediment core (~30 cm) was taken from the deepest part (north basin) of each lake using a modified gravity corer (Kliza and Telmer 2001), and was extruded in incrementals on site. The extruded sample was flushed with N_2 and kept in a cooler with ice bags to minimize the pigment degradation. After transportation to the laboratory, samples were preserved in a freezer (-80°C) until further analysis. Both cores were dated using ^{210}Pb dating techniques by α spectroscopy (Appleby and Oldfield 1978) at Mycore Scientific, Ottawa, Canada. The constant rate of supply (CRS) model was applied to the ^{210}Pb data (Appleby 2001).

Pigment analysis

Pigments were analyzed following the methods of Leavitt and Hodgson (2001) and Leavitt (1989) using high pressure liquid chromatography (HPLC). Pigment extractions of were performed by soaking ~100 mg of freeze-dried sediment in 5ml of degassed mixture (bubbling He through the solvent mixture for 5-10 min) of acetone:methanol:water (80:15:5 by vol.) in 10-20 ml glass tube. Samples were then flushed with N_2 and stored in the dark at -20°C for 12 hours. Four ml of the extract

were transferred into clean 20mL glass tubes and dried under N_2. Dried extracts were dissolved into 500 μL injection solution (Solvent A: 10% ion-pairing reagent in methanol by volume) and 500 μL of sudan II ($3.2 mg \cdot L^{-1}$) as an internal reference. The ion-pairing reagent was a mixture of 0.75g tetrabutyl ammonium acetate and 7.7g ammonium acetate in 100ml of distilled de-ionized water. One ml of dissolved extract was transferred into a brown 2ml vial, flushed with N_2 and cupped using Dionex cups. Vials were kept in a freezer until HPLC analysis.

The HPLC system included a DIONEX gradient pump, an AS50 Autosampler, a C-18 column (5 μm particle size; 15 cm length), and a PDA detector at 435 nm. Flow rate was 1.5 ml/min and the separation gradient was (i) isocratic for 1.5 min -10% IPR in methanol (Solvent A), (ii) a linear ramp to 100% of a mixture of 27% acetone in methanol (Solvent B) over 7 min and an isocratic hold for 15.5 min, and (iii) a linear return to 100% Solvent A over 3 min with isocratic hold for 12.5 min for column equilibration.

Pigment concentrations were quantified using equations derived from commercially available standards (DHI Water and Environment, Denmark). All pigment concentrations were normalized to their mass per gram of organic matter ($mg \cdot g^{-1}$ OM) where organic matter content in the sediment samples were measured as loss on ignition (LOI) at 550°C for 2 hours (Heiri et al. 2001).

Statistical analysis

For illustration and statistical analysis, time series from both sediment cores were grouped into two periods: pre- and post-disturbance regimes where 'pre-disturbance' refers to all years before 1900 and 'post-disturbance' refers to all years after 1900 and normalized to similar resolution. To determine the level of temporal coherence I conducted Pearson's correlations (using a randomization procedure) between the z-scores of each variable (pigments) between the two study lakes. High coherence indicates regional control of aquatic productivity, whereas low coherence suggests site specific controls (Rusak et al. 1999). To compare variation of paleo-indicators in pre- and post-disturbance periods, I ran a Levene's test on $\log_{10}$-transformed, median-scaled data (Cottingham et al. 2000). Samples with similar resolution (e.g., 1 cm) were selected from pre- and post- 1900 periods for Levene's test to be consistent throughout the cores. Data were re-combined for this analysis. Equal sample size (n = 15) for pre- and post- 1900 periods were used for both coherence and variability analyses.

Results

Sediment chronology

The ^{210}Pb profile shows a decrease in activity from the top layer of the sediment towards the bottom layer (~8 cm) (Figure 2.2). Errors of precision of ^{210}Pb dated years were found to be moderate: 95% confidence intervals were for the first 10 (±0.33 yr), 20 (±0.63 yr), 100 (±5.3 yr), and 150 (±16.2 yr). Results from sediment chronology indicate that 30 cm cores were long enough to establish reliable pre-1900

baseline conditions for lakes impacted by human activities during the 20th century on Vancouver Island.

Pigment stratigraphy

Fossil pigment analysis in the lake sediment samples revealed the presence of the following potential algal assemblages: Dinophyceae (chlorophyll c_2), Bacillariophyceae (diadinoxanthin), Chrysophyceae (fucoxanthin), Cryptophyceae (alloxanthin), Chlorophyceae (chlorophyll *b*), Cyanophyceae (zeaxanthin, echinenone), filamentous Cyanophyceae (canthaxanthin), and pigments present in all algae (chlorophyll *a*, pheophytin *a*, β-carotene). Chlorophyll c_2 was detected only in Shawnigan samples. A list of pigments detected in both study lakes have been compiled in Table 2.4. In both study lake sediments chlorophyll *a* was found in higher concentration compared to rest of the detected pigments.

Results from Sooke Reservoir sedimentary pigment records suggest that there have been a few changes in concentrations over the past 100 years. Major changes were observed within the uppermost 12 cm of the sediment core (Figure 2.3). In most cases, pigment concentrations in the uppermost 5 cm decreased gradually with depth in Sooke sediment samples. However, Pre-1900s sediment pigment profiles were found to be relatively unchanged in both study lakes.

In comparison, the overall fossil pigment concentrations in the post-1900 periods changed noticeably compared to the natural background levels in Shawnigan Lake

sediments (Figure 2.4). A few directional shifts in pigment concentrations have also been observed in Shawnigan sediment profiles. For almost all detected pigments, an increase between 0 and 5 cm preceded by a decrease around 8 cm and further increase between 12 and 15 cm was detected. Although most of the pigment concentrations, representing different algal groups, changed over the past 100 years, the most noticeable increase can be detected for cyanophyceae and bacillariophyceae communities. The chlorophyll derivatives (CD) to total carotenoids (TC) ratio (CD/TC) was lower in Sooke Reservoir sediment samples compared to that of Shawnigan samples. Overall, the ratio was lower during pre-1900 periods in both study lakes. The chl *a*: phyt *a* ratio in Sooke shows some shifts along the core within the uppermost 12 cm, where below that core depth it was in a more or less constant state (Figure 2.5). The overall trend between chlorophyll *a* and pheophytin *a* was found to be linearly related. The biggest shift in the chl *a*: phyt *a* ratio in Shawnigan is at approximately 5 cm and may be related to the age of the pigments where bacterial degradation can affect the fossil pigments (Hurley and Armstrong 1990; Leavitt and Carpenter 1990a, 1990b).

Variability

Trends in most of the algal groups inferred from fossil pigment concentrations were noticeably changed when compared to mean values for the recovered intervals of deposition (Figure 2.4). In both study lakes, changes in phytoplankton diversity have been observed in post-disturbance periods (i.e., post-1900s). However, it is more evident in Shawnigan Lake samples. Among all the phytoplankton groups,

cyanophyceae and bacillariophyceae (> 1000%) changed the most in Shawnigan Lake sediment samples. In contrast, variability during post-disturbance periods was subtle in Sooke Reservoir sedimentary profiles compared to Shawnigan samples. To determine whether these responses are site specific and to analyze temporal coherence, Pearson's correlation analysis was performed between individual pigment concentrations for the two lakes. Only alloxanthin ($r = 0.38$, $p < 0.001$), and zeaxanthin ($r = 0.53$, $p < 0.001$) were found to be significantly correlated between Sooke and Shawnigan (Table 2.5). Analysis with the median-log Levene's test indicated that for all algal communities, variability increased markedly in post-disturbance periods (Figure 2.6). Algal groups showed greater variability in Levene's test in Shawnigan Lake sediments compared to sooke sediments.

Discussion

Historical lake productivity

Results from this study revealed that contrasting watershed disturbances have had divergent effects on paleoproductivity. In Sooke Reservoir, seasonal succession following changes in water residence time might have played a key role in controlling algal production and variability in community structure. Several studies have shown that algal communities during pre-disturbance periods with short residence time are generally dominated by diatoms and cyanobacterial communities dominate in post-distrurbance periods with variations in flushing rates (Stockner and Benson 1967; Peterson and Stevenson 1989; Wetzel 2001). Additionally, the changes in phytoplankton diversity can also be dependent on the availability of growth limiting

resources. In general, there is strong evidence that in nutrient enriched systems diversity often goes down- not up, as a few groups become strongly dominant. The rapid colonization and resource competition by pioneer oligotrophic taxa, primarily cryptophyceae, and the highly variable immigration of other weak competitors over time following inundation, likely masked a peak in average richness along the flooding frequency gradient (Tilman 1982; Interland and Kilham 2001). The strategy that best allows species to exist under oligotrophic conditions may be one that allows for tolerance of low nutrients (Smith 1983; Interland and Kilham 2001). In recent years, when the disturbance levels are assumed to be higher due to increased human settlement and increased use for recreational purposes that lead to elevated nutrient loadings (e.g., P and N loading), some groups of phytoplankton cannot keep pace with the exploitive competitors, resulting in declining species diversity (Huston 1994). Additionally, this system is also phosphorus limited so increased inputs of total phosphorus may stimulate higher algal production. The ratio between primary and degraded chlorophyll *a* (pheophytin *a*) showed similar trends when compared with total chlorophyll *a* profiles in both study lakes, which reflect a shift in the productivity regimes (i.e., higher primary production, higher degraded pigments) and are not related to diagenetic transformation.

Oligotrophic lakes like the study lakes are generally dominated with less diverse algal groups, specifically Cyanophyceae (Weisse 1993). This is partly because small unicellular algae in the size range of picoplankton can outcompete larger ones at the oligotrophic extreme of the trophic gradient. One of the advantages of small cell-size

in low nutrient environments is reduced limitation by molecular diffusion of nutrients (Chisholm et al. 1988), through increased surface to- volume ratios (Raven 1986). The simple prokaryotic cell structure of cyanobacteria, which are the dominant algal community in the study lakes, has a low cost of metabolic maintenance thus providing a greater competitive advantage (Weisse 1993). Enhanced catchment export of nutrients due to raising water level accompanied by forest harvesting and road building, in addition to minor organic matter input from wildfire incidents might have enhanced lake primary production (Carignan et al. 2000; Patoine et al. 2000; Charette and Prepas 2003). Decomposition of submerged plant material and soil nutrient input through erosion is likely responsible for the subtle changes in algal production in recent Sooke Reservoir sediments (Gunkel et al. 2003). In contrast, initial changes in Shawnigan Lake productivity starting in the post-1900 periods might be due to shoreline erosion and runoff input of nutrients (Nordin and McKean 1984). The first automobile use and subsequent road construction as well as population increase began in the watershed during this time. These events were likely responsible for the changes in allochthonous nutrient loading which increased the productivity from its natural oligotrophic condition. Additionally, large amounts of dissolved nutrients were likely supplied to the lake from a large forest fire accompanied by sawmill burning, and these events may have changed algal productivity. In addition, point and diffuse nutrient loadings resulted in enhanced lake productivity in recent years. Lower CD/TC values in both sediment cores also suggests that cyanobacterial communities dominated mainly during pre-1900 periods

and in some instances, during post-1900 periods when the resource availability was limited (Waters et al. 2004).

Variability

Establishing a dam on a lake, accompanied by watershed flooding due to increasing water levels, leads to a transformation in aquatic productivity and a new equilibrium. Several factors, including: flushing rate changes, seasonal succession of algal communities, decomposition of plant litter and the release of nutrients from submerged soil, changes in water column depth, and turbidity are responsible for this change in productivity (Ostrofsky and Duthie 1978; Grobbelaar 1989). Inferred sedimentary fossil pigments indicated ecosystem variability responded to elevated water levels in Sooke Reservoir and watershed land use changes in Shawnigan Lake. In both lakes historical variability increased significantly for cyanophytes (zeaxanthin, echinenone) and bacillariophytes (diadinoxanthin). However, the variability was more evident in Shawnigan Lake sedimentary records. Changes in variability inferred from sediment pigment concentrations following disturbance were unrelated to the changes in pigment preservation. Rather, the trends were closely related to the corresponding productivity regimes and were consistent with chlorophyll (primary) to pheophytin (degraded) ratios. However, deviation of pigment concentrations (representing different phytoplankton groups) from the mean natural levels was not consistent throughout the post-disturbance periods in both study lakes. As demonstrated in previous work, increased variability may reduce the

predictive power of anthropogenic perturbation experiments on lakes and ecosystem functioning at whole ecosystem scale (Tillman et al. 1997; Cottingham et al. 2000).

The synchronous character of cryptophytes (alloxanthin) and colonial cyanobacteria (zeaxanthin) suggests that variability in spring climate had a major influence on these algae. This result is consistent with previous interpretations where it has been demonstrated increased coherence among lakes and increased interannual variability within a lake for cryptophytes and cyanobacteria (Cottinghum et al. 2000; McGowan et al. 2005) is influenced by regional climate. However, other factors including resource exploitation, thermal stratification, temperature-dependent development of herbivorous zooplankton communities, and watershed disturbances may have influenced variability along with regional climatic factors (George et al. 2000). The lack of correlation for most of the pigments between two lakes suggests that site-specific factors are more important than factors operating at a regional scale in regulating algal communities and productivity in the two study lakes.

Regulated water level *vs.* watershed land use change

Between the two different anthropogenic disturbances I reported in this study (water level changes and human settlement), results from the sedimentary pigment profiles show it is more likely that land use changes have had an impact on lake productivity. The reconstructed pigment stratigraphies indicate that primary production was lower during pre-1900 period compared to post-1900 periods. Pigment concentrations in SHL sediments were relatively higher compared to the SOL sediments. Lake specific

factors could have affected the absolute differences between fossil pigment concentrations in both study lakes (Cuddington and Leavitt 1999). These results were also consistent with the pre- and post-disturbance variability analysis, which suggested that variability in algal groups increased during post-disturbance periods regardless of the types of anthropogenic events. Only a few changes in paleoproduction were observed in Sooke Reservoir after changes in water level, whereas the algal production dramatically increased after human settlement in the Shawnigan Lake watershed. Increased inputs of nutrients from diffuse sources due to watershed disturbances, including shoreline erosion, and household wastes may have also contributed to these changes in Shawnigan Lake (Schindler 2006; Smith 2006). I suspect that regulated water levels played an important role in controlling the algal production in lakes. However, nutrient depletion resulted in resource limitation within this oiligotrophic system (i.e., Sooke Reservoir) when algal nutrients demands exceeded rates of supply after a few years of impoundment.

Conclusion

Ecosystem-level disturbances and changes in aquatic community structure is an emerging issue in modern ecological studies. Responding to recent modifications and disturbances of the environment, ecosystems have evolved into the variety of landscapes present today. From fossil pigment analyses, I showed that land-use changes in the Shawnigan Lake watershed had greater negative impacts on algal productivity and therefore, lake water-quality compared to regulated water levels in Sooke Reservoir. Results from this study confirm the application of fossil pigments to

compare temporal coherence and variability in two lakes with contrasting watershed land use histories (Cottingham et al. 2000; McGowan et al. 2005). Paleolimnological evidence from the analyses illustrate that impoundments due to raising the water levels in Sooke Reservoir affected water residence time and seasonal succession and subtly enhanced aquatic productivity. In contrast, evidence from Shawnigan Lake sediment pigment profiles compared with Sooke Reservoir profiles indicated that land use changes in the Shawnigan Lake watershed had greater effects than regulating water levels in Sooke Reservoir, in enhancing lake productivity due to input of nutrients from diffusive sources. Regardless, anthropogenic disturbances in both systems (i.e., regulated water level and human settlements) produced irregular aquatic productivity regimes, which were exhibited by the presence of diverse algal groups along with increased ecosystem variability. Fossil pigment data in lake sediments can provide information on temporal coherence and variability due to either natural or anthropogenic disturbances and thus can be used to guide and manage lake water quality.

Tables

Table 2.1. A comparison of the major historical events after 1900 in the two study lakes: Sooke Lake Reservoir (SOL) and Shawnigan Lake (SHL). It is assumed that pre-1900 events (including natural forest fires) would have had similar impacts on both watersheds. Sources: Original operational records of the Sooke Lake caretaker; Mr. Stewart Irwin (personal communication); Barraclough (1995); Greater Vancouver Water Department historical documents; British Columbia Water Commission minutes; Strategic Plan for Water Management Report (CRD 1999); Zhu et al. (2007).

Year	Sooke Reservoir	Year	Shawnigan Lake
1911	Construction of Canadian Northern Pacific Railway started.	1908	Entire shoreline had been deforested.
1911-1914	Construction of first dam and raising the water level by 3.7 m.	1910	First automobiles arrived at the lake.
1920	Kapoor Logging company begins operations.	1919	Sawmill on the north-eastern shore of the lake burnt down. Sawmill was rebuilt and expanded.
1968	Forest clearing around the reservoir begins.	1967	Approx. 1000 permanent residents in watershed
1970	Second dam on reservoir, Low precipitation year. Dam is raised to 13.2 m., raising the level of water by 7 m above the dam constructed in 1914.	1979	Approx. 2000 permanent residents in watershed
2002	Third and last dam-raising event completed. Raised water level inundated 360 hectares of land and converted this area into wetland by 2005.	1997	Approx. 5700 permanent residents in watershed

Table 2.2. Three successive dam periods on Sooke (1912, 1970, 2002) and summary of inundated area.

Events	Surface area (ha)	Volume (m^3)	Inundated area (ha)
Original lake	372.2	67.7×10^6	-
First dam in 1910	435.9	84.1×10^6	63.7
Second dam in 1970	607.1	120.0×10^6	171.2
Recent dam in 2002	750.6	170.0×10^6	131.0

Table 2.3. A compilation of morphological and limnological variables and parameters of the study watersheds. Values presented here are based on yearly average. Unit for chemical characteristics is $\mu g \cdot L^{-1}$. SOL = Sooke Reservoir, SHL = Shawnigan Lake, Z_{max} = maximum depth in meters, DOC = dissolved organic carbon, TP = total phosphorus, TN = total nitrogen, Chl *a* = chlorophyll *a*.

Lake		Z_{max}	Catchment area (km^2)	Surface area ($\times 10^6$ m^2)	Water exchange rate yr^{-1} (± 1 SD)	DOC (± 1 SD)	TP (± 1 SD)	TN (± 1 SD)	Chl *a* (± 1 SD)
SOL	Whole lake	70.0	87.0	6.0	0.7 (±0.27)	--	--	--	--
	North basin	70.0	--	4.3	--	2.0 (±0.3)	3.1 (±1.5)	80.9 (±13.3)	0.7 (±0.4)
	South basin	22.0	--	0.5	--	2.0 (±0.3)	3.3 (±1.5)	85.6 (±25.4)	0.9 (±0.3)
SHL	Whole lake	53.0	69.4	5.5	0.5 (±0.14)	--	--	--	--
	North basin	53.0	--	3.6	--	3.1 (±0.31)	4.9 (±1.8)	152.4 (±26.5)	1.3 (±0.64)
	South basin	27.0	--	0.6	--	3.1 (±0.29)	4.4 (±2.1)	153.4 (±24.2)	1.5 (±0.74)

Table 2.4. A list of the common pigments detected in the study lake sediments and their associated precursor organisms (modified from Rowan 1989 and Leavitt and Hodgson 2001).

Pigments	**Source organisms**	**Preservation in lake sediments**
Chlorophyll *a*	All higher plants and all algae	Excellent
Chlorophyll *b*	All higher plants, Chlorophyceae, Euglenophyceae	Moderate
Pheophytin *a*	Derivative of chlorophyll a	Excellent
β - carotene	All higher plants, all algae, some photoautotrophic bacteria	Excellent
Alloxanthin	Cryptophyceae	Moderate
Fucoxanthin	Chrysoyphyceae, Dinophyceae, Bacillariophyceae,	Moderate
Diatoxanthin	Bacillariophyceae, Dinophyceae	Moderate
Lutein	Chlorophyceae, Euglenophceae, higher plants	Moderate
Zeaxanthin	Cyanobacteria	Moderate
Myxoxanthophyll	Cyanobacteria	Poor

Table 2.5. Pearson's correlation coefficient (r) between pigments in Sooke Reservoir and Shawnigan Lake.

Pigments	Correlation coefficient (*r*)	Probability (*p*)
Fucoxanthin	0.237	0.440 ^{ns}
Diadinoxanthin	-0.056	0.637 ^{ns}
Alloxanthin	0.383	0.001*
Zeaxanthin	0.534	<0.001*
Canthaxanthin	0.106	0.372 ^{ns}
Chlorophyll *b*	-0.024	0.840 ^{ns}
Chlorophyll *a*	0.028	0.813 ^{ns}
Echinenone	-0.038	0.750 ^{ns}
α-carotene	0.072	0.543 ^{ns}
β-carotene	-0.175	0.139 ^{ns}

* significant at $\alpha \leq 0.05$, ns – not significant

Figures

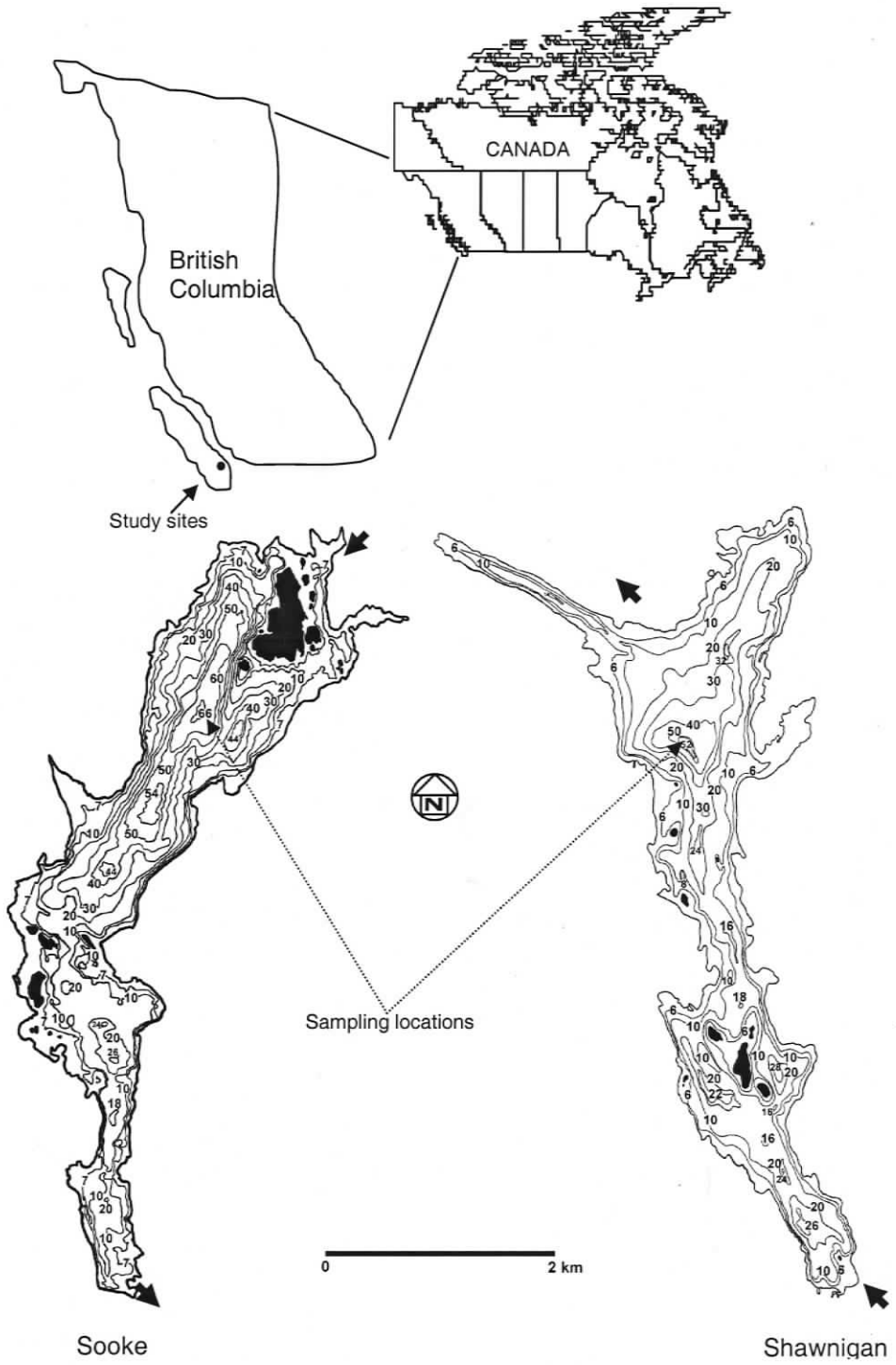

Figure 2.1: Location and bathymetry map of Sooke Reservoir and Shawnigan Lake in Vancouver Island, British Columbia, Canada. Bathymetries of the two study lakes are adapted from Spafard et al. (2002). The dark arrows indicate surface water flow directions.

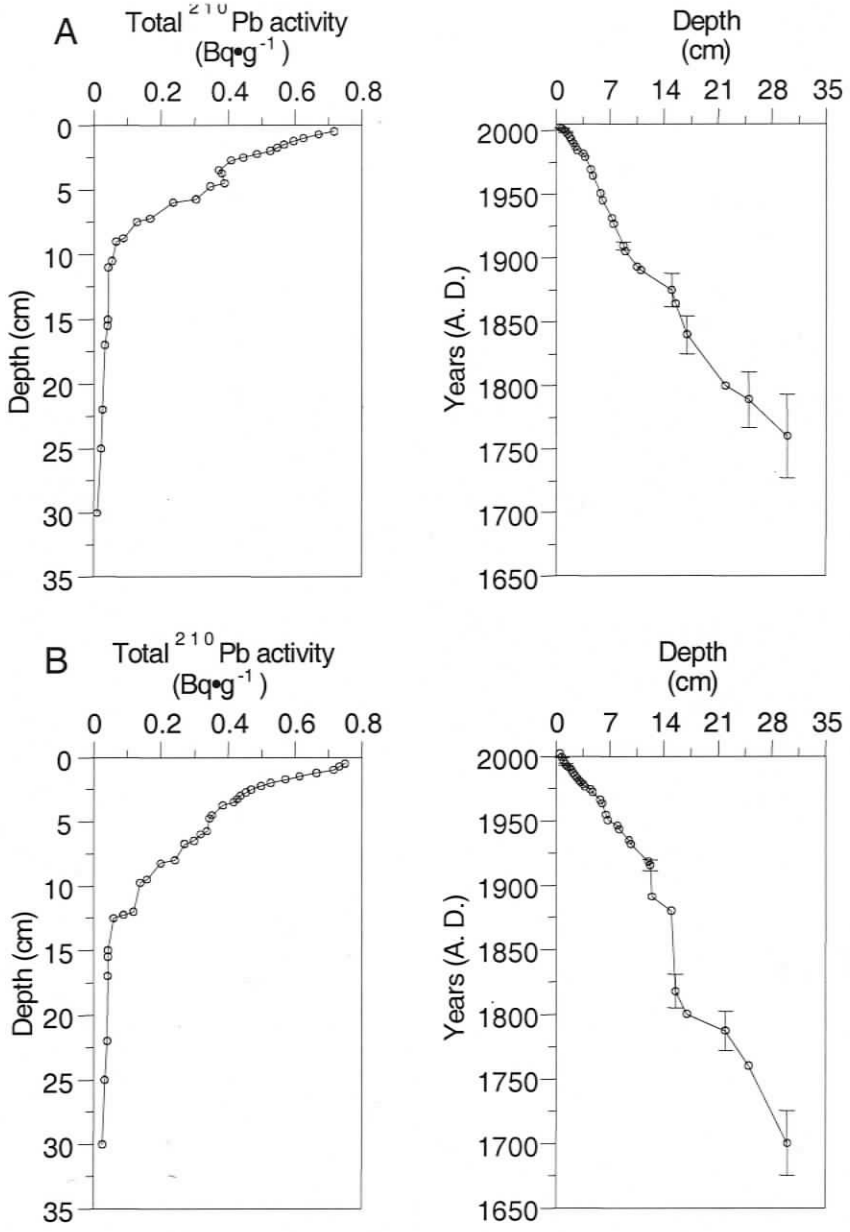

Figure 2.2: Activity of ^{210}Pb within in study lake sediment cores based on constant rate supply (CRS) modeled yeas (a: Sooke Reservoir, b: Shawnigan Lake). Error bars indicate 95% confidence intervals.

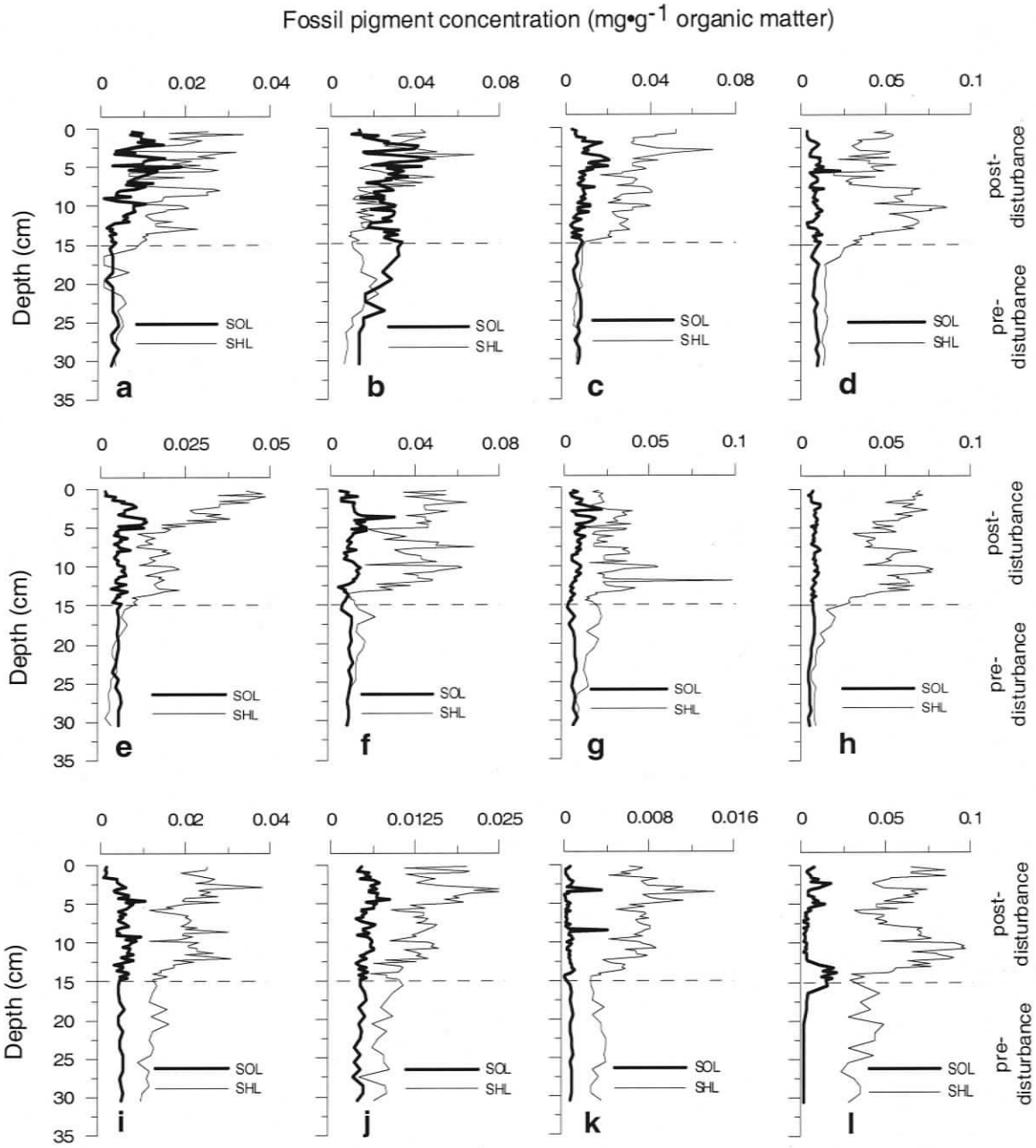

Figure 2.3: Fossil pigment stratigraphy from the study lakes. Horizontal dashed lines indicate the separation between pre- and post- 1900 periods. (a. fucoxanthin, b. diadinoxanthin, c. alloxanthin, d. lutein-zeaxanthin, e. canthaxanthin, f. chlorophyll *b*, g. chlorophyll c_2, h. chlorophyll *a*, i. echinenone, j. pheophytin *a*, k. α-carotene and l. β-carotene) (SOL = Sooke Reservoir and SHL = Shawnigan Lake).

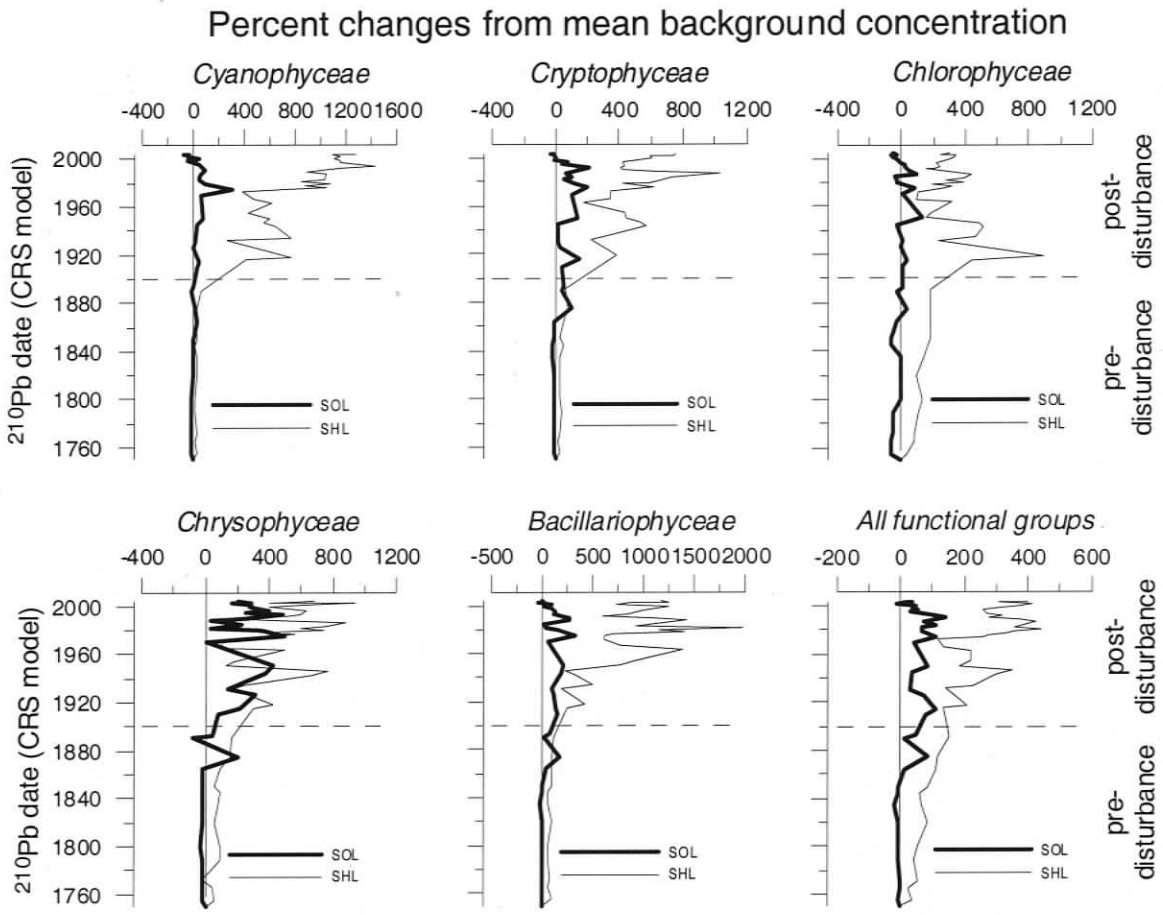

Figure 2.4: Sedimentary profiles of percent changes in algal group profiles (inferred from fossil pigment concentrations) from its mean natural background levels in study lakes. Refer to Table 3 for description of pigments and representing algal function groups. Horizontal dashed lines indicate the separation between pre- and post- 1900 periods. (SOL = Sooke Reservoir and SHL = Shawnigan Lake). Natural background levels were based on the ^{210}Pb modeled dates and major historical events.

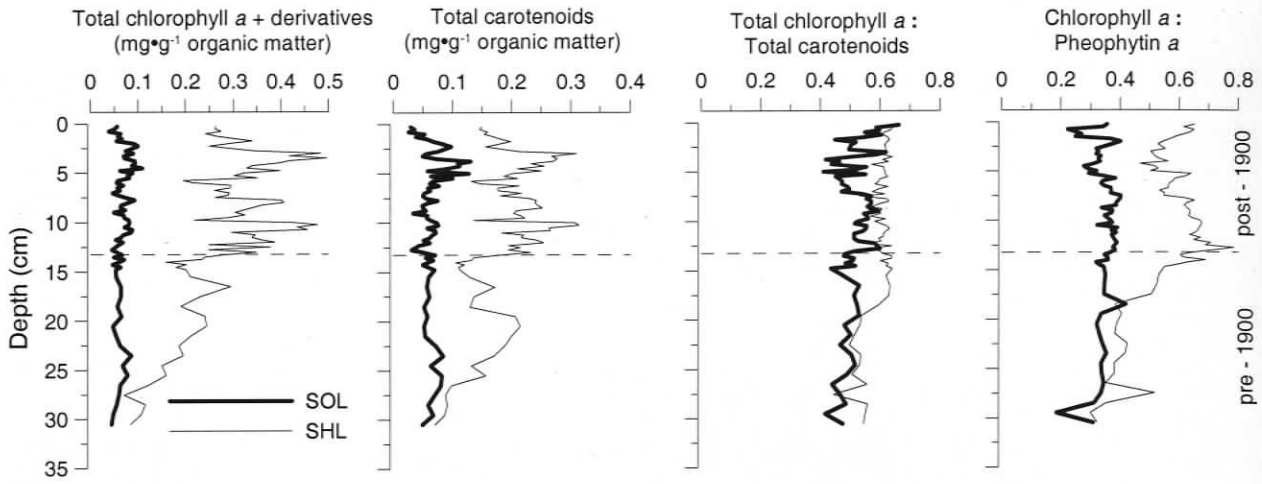

Figure 2.5: Sediment profiles for total chlorophyll *a* and its all derivatives concentration, total carotenoids concentration, chlorophyll derivatives (CD) to total carotenoids (TC) ratio and chlorophyll to pheophytin ratio. Horizontal dashed lines indicate the separation between pre- and post- 1900 periods. (SOL = Sooke Reservoir and SHL = Shawnigan Lake).

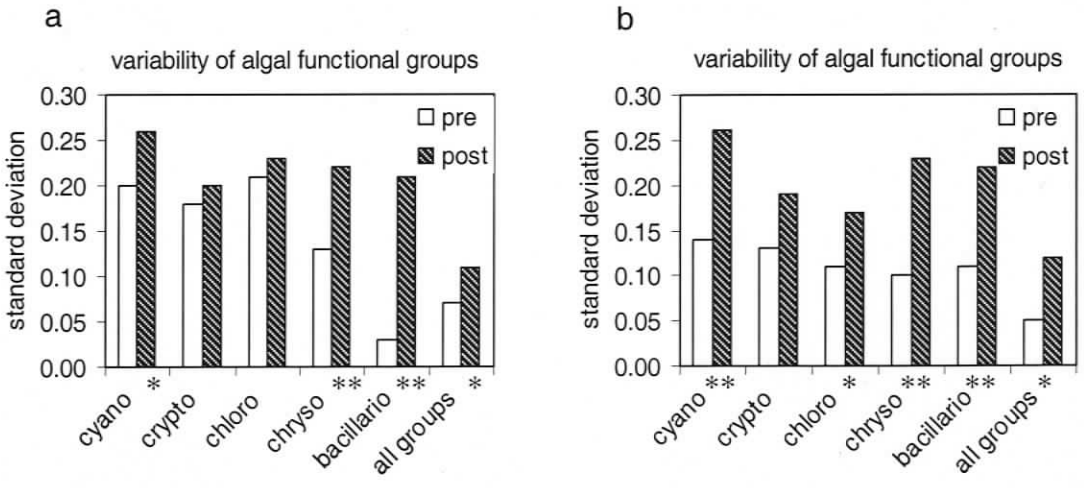

Figure 2.6: Pre (dark bars)- and post-disturbance (open bars) variability based on median-log Levene's test. Asterisks below the bar indicate the *P* values (Refer to Table 3 for description of pigments and representing algal function groups). * for $P \leq 0.05$, ** for $P \leq 0.01$. Absence of asterisks indicates the variability was not significant at $\alpha \leq 0.05$. (a: Sooke Reservoir, b: Shawnigan Lake) (cyano = Cyanophyceae, crypto = Cryptophyceae, chloro = Chlorophyceae, chryso = Chryophyceae, bacillario = Bacillariophyceae)

Chapter 3: Anthropogenic disturbance history influences the temporal coherence of paleoproductivity in two lakes

Abstract

I investigated how the history of local disturbances in a watershed can influence the regional coherence of ecosystem properties in lakes that have similar morphometry and climatic conditions. Sedimentary $\delta^{13}C$, $\delta^{15}N$, C:N and $\%BSiO_2$ were measured in Sooke Lake Reservoir (SOL) and Shawnigan Lake (SHL), which are located within 4 km of each other on Vancouver Island, Canada. SOL is an impounded lake whose watershed has been fully protected over the last century, although the lake level has been raised three times via impoundment during this period. SHL has a similar limnological regime but the surrounding watershed has been developed extensively for residential uses. It was investigated how a pulse disturbance regime in SOL (i.e. repeated dam raising) and a press disturbance regime in SHL (i.e. persistent development) influenced the variability of paleoindicators in each system over time. Results from this study demonstrated that these contrasting disturbance regimes reduced the regional temporal coherence of aquatic productivity between the two lakes (indicated by $\%BSiO_2$), but did not influence the regional coherence of nutrient status or the main carbon sources of the lakes (indicated by %C, %N and $\delta^{13}C$). In contrast, indicators of the sources and cycling of nitrogen (indicated by $\delta^{15}N$) showed increased coherence. Local disturbances also affected the variability of the paleoindicators within each system over time. In SOL impoundments led to both declines (%N, $\delta^{15}N$) and increases ($\delta^{13}C$) in the variability of paleoindicators. In SHL, persistent watershed development led to lower variability of two paleoindicators (%N, $\%BSiO_2$). Overall, the data suggest that local disturbances can

influence the $\%BSiO_2$ and C:N ratio of lake sediments, but is less likely to alter the regional coherence of %C, %N and $\delta^{13}C$ between lakes.

Introduction

The analysis of variability in ecosystem properties over space and time can help ecologists understand the factors that influence ecosystem dynamics and stability. Comparisons of variability across spatially separated systems allow the identification of ecosystem regulators acting over distinct spatial scales (Patoine and Leavitt 2006). Alternatively, comparisons of variability over time allow the identification of influencing factors that cause shifts in ecosystem dynamics within a given location (Cottingham et al. 2000).

When comparing dynamics across locations, synchrony in the variation of ecosystem properties, called "temporal coherence", is thought to be caused by regional, extrinsic regulators such as climate or geology (Kratz et al. 1987; Magnuson et al. 1990; Rusak et al. 1999; Patoine and Leavitt 2006). Conversely, unique local influencing factors are thought to cause the de-coupling of variation in ecosystem properties across sites. Local regulators can be either intrinsic (i.e. ecological interactions) or extrinsic (e.g. nutrient loadings) to the ecological community (Patoine and Leavitt 2006).

Ecosystem properties and their variability can be determined locally by the species composition and diversity of the biological community (Tilman et al. 1997 and Tilman et al. 2006 respectively), or by the types of disturbances experienced by the ecosystem, e.g. fire, flood or human development (Bender et al. 1984; Underwood 1991). For instance, increased nutrient loading is an extrinsic disturbance that may cause increased variability (Rosenzweig 1971; Carpenter et al. 1998; Cottingham et

al. 2000; Carpenter and Brock 2006). The type and duration of a disturbance may also affect the variability over time (Bender et al. 1984). For instance, pulse disturbances may increase the variability of ecosystem properties temporarily, after which a new stable state may be achieved. However, a press (i.e. prolonged) disturbance may increase the potential for time-lagged dynamics and complex ecological feedbacks, and could lead to a persistent destabilizing effect on the variability of an ecosystem property over time (DeAngelis and Waterhouse 1987; Carpenter et al. 1998; Carpenter and Brock 2006).

In this paper, it was investigated how unique, local anthropogenic disturbances affected the temporal coherence of various ecosystem properties between two adjacent and very similar lakes in order to determine whether local or regional drivers governed these ecosystem properties. It was also investigated whether these local disturbance regimes affected the within-lake variability of ecosystem properties over time. The two lakes that were chosen for this study are located on Vancouver Island, British Columbia, Canada. The lakes are very similar in terms of their climate, geography, morphometry and limnology (Spaphard et al. 2002; Davies et al. 2004; Nowlin et al. 2004).

Sooke Lake Reservoir (hereafter, SOL) has experienced three increases in water level over the last century (pulse disturbances), but there has never been residential or other development within its watershed. Impoundment was considered to be an anthropogenic disturbance because water level changes and catchment flooding

following impoundment can alter nutrient inputs to lakes from multiple sources including terrestrial plant decomposition and soil erosion (Glazebrook and Robertson 1999; Larmola et al. 2004). Previous studies on the allochthonous dissolved organic carbon from littoral wetlands have suggested that these are the largest continuous nutrient loads to reservoir ecosystems (Glazebrook and Robertson 1999). By comparison, nearby (< 4 km) Shawnigan Lake (hereafter, SHL) is similar to SOL (see Methods for details) but has experienced steady deforestation and increasing residential development (press disturbance) in its watershed since 1910 (Barraclough 1995). SHL has never been impounded. However, logging and residential development within a watershed can increase nutrient loading and in turn, significantly increase nutrient status of the lake (Bradbury and Van Metre 1997; Douglas et al. 2002; Rosenmeier et al. 2004).

Because these two lakes are limnologically very similar and share regional climatic influences (Nowlin et al. 2004; Davies et al. 2004), I hypothesized that if the measured ecosystem properties (discussed below) were driven by local forces, then temporal coherence would decrease in the post-disturbance period. However, if a given ecosystem property is driven by regional forces, then its temporal coherence would be unaffected by local disturbances within each watershed. For those ecosystem properties whose temporal coherence was unaffected by disturbance, regional temporal coherence was tested between lakes using the entire sediment chronology (as in Rusak et al. 1999).

I also hypothesized that changes in the variability of ecosystem properties, as reflected by the paleoindicators, would depend on the disturbance regime experienced by the ecosystem. To test this, variability of the paleoindicators before and after anthropogenic disturbance in each lake were compared. The effects of the different types of local disturbance on the variability of the paleoindicators were also compared across lakes in order to determine whether the response of the indicator depended on the type of disturbance.

Six sedimentary variables were used as paleoindicators of ecosystem properties from a single high-resolution sediment core removed from each lake. These were: carbon and nitrogen stable isotopes ($\delta^{13}C$ and $\delta^{15}N$), percent carbon and nitrogen composition (%C, %N), the molar ratio of carbon to nitrogen (C:N), and biogenic silica concentration (%$BSiO_2$). This suite of paleoindicators is capable of providing important information about a lake ecosystem, but the specific interpretation of each indicator is still debated (Meyers 1994; Kaushal et al. 2006). $BSiO_2$ is linked to both the biogeochemical weathering of silica and diatomaceous primary production (Conley and Malone 1992; Chmura et al. 2003). Generally, the indicators provide information about lake productivity (%$BSiO_2$), the source and magnitude of nutrient loading ($\delta^{15}N$ and C:N and N respectively), and the source of organic matter ($\delta^{13}C$) .

The prediction was %$BSiO_2$ would display the greatest decline in temporal coherence due to disturbance because it can vary significantly due to changes in both the productivity and biotic community composition in a lake (Kratz et al. 1987;

Magnuson et al. 1990; Rusak et al. 1999). However, *a priori* predictions regarding the temporal coherence of $\delta^{15}N$, $\delta^{13}C$ and C:N were not possible because, while these variables could each have been affected by the anthropogenic disturbances experienced locally in each watershed, regionally-shared forces such as precipitation and timing of mixing could also have caused strong temporal coherence across the lakes, overriding the local effects of development on nutrient status and productivity (Patoine and Leavitt 2006).

Finally, the prediction was variability of productivity and nutrient status of each lake in the post-disturbance as compared to the pre-disturbance period would have depended on the persistence and variability of anthropogenic disturbance. Specifically, it was expected that human settlement in SHL (a press disturbance) would have had longer-term effects, increasing the variability of ecosystem properties over an extended period of time. Conversely, the prediction was short-term nature of the human disturbance in SOL (shoreline logging and impoundment of the lake) would result in more transient effects on the variability of ecosystem properties (Underwood 1991; Carpenter et al. 1998).

Materials and Methods

Study sites

Both SOL (48°33′N latitude and 123°42′W longitude) and SHL (48°37′N latitude and 123°38′W longitude) are located on southern Vancouver Island, British Columbia, Canada (Figure 2.1). The study lakes lie within the Insular and Coastal Mountain

limnological region of south-eastern Vancouver Island (CRD 1999). Description of the study lakes has been also included in Chapter 2.

The water residence time of SOL is 1.4 years. The total catchment and lake surface areas of this reservoir are approximately 87 km^2 and 6 km^2 respectively, giving a ratio of terrestrial to lake area of 13.5:1 for the catchment (Nowlin et al. 2004). The SOL watershed is principally comprised of Metchosin volcanic materials including basalt flows, tuffs, and agglomerates of Devonian and Carboniferous origin (CRD 1999). The catchment vegetation is characterized by Western Hemlock stands interspersed with Coastal Douglas Fir and Western Red Cedar (Barraclough 1995; CRD 1999). The region experiences mild winters and cool summers due to the moderating influence of the ocean. The area is in a rain shadow created by the Olympic Mountains (Tuller 1979). The watershed receives about 1,226 mm of precipitation per year, with maximum stream flows occurring during winter months due to heavy rainfall (MacKay 1966; Nowlin et al. 2004). Sooke Lake Reservoir is classified as oligotrophic, with a conductivity of approximately 45 $\mu S \cdot cm^{-1}$, total phosphorus of around 3 $\mu g \cdot L^{-1}$, and standing biomass of around 0.7 $\mu g \cdot L^{-1}$ of chlorophyll-*a* (Nowlin et al. 2004).

SHL is similar to SOL in many ways. SHL is also classified as oligotrophic (~ 48 $\mu S \cdot cm^{-1}$ for conductivity, 4.9 $\mu g \cdot L^{-1}$ for TP and 1.3 $\mu g \cdot L^{-1}$ for chlorophyll *a*) and both lakes are monomictic (Nowlin et al. 2004). Both lakes have one relatively deep and one shallow basin (Figure 2.1). Because the two lakes are located within 4 kilometers

of each other, the climate and the natural watershed vegetation are essentially the same for both catchment areas. The average forest age is currently 124 years for SOL and 129 years for SHL (Zhu et al. 2007). However, SHL has smaller total catchment and lake surface areas (69.4 km^2 and 5.5 km^2 respectively) than SOL, with a ratio of 11.6:1 of terrestrial to lake area for the catchment (Nowlin et al. 2004). SHL is fed through a different major inflow, namely Shawnigan Creek, and has a slightly longer residence time (~ 2.0 years) than SOL. Geologically, most of the SHL watershed is made-up of Wark and Coquitz Gneiss complexes and is of Devonian origin (Barraclough 1995; CRD 1999). SHL soils contain less material of colluvial origin than in SOL, and the drainage is imperfect, whereas drainage in SOL is moderated to rapid (Zhu et al. 2007).

Both lakes have been impacted by human activities since the turn of the 20^{th} century. The first dam on SOL was constructed in 1910 to supply drinking water to the city of Victoria. Since the initial dam construction, the water level in SOL has been raised twice, once in 1970 by 5 meters and once in 2002 by 6 meters. The SHL shoreline had been fully deforested by 1908 and has since been developed for residential use. See Table 1 for a more complete chronological listing of major events in each watershed.

Sampling and sediment chronology

Sediment cores were collected from the deepest part of the lakes using a modified gravity corer (as in Kliza and Telmer 2001) and extruded them on site. The sampling

resolution was 1 cm throughout the core. Samples were transported to the laboratory on ice, where it was preserved in a freezer (-20°C) until further analysis. Sediment cores were dated using ^{210}Pb dating techniques by α-spectroscopy (as in Appleby and Oldfield 1978). The constant rate of supply (CRS) model was applied to the ^{210}Pb data (as in Appleby 2001). The 95% confidence interval for the dating was based on counting error. Sediment accumulation rate was calculated by applying the CRS model to the ^{210}Pb activity in the sediment samples.

Sediment organic matter and stable isotope characterization

Percent carbon (%C), percent nitrogen (%N), carbon to nitrogen molar ratio (C:N), and the stable isotopic compositions of carbon (δ^{13}C) and nitrogen (δ^{15}N) of the sediment samples were measured using a continuous flow, high-temperature elemental analyzer coupled to a DELTA^{plus} Advantage mass spectrometer. The reproducibility of duplicate analyses was ±0.1‰.

The measured values of δ^{13}C are dependent on the historic isotopic signature of dissolved inorganic carbon at the time when the organic carbon is produced photosynthetically (Meyers and Ishiwatari 1993). As a result, the data for the δ^{13}C were normalized to account for the historic depletion of δ^{13}C in atmospheric CO_2 due to fossil fuel burning (the 'Suess Effect') as recorded by fossil air trapped in ice cores (Friedli et al. 1986). I applied the following polynomial equation to correct for the Suess Effect, where t is time in years (as in Friedli et al. 1986):

$$\delta^{13}C = -7.000\,t^3 - 3.000\,t^2 + 7.343\,t - 4547.200 \qquad [1]$$

I subtracted the calculated time-dependent depletion in $\delta^{13}C$ since 1840 from the measured $\delta^{13}C$ for each dated sediment section.

Biogenic silica

For $BSiO_2$ analysis, 30 mg of each freeze-dried sediment sample was transferred into a 125 mL polypropylene round bottle. Organic matter from the samples was removed by adding 30% H_2O_2 and letting the samples stand at room temperature for 4 days. $BSiO_2$ was then dissolved by adding 40 mL of 1% NaOH to each sample and oscillating them at a speed of 100 rpm at 85°C in a heated shaker. Caps were loosened slightly to vent gasses. Aliquots were examined from the samples under a compound microscope at 400 x magnification every half-hour until all of the diatom frustules had been dissolved. Upon complete digestion of $BSiO_2$ (after ~ 5 hours), slurries were centrifuged. 1.0 mL aliquots of supernatant from each sample were neutralized with 9.0 mL of 0.021 N HCl. Total dissolved silica was measured using molybdate blue reduction (Conley and Schelske 2001). The measured $BSiO_2$ was converted to a percentage of the original sample in terms of dry mass (hereafted reported as % $BSiO_2$.

Statistical analysis

Data were grouped from each core into two periods, pre- and post-disturbance, where 'pre-disturbance' refers to all years before 1900 and 'post-disturbance' refers to all years thereafter. Data were matched between lakes by date. Exact matches by year were not possible for all dates. As a result, in the pre-disturbance period was aimed to

maximize the number of matched sections according to date while maintaining differences in dates between the lakes that were less than the half-width of the 95% confidence interval for the ^{210}Pb date (see Results). To estimate a conservative half-width of the confidence interval for a given match, the date was used that was most recent between the two cores. An exponential function was fitted to the estimated half-widths of the confidence intervals (H) for the ^{210}Pb dates (t) of the cores (see Results). The following function fit the data with an r^2 of 0.99.

$$H = 0.310 \bullet e^{0.027\,t} \qquad [2]$$

This function was used to calculate the maximum allowable difference between the dates of comparable sections of the two lakes. According to this matching process, one match was included that differed by a maximum of twenty years in the pre-disturbance period. This match occurred between the section of the SHL core dated to 1817 and the section of the SOL core dated to 1837. The conservative measure of the half-width for 1837 is twenty-six years, and so the difference between the dates is within the precision of the estimate. All other matches for pre-disturbance dates differed by less than seven years. The level of precision for the estimates of the post-disturbance dates exceeded the resolution of many of the matches because the half-width of the dating confidence intervals were less than one year for all dates after 1958. As a result, for the post-disturbance period I matched dates so as to maximize the number of matches while tolerating a maximum difference in the ^{210}Pb dates between the cores of three years.

To determine the level of temporal coherence of the proxies between the two lakes Pearson's correlation analysis was conducted between the z-scores of each variable ($\delta^{13}C$, $\delta^{15}N$, %C, %N and biogenic silica) (as in Rusak et al. 1999). To determine whether the temporal coherence of the proxies had significantly changed after the disturbance, data were split into pre- and post- disturbance periods and calculated the difference between the coefficients of determination in each period (Δr^2).

$$\Delta r^2 = r^2_{pre} - r^2_{post} \quad [3]$$

The probability of getting a value of Δr^2 as large as, or larger than the one was observed was measured using randomization. For randomizations, randomly sampled matched data were considered from the time series without replacement, creating 10,000 randomly re-ordered time series. The Δr^2 for each time series was calculated by comparing the number of randomizations that yielded results as or more extreme than ours to the total number of randomizations (see Edginton 1987). R^2 was used as a measure of temporal coherence instead of r in this analysis because I was only interested in changes in the magnitude of the strength of the relationship, not the direction, and while r can vary between negative one and one, r^2 only varies between zero and one. R^2 was also a meaningful metric because it is indicative of the amount of variability in the data that is accounted for by the correlation (Zar 1999). R software, version 2.6.2, was used for this analysis (R Development Core Team 2008).

When variables did not show significant changes in temporal coherence between time periods, regional correlation was tested between lakes over the entire time series.

Again, 10,000 randomizations were used as above, however, for this analysis only the SHL values were randomized for a given paleoindicator while holding the SOL values constant in order to test for the significance of the correlation (Edginton 1987).

To compare variation in the paleoindicators between pre- and post disturbance periods a Levene's test was conducted on $\log_{10}$-transformed, median-scaled data (as in Cottingham et al. 2000). Samples from transitions years (1891 to 1910) were excluded for this analysis. A linear transformation was applied prior to log transformation for $\delta^{13}C$ and percent nitrogen, so as to avoid negative values. SPSS software, version 15.0, was used for this analysis (SPSS Inc. 2008). The α was set at 0.05 for all analyses.

Results

Sediment chronology

The ^{210}Pb profile for SOL showed a decrease in activity from the top sediment layers downwards (Figure 3.1). Although the cumulative ^{210}Pb activity differed between the cores, there was an increasing trend in the total ^{210}Pb activity in the uppermost 8 cm and 12 cm of SOL and SHL, respectively. The sediment accumulation rates increased from 1850 onwards, and this effect was more pronounced during the post-disturbance period (after1900) for both study lakes (Figure 3.1). Changes in the sediment accumulation rate in both lakes confirmed the importance of using the CRS model. The precision of the ^{210}Pb dating technique was moderate. The 95% confidence intervals were: for SOL first 10 (±0.33 yr), 20 (±0.63 yr), 100 (±5.3 yr), and 150

(±16.2 yr) years and for SHL first 10 (±0.42 yr), 20 (±0.71 yr), 100 (±4.9 yr), and 150 (±16.7 yr) years. The results of the sediment chronology indicate that 30 cm cores were long enough to establish the pre-1900 baseline conditions for each lake.

Carbon and nitrogen

There was a slight increase in %C from the pre- to the post-disturbance period in SOL (mean of 8.32% to 9.05%) (Figure 3.2). SHL experienced a decrease in %C (mean of 12.53% to 11.01%). The %N was relatively stable in both watersheds, with a small decrease in the post-disturbance period in SOL (from a mean of 0.59% to 0.66%), and a slight increase in SHL (0.93% to 1.00%).

Changes in the molar C:N ratios in the sediment cores occurred concurrently with the anthropogenic activities in both SOL and SHL (Figure 3.2). In SOL, there was a sharp decline in the C:N just after both the first and second dam-raising events (in 1910 and 1970 respectively), indicating relative nitrogen enrichment (Figure 3.2A). However, this effect was short-lived for both dam-raising events and the molar C:N returned approximately to pre-disturbance levels within twenty years. SOL had relatively stable and slightly elevated %N for all post-disturbance years. The %C in SOL was negatively correlated with dam-raising events, and it was more variable than the %N in post-disturbance years. In SHL, the %C showed a decreasing trend, %N showed an increasing trend, and the C:N molar ratio showed a strong decreasing trend in post-disturbance years (Figure 3.2B).

Isotopes

The stable isotopic signatures were relatively enriched in the post-disturbance period in both lakes (Figure 3.2). Sediment $\delta^{13}C$ values ranged from -27.5‰ to -24.8‰ in SOL samples and from -27.2‰ to -24.7‰ in SHL samples (Figure 3.2). The mean $\delta^{13}C$ values during pre- and post-disturbance periods in SOL were –27.1‰ and -25.8‰ respectively, and in SHL they were -26.7‰ and -25.4‰ respectively. The $\delta^{15}N$ values ranged from 1.0‰ to 2.7‰ for SOL and from 1.0‰ to 2.6‰ for SHL. Mean values of $\delta^{15}N$ during pre- and post-settlement periods were 1.4‰ and 2.1‰, respectively in SOL, and 1.2‰ and 1.7‰, respectively in SHL.

Diagenetic artifacts

A major concern in interpreting changes in the levels of organic paleoindicators is the possibility of post-depositional decay, which may confound the interpretation of sedimentary isotopic profiles (Lehmann et al. 2002). However, it is thought that $\delta^{13}C$ values do not tend to display diagenetic shifts within systems of typical organic carbon content (i.e., <15%) (Meyers and Ishiwatari 1993; Lehmann et al. 2002). The most conspicuous early-diagenetic process for $\delta^{15}N$ is sediment denitrification (Lehmann et al. 2002), which strongly favours ^{14}N and leaves the remaining substratum enriched in ^{15}N. Further, there is some evidence that systems with elevated nutrient inputs, and hence biomass production, are enriched with heavier C and N isotopes, which results in higher $\delta^{13}C$ and/or $\delta^{15}N$ sediment values (Lehmann et al. 2002).

There was no significant linear relationship between $\delta^{13}C$ and %C in either lake in either period (i.e. pre- or post-disturbance), suggesting that the $\delta^{13}C$ signatures were independent of the nutrient loads and biomass production of the lakes (Figure 3.3). No significant relationship was also observed between $\delta^{15}N$ and %N in either lake or period (Figure 3.3). Therefore, the variability in the $\delta^{13}C$ and $\delta^{15}N$ signatures can be confidently interpreted as being reflective of changes in the sources of carbon and nitrogen rather than diagenetic processes (see Finney et al. 2000; Teranes and Bernasconi 2000).

Biogenic silica

Percent biogenic silica ($\%BSiO_2$) in both watersheds showed pronounced elevated concentrations in the post-disturbance periods (Figure 3.2). The $\%BSiO_2$ increased in post-disturbance samples in both lakes (from a mean of 12.0% to 14.4% in SOL and 7.9% to 18.2% in SHL). The $\%BSiO_2$ became significantly less variable in SHL in the post-disturbance period (Figs. 3.2 and 3.5, Table 3.2B). Much like for the C:N molar ratio in SOL, there was evidence of sharp, but transient, declines in $\%BSiO_2$ following dam-raising events.

Temporal coherence and within-lake variability

The temporal coherence declined in the post-disturbance period for all of the paleoindicators (positive Δr^2 in Table 3.1, see Figure 4.4) except for %N and $\delta^{15}N$. This decline in coherence was only significant for $BSiO_2$. Contrary to the predictions however, Δr^2 was negative for %N and $\delta^{15}N$, indicating greater temporal coherence in

the post-disturbance period than in the pre-disturbance period. This effect was significant for $\delta^{15}N$. The temporal coherence of %C, $\delta^{13}C$ and %N did not significantly change between periods. However each of these indicators did show a significant correlation between lakes when the data between the two periods were pooled (%C: r=-0.49, p=0.001; $\delta^{13}C$: r=0.64, p<0.001; %N: r=0.47, p=0.004).

Also contrary to predictions, variability did not generally increase significantly after disturbance (Table 3.2, Figure 3.5). While there were qualitative increases in the variability of %C, $\delta^{13}C$ and $\delta^{15}N$ in SHL, and $\delta^{13}C$ and $BiSO_2$ in SOL, the increase was only significant for $\delta^{13}C$ in SOL (Table 3.2A). I found lower post-disturbance variability for %N in both SOL and SHL, for $\delta^{15}N$ in SOL, and for $\%BiSO_2$ in SHL (Table 3.2, Figure 3.5).

Discussion

Temporal coherence

It was found that the history of anthropogenic disturbances that occurred in two limnologically similar lakes led to changes in the temporal coherence of two paleoecological proxies, namely $\%BSiO_2$ and $\delta^{15}N$ (Table 3.1, Figure 3.4). The temporal coherence of %C, $\delta^{13}C$ and %N were not significantly changed after disturbance. All possible variations of the changes in temporal coherence were found: a significant decrease (positive Δr^2), a significant increase (negative Δr^2), and no change at all ($\Delta r^2=0$). The interpretation was that a significantly negative Δr^2 as

evidence of local control. This interpretation assumed that the two lakes had identical local attributes with respect to factors driving the particular ecosystem property in the pre-disturbance period (I must assume this because it cannot be tested). The interpretation for a significantly positive Δr^2 was as indicating either local control, or a switch from local to regional control. Unfortunately, it was not possible to distinguish these two possibilities with the present analysis. Finally, it could be interpreted no change in Δr^2 as evidence of either local or regional control, and so for those properties where there was no significant change in Δr^2, a test was conducted for a significant linear correlation of the property across lakes over the entire time series. A significant correlation was as evidence of regional temporal coherence (as in Rusak et al. 1999).

The temporal coherence of $\%BSiO_2$ declined after 1900, which was the onset of human involvement in both watersheds (Figure 3.4E). This confirmed the original prediction that in the absence of disturbance, the two lakes would show relatively synchronous fluctuations in productivity, and that the damming in SOL and settlement in SHL, would lead to divergent patterns of primary productivity. The divergence in the $\%BSiO_2$ between lake profiles could have been caused either by asynchronous changes in lake productivity, the biotic community composition, or both (Kratz et al. 1987; Magnuson et al. 1990; Rusak et al. 1999). Generally, high biogenic silica content in the sediment can be taken to indicate trophic enrichment and increased productivity because diatoms tend to require nutrient-rich waters (Reynolds 1984), and as the waters become nutrient-depleted other algal groups

replace diatoms. It has been recommend that future studies measure other sedimentary variables that might aid the further interpretation of the %BSiO2 data. For instance, %P may be another useful indicator of productivity because it is thought that phosphorus is the major limiting nutrient in freshwater systems (Hecky and Kilham 1988). Also, identification of species, or coarser taxonomic groupings, from the frustules of the remaining diatoms would provide information about how diatom communities are changing over time.

The temporal coherence of $\delta^{15}N$ also appears to have been sensitive to local disturbances (Table 3.1), however, contrary to the predictions, the temporal coherence of this paleoindicator increased in the post-disturbance period (Figure 3.4D). This increase indicates that while the local disturbances in each lake have been different, the signatures of their nitrogen sources have become more similar (Fig 3.2). Atmospheric nitrogen is considered to have a relatively constant isotopic signature around the globe (Mariotti 1984). However, it is possible that the increased coherence is the result of increased fossil fuel emissions in the 20^{th} century. Fossil fuel emissions can be a source of enriched nitrogen (in the form of nitrate or ammonium) and they could be regionally transported in precipitation over the watersheds (Peterson and Fry 1987).

However, both the %N and the $\delta^{15}N$ increased in post-disturbance period in SHL (Fig 3B), and this is indicative of both increased nitrogen loading and changing nitrogen sources (Cairns 1995; Kaushal et al. 2006). Elevated household wastewater inputs to

the lake due to the residential development within the watershed are likely responsible for the larger load and relative enrichment of the sources of nitrogen entering the lake (Lake et al. 2001). It was not anticipated that the elevated %N and enriched $\delta^{15}N$ evident in the recent sediment samples from SOL, given that the watershed is protected from human access and development. However, large amounts of dissolved organic carbon and nitrogen can be released into lakes from inundated wetlands created as a result of raised water levels following impoundment (Glazebrook and Robertson 1999; Langhans and Tockner 2005). The elevated nitrogen concentrations and $\delta^{15}N$ in the post-disturbance period may have resulted from the inundation of terrestrial soils (see Table 2.1 for inundated terrestrial area in 2002). Lake water measurements from SOL showed an increase in the total concentration of nitrogen after the third dam-raising event from 85 µg/L in 2001 to 124 µg/L in 2005 (Zhu et al. 2007). The nitrogen in mineral soils is isotopically relatively enriched (Fry 1991) and SOL's watershed contains mineral soil types (Zhu et al. 2007). It is therefore possible that leaching from the inundated soils caused an increased $\delta^{15}N$ in the post-disturbance period. In this case, the increased temporal coherence of this paleoindicator may have resulted from the similar timing of the two completely independent local changes in the sources and transformations of nitrogen in the watershed. As a result, the increase in temporal coherence may not indicate that the nitrogen sources for the lakes became increasingly controlled by regional forces such as the enrichment of the isotopes of nitrogen falling in precipitation.

While there were no significant changes in the temporal coherence of %C, $\delta^{13}C$, or %N, this alone is not sufficient evidence to conclude that drivers acting on a regional scale controlled these paleoindicators. This is because it is also possible that the drivers were influenced by local factors both before and after 1900; leading to an absence of a significant change in the coherence of the paleoindicators. However, upon further investigation, it was found that all three paleoindicators were significantly correlated across lakes over the full time series (Figure 3.4A, B and C). This provides evidence that regional forces did drive the ecosystem properties characterized by these indicators.

As an aside, the results support the findings of previous studies showing that the C:N ratio of sediments is relatively sensitive to human disturbance of watersheds (Sollins et al. 1984; Aller 1994; Meyers 1994), and that trends in this ratio reflect the type of disturbance experienced by the system. In general, the C:N ratios in both lakes were greater than the typical ratios for phytoplankton, but lower than the ratios for terrestrial vegetation, indicating that some allocthonous organic material contributed nutrients to the lakes (Figure 3.2) (see Meyers 1994). The C:N ratio declined in the post-disturbance periods for both lakes. In SOL this trend was due predominantly to declines in the %C in the sediment in post-damming years, and in SHL it was due to a combination of declining %C and increasing %N over the post-disturbance period (Fig 3.2). In SOL, this trend was transient (pulse disturbance), lasting less than twenty years after each dam-raising event (Figure 3.2B). In SHL, the C:N has declined quite steadily reflecting the nature of the press disturbance experienced in this watershed

(Figure 3.2B). I found it noteworthy that this indicator responded uniquely both to the type and duration of these disturbances.

It has been hypothesized that anthropogenic activities may increase ecosystem variability (Cottingham et al. 2000; Carpenter and Brock 2006). However, the data do not support this hypothesis. Those paleoindicators whose variability changed significantly all showed declining variability, except for $\delta^{13}C$ in SOL (Tables 3). The significant changes in variability were also generally unique to each lake, and were therefore likely attributable to the particular local disturbances.

For instance, the significant decline in the variability of $\%BSiO_2$ in SHL (Figure 3.5 Table 3.2B) may be indicative of a decline in the strength of resource competition due to elevated nutrient loading (Tilman and Sterner 1984), or a decline in the frequency of external disruptive disturbances (Gaedeke and Sommer 1986). Based on the rate of development in SHL, and assuming that this development entails an increased frequency of disturbance, the assumption was that the cause of the decline is not the latter. The decline in variability in SHL is not replicated in SOL, further supporting the conclusion that productivity is driven by local factors. The variability in $\delta^{15}N$ also showed a unique and significant decline, but it occurred in SOL (Figure 3.5, Table 3.2A). Building dams on SOL increased the volume of the lake, which may have increased the water residence time, causing decreased nutrient renewal (Schindler et al. 1978) and resulting in decreasing variability in both %N and $\delta^{15}N$ signatures. Essentially, the increased volume of the SOL could have increased the buffering

capacity of the ecosystem to extrinsic disturbances. While the variability of $\delta^{15}N$ declined in SOL, it increased (though not significantly) in SHL, lending support to the conclusion that $\delta^{15}N$ is locally driven.

In contrast to the $\delta^{15}N$ signature, the variability of $\delta^{13}C$ increased significantly during post-disturbance periods in SOL (Table 3.2A). This may have been the result of wetland inundation in SOL and the subsequently variable input of carbon from previously unavailable diffuse sources of carbon into the water body (Jeppesen et al. 1999). The positively shifted $\delta^{13}C$ signature of the SOL profile in post-disturbance years, which is indicative of a greater terrestrial input of carbon, supports this explanation.

The assumption was that the concurrent declines in the variability of the %N in both lakes (Table 3.2, Figure 3.5) are the result of steady and elevated nitrogen inputs resulting from local anthropogenic disturbances. However, based on the presence of a significant regional temporal coherence in %N ($r=0.47$, $p=0.004$), it is also possible that the factors driving the nitrogen concentration are regional and could include deposition from rain, as for $\delta^{15}N$ (Peterson and Fry 1987). Therefore, it was not possible to determine whether local or regional factors are more important in driving %N at this point.

Conclusion

It has been demonstrated that productivity (as indicated by %BSiO2) is controlled on a local scale. There was evidence of regional control for %C, $\delta^{13}C$ and %N. However, the variability in these paleoindicators explained by their regional correlations was not large (%C r^2=0.24, $\delta^{13}C$ r^2=0.42 and %N r^2=0.22). Process and measurement error could have reduced the regional correlation between these paleoindicators (Hilborn and Mangel 1997), but the possibility that some of the remaining unexplained variability may have been accounted for by local processes may not be excluded.

The difficulty in interpreting the change in temporal coherence of the $\delta^{15}N$ data exemplified one crucial weakness in this method; namely that the expected impacts of the local disturbances on a given ecosystem property must be unique. In this case, the nature of the impact of wetland inundation in Sooke Lake Reservoir was overlooked. The effect of this local disturbance may have given a very similar signature to impact of local watershed development in Shawnigan Lake. When local disturbances have similar impacts, it impedes the ability to detect the relative importance of local versus regional drivers. It is recommend, therefore that this method be used in future studies where local disturbances are expected to have had unique impacts, or where one ecosystem was maintained in the reference state (i.e. without disturbance), while the other was disturbed.

It was found that the variability in the paleoindicators was uniquely affected by the local disturbances in those cases where evidence of local control of the ecosystem

property (namely for $\%BSiO_2$, and $\delta^{15}N$) has been demonstrated. The only exception to this finding was that there was a uniquely significant effect for $\delta^{13}C$ in SOL, for which there was evidence of regional control, but the same effect did occur in the other lake, it was simply not statistically significant.

Lakes are particularly good study systems for this type of analysis because the 'local' and 'regional' scales are clearly defined. However, the use of this method is recommended in any system wherein the local scale can be shown to be relatively discrete, giving independence of the local units on the regional scale. Future studies using this technique in other systems and with other paleoindicators, to explore the scales at which a wider array of ecosystem properties is regulated, would be valuable to ecologists and natural resource managers alike. In addition, synchronous or asynchronous behavior of ecosystem properties within two basins of each lake (Sooke and Shawnigan) can be explored.

Tables

Table 3.1: Pearson's correlation coefficient (r) and the difference between the coefficients of determination for pre- and post-disturbance paleoindicators (Δr^2) compared between Sooke Lake Reservoir (SOL) and Shawnigan Lake (SHL) ($n_{pre\text{-}disturbance} = 9$, $n_{post\text{-}disturbance}=24$). Probabilities (p) are the proportions of 10,000 randomizations that gave differences in the coefficients of determination equal to or more extreme than the differences in this data.

Paleoindicator	r_{pre}	r_{post}	Δr^2	p
%Carbon	-0.45	-0.10	0.196	0.272
$\delta^{13}C$	-0.49	-0.33	0.133	0.368
%N	0.25	-0.34	-0.049	0.322
$\delta^{15}N$	0.31	0.92	-0.753	0.001
$\%BiSiO_2$	-0.65	0.09	0.416	0.023

Table 3.2: Test of homogeneity of variances for sediment core data between pre- and post-disturbance periods. **A.** SOL (n_{pre}=13 and n_{post}=30) **B.** SHL (n_{pre}=10 and n_{post}=34). The data were log-transformed and then scaled to the median before conducting a Levene's Test as for a one-way ANOVA (as in Cottingham et al. 2000).

Paleoindicator	Levene Statistic	P
A.		
%C	0.128	0.723
$\delta^{13}C$	4.639	0.037
%N	16.815	<0.001
$\delta^{15}N$	5.071	0.030
$\%BiSiO_2$	1.035	0.315
B.		
%C	0.383	0.539
$\delta^{13}C$	0.686	0.412
%N	11.895	0.001
$\delta^{15}N$	0.744	0.393
$\%BiSiO_2$	36.012	<0.001

Figures

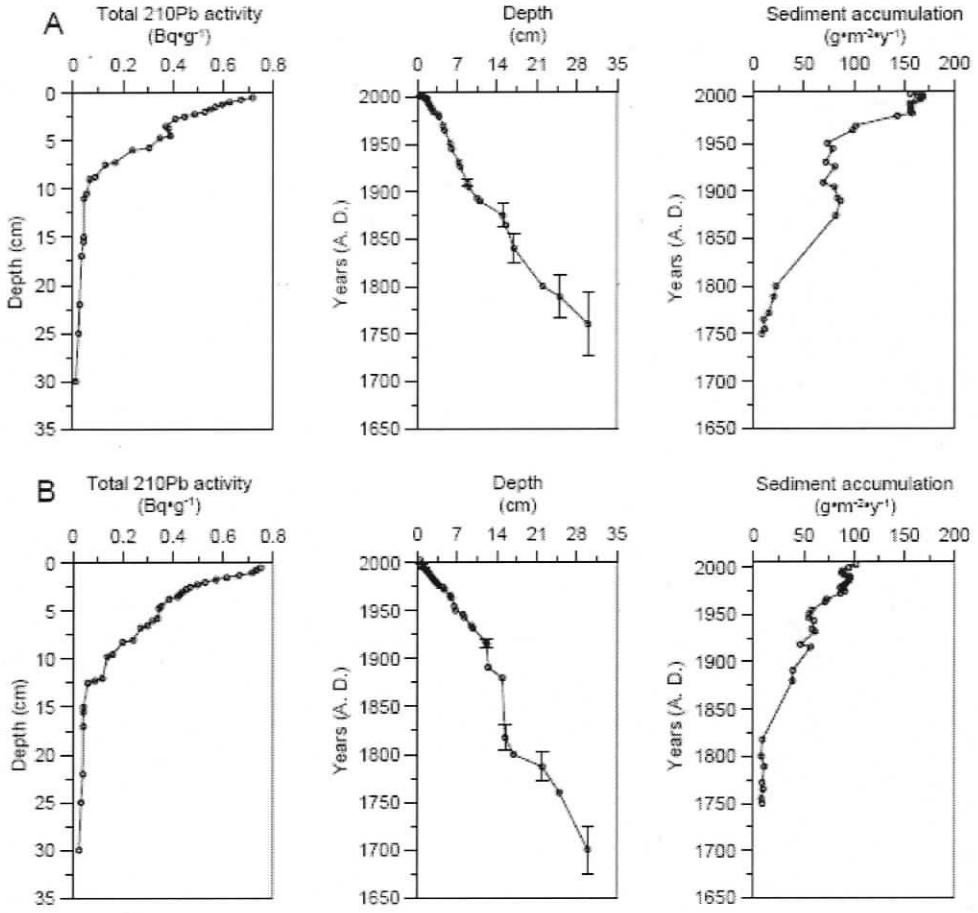

Figure 3.1: Activity of ^{210}Pb within the sediment core, the constant rate supply (CRS) model dating of samples, and the sediment accumulation profiles for both watersheds (from left to right respectively). **A**. SOL (Sooke Reservoir), **B.** SHL (Shawnigan Lake). Error bars indicate 95% confidence intervals.

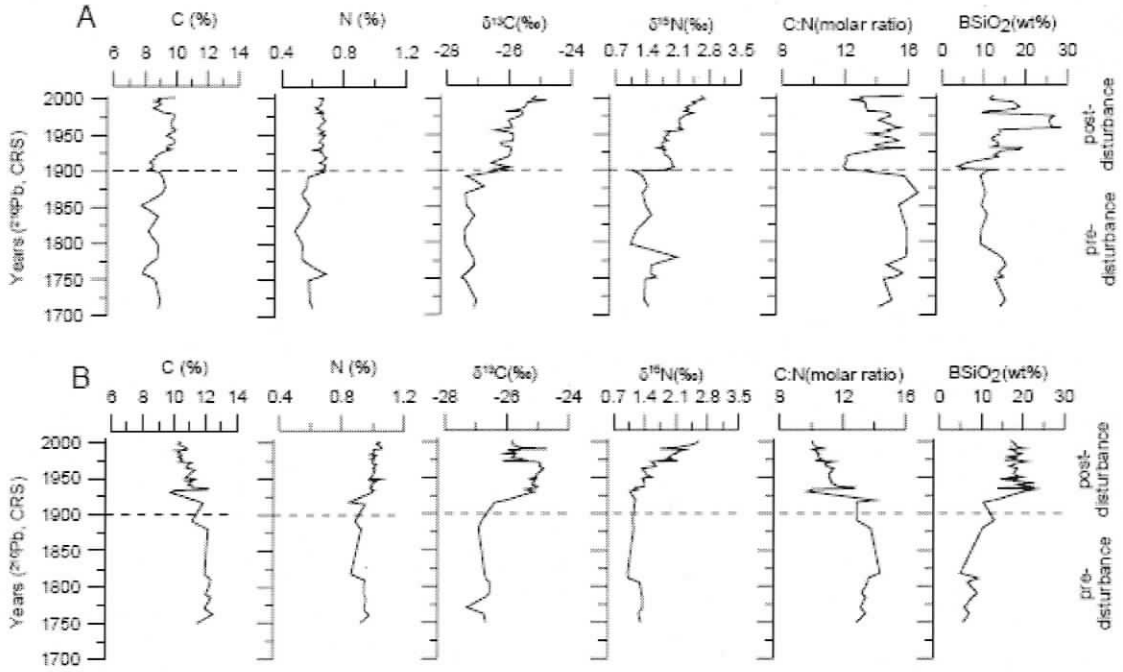

Figure 3.2: Sedimentary geochemical (%C, %N, $\delta^{13}C$, $\delta^{15}N$), C:N ratio and percent biogenic silica (%$BSiO_2$) profiles of samples collected from **A**. SOL (Sooke Reservoir), **B.** SHL (Shawnigan Lake). Years in Y-axis are based on ^{210}Pb activity and the CRS model, and horizontal dashed lines separate pre- and post-disturbance periods.

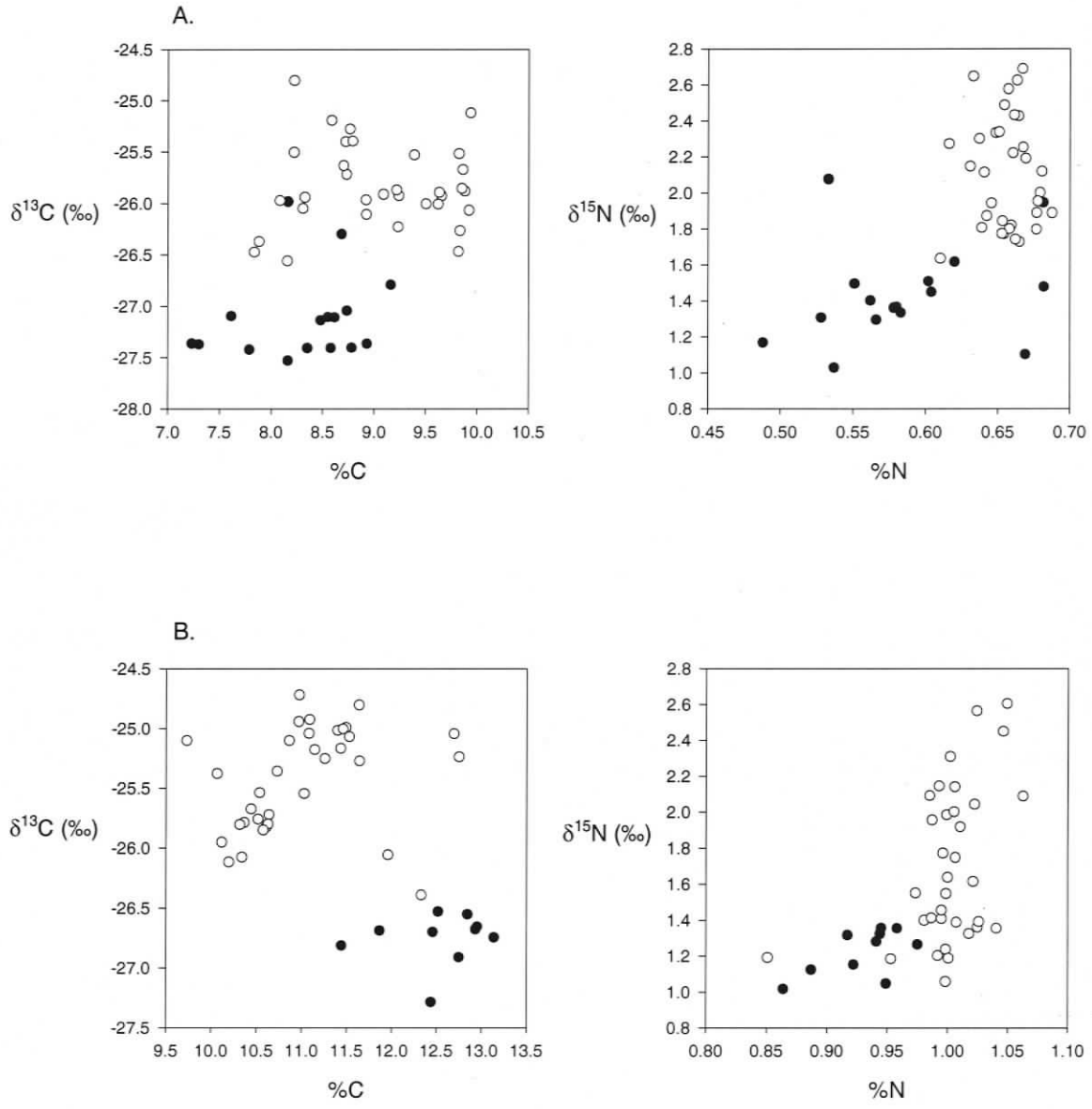

Figure 3.3: Relationships between sediment $\delta^{13}C$ and %C, and $\delta^{15}N$ and %N signatures in **A**. SOL (Sooke Reservoir), **B.** SHL (Shawnigan Lake) gravity cores, arranged as samples deposited in pre- (closed circles) and post- (open circles) disturbance periods.

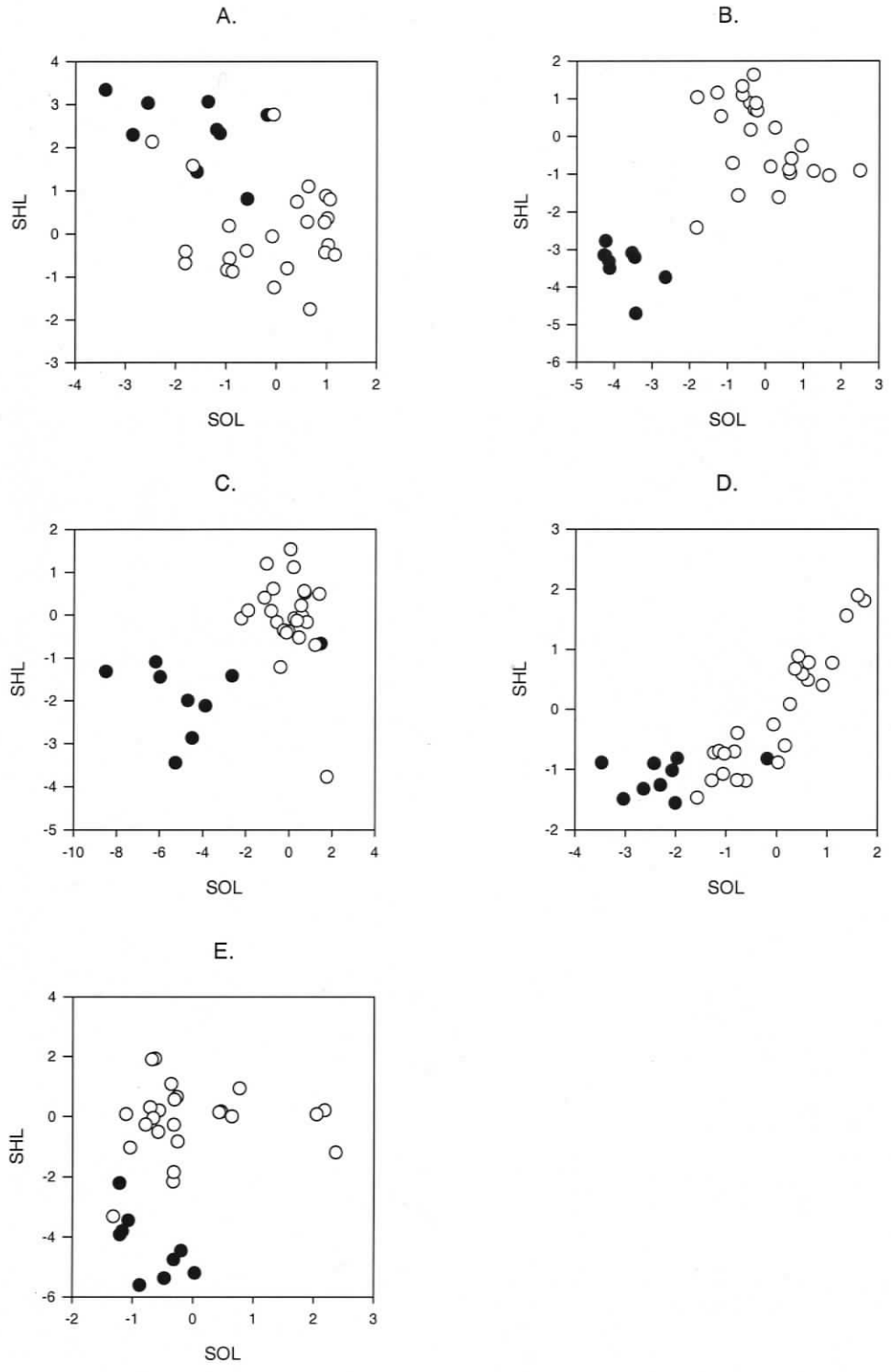

Figure 3.4: The relationship between z-scores of the five paleoindicators for SOL (Sooke Reservoir) and SHL (Shawnigan Lake). Closed circles indicate pre-

disturbance periods and open circles represent post-disturbance periods. **A.** %C, **B.** $\delta^{13}C$, **C.** %N, **D.** $\delta^{15}N$, and **E.** $\%BSiO_2$.

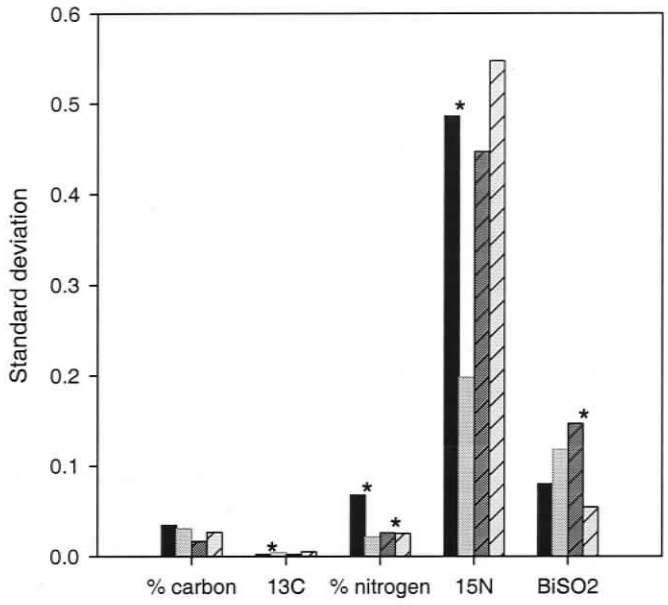

Figure 3.5: Pre- (dark bars) and post-disturbance (light bars) variability as shown by the standard deviation of log-transformed and median scaled values. Open bars indicate SOL and hatched bars indicate SHL. An asterisk above two bars indicates a statistically significant difference in the homogeneity of variances according to the Levene's Test at $\alpha < 0.05$.

Chapter 4: Relationship between phytoplankton paleo-production and diversity in contrasting trophic states

Abstract

With the increasing rate of species extinctions following anthropogenic perturbation, there has been growing interest in biodiversity research among ecologists. Although production and species richness relationship have been applied in contemporary aquatic ecological studies, none have been applied to paleoecology with contrasting trophic states. The present study explores the applicability of contemporary production and species richness relationship in high-resolution paleoecological records with low, intermediate and mid to high productive aquatic systems. Results from the study reveal that diatom species richness was positively correlated in low to intermediate productive lakes. In contrast, the relationship was hump shaped (or unimodal) in a mid to high productive system concurrent with the species diversity analyses. Contrasting relationships between diatom species richness and stable isotope records ($\delta^{13}C$ and $\delta^{15}N$) suggested that the nutrient biogeochemical cycle might play an important role in controlling species richness. From fossil pigment records I also demonstrated that the variations in algal functional group signatures were highest in the intermediate state. Collectively, these results suggest that the hump shaped (or unimodal) relationship between diatom species richness and production might be limited to high productive systems with maximum richness and diversity in intermediate states, which is also supported in contemporary studies. Moreover, fossil pigment records as proxies for algal functional groups reveal that in a mid to high productive system with intense watershed scale disturbances, community composition of algal functional groups declined favoring certain diatoms. The results of this study demonstrated the applicability of production and diversity

relationship theory in paleo-perspective and that recent watershed scale land use changes might affect the species diversity in aquatic systems.

Introduction

Ecosystem-level disturbances and changes in species and/or community structure are emerging issues in modern ecological studies. Species composition can be influenced by both natural factors (Shurin 2001; Bruno et al. 2003) and human activities (Proulx et al. 1996; Dodson and Lillie 2001). Lakes are model systems to study these types of effects on aquatic community structure. In part, because most lakes are somewhat isolated with a defined boundary and drainage areas and are easily accessible (Hoffmann and Dodson 2005). Accordingly, lake production and species richness is often used as a measure of aquatic environmental health. In the literature, two different approaches have been demonstrated to determine the relationship between productivity and species richness. One approach has examined how the contrasting ecosystem processes affect the species number (Tilman and Pacala 1993; Huston 1994) and community composition and the other focused on the affect of community composition on ecosystem functioning (Tilman et al. 1997). The purpose of the present study is to explore the relationship between algal production and diversity in a century scale timeframe with contrasting aquatic systems.

Hypothesized production-diversity relationships can be positive (Abrams 1995), negative (Rosenzweig 1971) or unimodal (Tilman and Pacala 1993) and are applicable in both species and functional group level (Weithoff et al. 2001; Weithoff 2003). Species richness in lakes might be influenced by primary production. Species richness initially increases but eventually decreases with productivity, producing a hump shaped relationship (Tilman 1982). For example, a eutrophic system with a

stressed environment typically has a lower number of species with one or two species (those adapted to the stress) having many more individuals than the other species (Dodson et al. 2000). Additionally, other factors including the lake morphological characteristics can also affect the aquatic community composition (Dodson 1992). A meta-analysis by Proulx and Mazumder (1998) demonstrated that species richness is influenced by the grazing activity and level of productivity. Diversity and species richness may also depend on the disturbance type, frequency and of generation time (Gaedeke and Sommer 1986). In the literature it has been demonstrated that, (a) species diversity is reduced in the absence or very intensive disturbances, and (b) maximum diversity at intermediate disturbance levels (Kondoh 2001). Recently, Rusak et al., (2004) assessed the richness-production relationship on a millennial scale timeframe. Although this study is considered to be the pioneer in the application of contemporary diversity-production theory on a millennial-scale, the study period was limited to higher production regimes without comparing varying trophic states.

Fossil algal remains, specifically diatoms and pigments, are confidently and consistently used in reconstructing community structure and paleoproduction in lentic systems (Leavitt and Hodgson 2001; Das et al. 2005). Additionally, diatom and pigment records in lake sediments can be used to track changes in species richness and functional group structures, respectively, responding to contrasting watershed-scale land-use changes (Quinlan et al. 2002; Itoh et al. 2003; Saros et al. 2003). The current study is based on the contemporary species richness and production relationship, to see whether similar responses can be reconstructed from fossil

remains in lake sediments responding to different anthropogenic events. In particular, I focused on the following three questions in a century scale timeframe: (1) Is the relationship between diatom productivity and species richness linear (positive or negative) or quadratic hump shaped (unimodal)? (2) Do these relationships vary with contrasting trophic states? (3) Can fossil pigments be used to reconstruct the temporal changes in algal functional groups?

Methods

Sampling locations

Watershed land use of two (Sooke Reservoir and Shawnigan Lake) of the three study lakes have been described in Chapters 2 and 3. The third lake, Elk Lake (48°31′N latitude and 123°23′W longitude) is located on the Vancouver Island, British Columbia, Canada. Sooke Reservoir is an ultra-oligotrophic lake. Shawnigan Lake is classified as oligotrophic to mesotrophic. Elk Lake is a mesotrophic lake (Table 4.1) influenced by different types of anthropogenic activities and under constant pressure from the recreational activities undertaken on and in both the lake and watershed. It has high water-residence time varied between 4.4 (McKean, 1992) to 7.5 (Nordin, 1981) years. Its drainage basin lies within the coastal Douglas fir biogeoclimatic zone, which has mild wet winters and dry summers (McKean, 1992). The most important developments influencing the lake system were the construction of the Victoria waterworks between 1873 and 1879 and the Patricia Bay Highway in the 1950s.

Sampling and sediment chronology

Sediment cores were taken from the deepest part of the lakes using a modified gravity corer (Kliza and Telmer 2001) and were extruded on site. Brief descriptions of sample collection and dating methods have been described in Chapters 2 and 3.

Sediment stable isotope characterization

The isotopic compositions ($\delta^{13}C$ and $\delta^{15}N$) of sediment samples were analyzed using a continuous flow system high-temperature elemental analyzer coupled to a DELTA^{plus} Advantage mass spectrometer. Reproducibility of duplicate analyses was $\pm 0.1‰$. Measured values for $\delta^{13}C$, are dependent of the historic isotopic signature of dissolved inorganic C when organic C is produced photosynthetically. An acidification test confirmed that inorganic C was of minor importance in the bulk sediments. Data for $\delta^{13}C$ were normalized to account for historic depletion of $\delta^{13}C$ in atmospheric CO_2, due to fossil fuel burning as recorded by fossil air trapped in ice cores (Friedli et al. 1986); this effect is termed the Suess effect. I applied the following polynomial equation (Friedli et al. 1986) to remove the Suess effect, where t is time (in yr):

$$\delta^{13}C = -4{,}577.8 + 7.3430t - 3.9213 \times 10\text{-}3t^2 + 6\ .9\ 812 \times 10\text{-}7t^3$$

The calculated time-dependent depletion in $\delta^{13}C$ since 1840 was subtracted from the measured $\delta^{13}C$ for each dated sediment section.

Diatom analysis

Sediment samples were digested and fossil diatom frustules were identified and counted following standardized paleolimnological protocols. A brief description of the digestion of sediment samples and diatom identification is as follows. To oxidize carbonate from homogenized sediment sub-samples (wet: 0.700-1.200 g), 10% HCl (~10 mL) was added and left undisturbed for 24 hours before the remaining HCl was removed by aspiration. The vials were then placed in a support rack and ~15mL of a 1:1 mixture of concentrated nitric and sulphuric acid was slowly added up to the one-half or three quarter mark on each vial. The samples were stirred and left for at least 24 hours before being placed in a water bath (~90°C) for 3 hours. On each of 6 consecutive days, the samples were stirred and aspirated down to 1 cm depth above the sediment, topped up with distilled water, stirred, and allowed to settle for at least 24 hours, until all acid was removed. A portion of the resulting slurry was then pipetted, in a series of dilutions, onto cover slips and allowed to evaporate on a hot plate. The dried cover slips were then mounted using Hyrax ® mounting medium (refractive index = 1.71). Between 300 and 500 diatoms were counted using an Olympus IMT-2 inverted microscope, at 1000x and 1500x magnification on each of the prepared slides. Diatom diversity was standardized to 300 valves count. During the counts, the diatoms were also identified, primarily following Patrick and Reimer (1966) and Cumming et al. (1995). Consecutively, the relative abundance of each species was determined by dividing the number of valves of the species encountered by the total number of valves counted on the slide. Species richness was counted as the total number of individual taxa identified in a sample.

Diversity estimate

The Shannon-Weaver index is a distribution-free measure of diversity. A narrow range of diversity index values implies minor changes in distribution, which also supports the hypothesis that 'diversity is maximal when all species have equal relative abundance (i.e., maximum number of niches occupied)'. The Shannon-Weaver diversity index, which accounts for both relative abundance as well as the total number of species in a population, has been used to estimate diatom diversity in study lake sediments (Wetzel 2001). The following equation was used for the Shannon-Weaver diversity estimate (H′).

$$H' = - \Sigma p_i \log p_i$$

Where p_i is estimated from n_i / N as the proportion of the total population of individuals (N) belonging to the i^{th} species (n_i) (Shannon and Weaver 1949).

Pigment analysis

Pigments were analyzed following the methods of Leavitt and Hodgson (2001) and Leavitt (1989) using high pressure liquid chromatography (HPLC). Pigment extraction and quantification procedures have been described in Chapter 2. Briefly, pigment extractions were performed by soaking ~100 mg of freeze-dried sediment in 5ml of degassed mixture of *acetone:methanol:water* (80:15:5 by vol.). Samples were then flushed with N_2 and stored in the dark at -20°C for 12 hours. Four mL of the extract were transferred into clean 20mL glass tubes and dried under N_2. Dried extracts were dissolved into 500 µL of injection solution (*Solvent A*: 10% ion-pairing

reagent in methanol by volume) and 500 μL of 3.2 ppm solution of *Sudan II* as an internal reference. Sediment samples were thoroughly soaked with extraction solution and washed with solvent after each decanting. The ion-pairing reagent was a mixture of 0.75g tetrabutyl ammonium acetate and 7.7g ammonium acetate in 100ml of distilled de-ionized water. One mL of dissolved extract was transferred into a brown 2ml vial, flushed with N_2 and cupped using Dionex cups. Vials were kept in a freezer until HPLC analysis. The HPLC system consisted of a DIONEX gradient pump, an AS50 Autosampler, a C-18 column (5 μm particle size; 15 cm length), and a PDA detector at 435 nm. Flow rate was 1.5 ml/min and the separation gradient was (i) isocratic for 1.5 min in 10% IPR in methanol *(Solvent A)*, (ii) a linear ramp to 100% of a mixture of 27% acetone in methanol *(Solvent B)* over 7 min and an isocratic hold for 15.5 min, and (iii) a linear return to 100% *Solvent A* over 3 min with isocratic hold for 12.5 min for column equilibration.

Pigment concentrations were quantified using equations derived from commercially available standards (DHI Water Environment). Diatoxanthin pigments representing diatom communities were used as a proxy of diatom production. All pigment concentrations were normalized to their mass per gram dry weight of organic matter ($mg \cdot g^{-1}$ OM) where organic matter content in the sediment samples were measured as loss on ignition (LOI) at 550°C for 2 hours (Heiri et al., 2001).

Before regression analysis, all variables except species richness were log transformed to normalize distributions. Because the quantified pigment concentrations were too

low and $\delta^{13}C$ values were negative, a constant ($\log_{10}[x + 1]$ for pigments and $\log_{10}[x + 30]$ for $\delta^{13}C$) were added, respectively before transformation.

Results

Changes in diatom species richness and production

Historical profiles of diatom species richness, production and $\delta^{13}C$ and $\delta^{15}N$ signatures in all three study lakes illustrate noticeable changes in recent years (Figure 4.1). In Sooke Reservoir sediment samples, an increase in species numbers was observed around 1860 (Figure 4.2). This increasing trend continued for a while and then retreated back after 1900, coinciding with diatom production and $\delta^{13}C$ and $\delta^{15}N$ signatures. In Shawnigan Lake samples, the species numbers were unchanged in pre-1920 periods, whereas an increase was observed post-1920. Species richness also coincides with the diatom production and $\delta^{13}C$ signatures for Shawnigan Lake samples. Interestingly, a decrease in diatom production and $\delta^{13}C$ signatures, with decrease in species richness, was observed in surface samples. Abrupt changes in species richness (Figs. 4.1, 4.2), diatom production, and $\delta^{15}N$ signatures were found during post-1920 periods in Elk Lake samples.

Richness-production relationship

Regression analyses indicated that the species richness-productivity relationships differed among the three systems responding to their trophic states (Figure 4.3). A hump shaped or unimodal relationship was observed for recent samples in Elk Lake.

In contrast, samples from Sooke Reservoir showed a non-significant linear relationship whereas in Shawnigan Lake a significant linear relationship was observed. When the species richness values were plotted against $\delta^{13}C$ and $\delta^{15}N$ (Figure 4.3), contrasting responses were evident in the three different systems. Species richness was weakly correlated with both $\delta^{13}C$ and $\delta^{15}N$ in Sooke Reservoir samples. In contrast, samples from Shawnigan Lake and Elk Lake showed significant positive linear relationships.

Changes in diatom species diversity

Although there were no differences in the Shannon-Weaver diversity index values during pre-disturbance regimes (pre-1900), they differ over time in individual lake as well as between lakes (Figure 4.4). Accordingly, the Shannon index values increased following the increasing productivity of individual lake. The highest values were reported both in Shawnigan and Elk Lake sediments (Figure 4.4). Interestingly, diatom diversity decreased after 1970 in the Elk Lake sediment profile.

Changes in algal functional groups

In this study, the production of different algal functional groups were reconstructed from the sedimentary fossil pigment records and were restricted to following algal functional groups: alloxanthin (cryptophyceae), diatoxanthin (mainly diatoms), lutein-zeaxanthin (chlorophyceae and cyanophyceae), canthaxanthin (nostocales cyanophyceae), echinenone (total cyanophyceae), chlorophyll *a* and pheophytin *a* (all algae). Fossil pigment records indicate an increasing trend in historical production,

from low (Sooke Reservoir), moderate (Shawnigan Lake) to high (Elk Lake) that also justifies the selection of sampling locations. The temporal profile of percent changes from natural background levels (bottom of each core and based on ^{210}Pb dates and disturbance histories) of different algal functional groups differs markedly among lakes and groups. When comparing all three lakes, the most noticeable changes were detected for chlorophyceae, filamentous cyanophyceae and overall algal productions and these changes were clearly detectable in Shawnigan Lake sediment samples (Figure 4.5). For most of the algal functional groups, the highest change occurred at intermediate disturbance (transition period between pre- and post-1900) levels, while some change at high disturbance levels was also detected. To compare the relative production contribution of algal functional groups to overall algal production, $\log_{10}$ transformed production of each of the functional groups were plotted against $\log_{10}$ overall algal production as inferred from chlorophyll *a* and all derivatives (Figure 4.6). Noticeable differences can also be seen in these plots. For both oligotrophic lakes (Sooke Reservoir and Shawnigan Lake), the relationships were significant in most cases. In contrast, for the mesotrophic system (Elk Lake), relationships were mostly scattered with the exception of diatoms and cyanophyceae, where significant correlations were present.

Discussion

Diversity-paleoproduction relationship

Lake sediments preserve fossil remains (Leavitt and Hodgson 2001; Das et al. 2005), and thus may provide a unique opportunity for evaluating the effects of production on

species richness. This study concentrated on demonstrating the relationship between paleo-production and a) diatom species richness, and b) inference of algal functional groups. The results demonstrate that the contemporary ecological hypotheses on species richness-production relationships can be applied in paleo-ecology with varying trophic states inferred from fossil diatom records and pigment remains in lake sediments.

Species richness responded to contrasting trophic states in a significant linear or hump shaped (unimodal) fashion (Figure 4.3). In Sooke Reservoir, seasonal succession following changes in water residence time might have played a key role in controlling diatom diversity and algal functional groups. Several studies have shown that algal communities during pre-disturbance periods with short water-residence times are generally dominated by diatoms and eventually, cyanobacterial communities dominate in post-distrurbance periods with variations in flushing rates (Stockner and Benson 1967; Peterson and Stevenson 1989; Perry et al. 1990). Additionally, the changes in phytoplankton diversity can also be dependent on the availability of growth limiting resources. The basic idea is that availability of elevated resources could support additional species in aquatic systems. However, the rapid colonization and resource competition by pioneer oligotrophic taxa, primarily cryptophyceae, and the highly variable immigration of other weak competitors over time following inundation, likely masked a peak in average richness along the flooding frequency gradient (Tilman 1982; Interland and Kilham 2001). The strategy that best allows species to exist under oligotrophic conditions may be one that allows

for tolerance of low nutrients (Interland and Kilham 2001). This is also evident in the relationship between species richness and $\delta^{13}C$ and $\delta^{15}N$, where a weak but positive linear response was observed. This might also be related to two different reasons. Firstly, carbon and nitrogen inputs from different sources (e.g., decomposed plant litter and catchment soil) influence stable isotope signatures differently. Secondly, contributions from denitrifying cyanobacterial communities following impoundments may have resulted in higher values of $\delta^{15}N$ (Figure 4.3). Growth limiting resource availability with contrasting flooding durations (i.e., time) (Tilman et al. 1982) might also have occurred in Sooke Reservoir.

In Shawnigan Lake, a significant linear relationship between species richness and production was observed. The result coincides with the diversity-productivity hypotheses (Dodson et al. 2000; Mittelbach et al. 2000). Species richness reached a maximum in mid-productive states. In the mid to high productive system (Elk Lake), a significant linear relationship was observed initially from the core samples. Although the species diversity increased linearly with production, the relationship between production of algal functional groups and overall algal production was only found to be significant for diatoms and cyanophytes as reconstructed from fossil pigment records (Figure 4.6). Such relationships could be related to several factors associated with either changes in food web structure and productivity (Proulx and Mazumder 1998) or competitive exclusion due to dominance by few algal functional groups (Tilman 1982). In recent years, when the disturbance levels are assumed to be higher due to increased human settlement and increased use for recreational purposes

that lead to elevated nutrient loadings (e.g., N loading), some functional algal groups could not keep pace with the exploitive competitors, resulting in declining species diversity (Huston 1994). The spatial structure may also play an important role in shaping community structure in the Shawnigan Lake ecosystem (Tilman et al. 1994; Comins and Hassell 1996; Pacala and Levin 1997). However, selective grazing pressure and exploitative competition over resources may eventually lead to loss of weak competitors resulting in loss of diversity. It is quite problematic to explain such processes from paleoecological data. If one considers longer time scales, nutrient depletion often induces shifts in community structure (e.g. from diatom dominated systems to picoplankton), favoring species (e.g. cyanophytes) that are more efficient at scavenging the limiting nutrient or do not require it (Tilman et al. 1994).

The watershed disturbances and relatively high productive state in Elk Lake may have contributed to the change in linear relationship between species richness and productivity into a hump-shaped curve. Responses to changes in higher trophic levels and grazing activity may also play a key role in controlling species richness in Elk Lake (Proulx and Mazumder 1998). As predicted by food web theory, the responses to increased productivity levels at the base of the food chain are manifested most strongly in the population densities, biomass and size structure of the top trophic level (Abrams 1995; Proulx and Mazumder 1998). Relative changes in available nutrient concentrations may create conditions conducive to further proliferation of cyanobacteria along with other algal communities (Smith 1983; Kotak et al. 1995; Watson et al. 1997; Downing et al. 2001). When considering all three low, mid and

mid to high productive systems demonstrated in this study, it is evident that in addition to resource competition, light limitation relating turbidity may play a key role in contributing to changes in the composition of phytoplankton communities (Leibold 1997).

Additional analyses indicate that diversity differs in contrasting trophic states. The greater variability in diversity during post-1900 periods in the study lakes might be related to alterations in nutrient loading in the water bodies. In all three cases during post-1900 periods, the relative abundance of both nutrient rich species *Tabellaria fenestrata* and *Asterionella formosa* increased (data not shown) compared to other oligotrophic species (e.g., *Cyclotella* sp.) over time resulting in changes in Shannon diversity index values. Additionally the narrow range of diversity index values in Sooke Reservoir samples implies that the abundance of diatom species might have changed over time, but the species evenness values were always in approximately the same proportions. In contrast, higher trophic states resulted in higher diversity ranges, which is evident in the Elk Lake sediment profile. Overall, the elevated trends are evident in Shawnigan and Elk Lake sediment diatom diversity profiles. A decrease in the diversity in recent sediment samples of Elk Lake (Figure 4.4) reflects the rapid growth rate of both *T. fenestrata* and *A. formosa*. Although a decrease in abundance of *Cyclotella* sp. was detected, the growth rate of *T. fenestrata* and *A. formosa*, along with other nutrient rich species was more rapid resulting in decreases in diversity.

The overall results from this study supports that the contemporary diversity-production hypotheses can also be applied to paleoecological research (Rusak et al. 2004). However, the question still remains unanswered as to whether these relationships could be related to relative disturbance levels (i.e., watershed development). Here I demonstrated the changes in algal diversity reconstructed from fossil pigment records with contrasting watershed land use histories. In ecosystem ecology, the idea that disturbance can help maintain species coexistence is largely based on the assumption that, without disturbance, competitively dominant species tend to monopolize resources such as space and food, and consequently drive less competitive species to local extinction (Tilman et al. 1994). Thus, disturbance might be regarded as a mediator in competitive assemblages, operating as a reset mechanism whereby populations of competitive dominants are periodically curtailed and resources are released for less dominant species to maintain their populations (Tilman et al. 1994; Pacala and Levin 1997). This is supported in the data from the study lakes. Temporal profiles illustrated that species richness in all three study lakes were likely to follow natural variability during low disturbance periods. Species diversity may increase at low levels of watershed disturbance due to limiting nutrients in lake (Rosenzweig). In contrast, species diversity may be reduced by eutrophication and contamination along with species competition during high levels of watershed disturbances (Wilson et al. 2003).

The results of this study differ from the previous report (as in Rusak et al. 2004), where it has been demonstrated that temporal profiles of diversity-production

relationship would differ over millennia scale compare to smaller scale studies. This could be due to two separate reasons. Firstly, the reported study was limited to lakes with high primary productivity regimes, and secondly, the study lakes were saline in nature. Therefore, more study lakes combining different trophic states and limnological regimes would help to justify whether the diversity-production relationship differs over spatial and temporal scales.

Conclusion

Watershed disturbance and the subsequent habitat destruction is a major threat to biodiversity in aquatic systems. Biodiversity could also be affected by varying trophic status. I compared the results at three different limnological regimes with contrasting watershed disturbance histories: low (ultra-oligotrophic), mid (oligotrophic to mesotrophic), and mid to high (mesotrophic) productive systems. Results from this study reveal that a unimodal relationship could be limited to mid to high productive systems at high levels of watershed disturbance. Additionally, with increased disturbance and primary production, diversity of algal functional groups would decline favoring certain diatoms and filamentous cyanobacterial growth. This suggests that the phytoplankton diversity could also govern overall primary production.

Tables

Table 4.1. A comparison of selected limnological variable and parameters of the study lakes.

Lake name	pH	DOC ($\mu g \cdot L^{-1}$)	TP ($\mu g \cdot L^{-1}$)	TN ($\mu g \cdot L^{-1}$)	Chl *a* ($\mu g \cdot L^{-1}$)
Sooke	6.8	2.5	4.6	18.2	0.5
Shawnigan	7.0	3.2	6.0	75.6	1.7
Elk	8.2	5.4	17.6	401.5	3.5

Figures

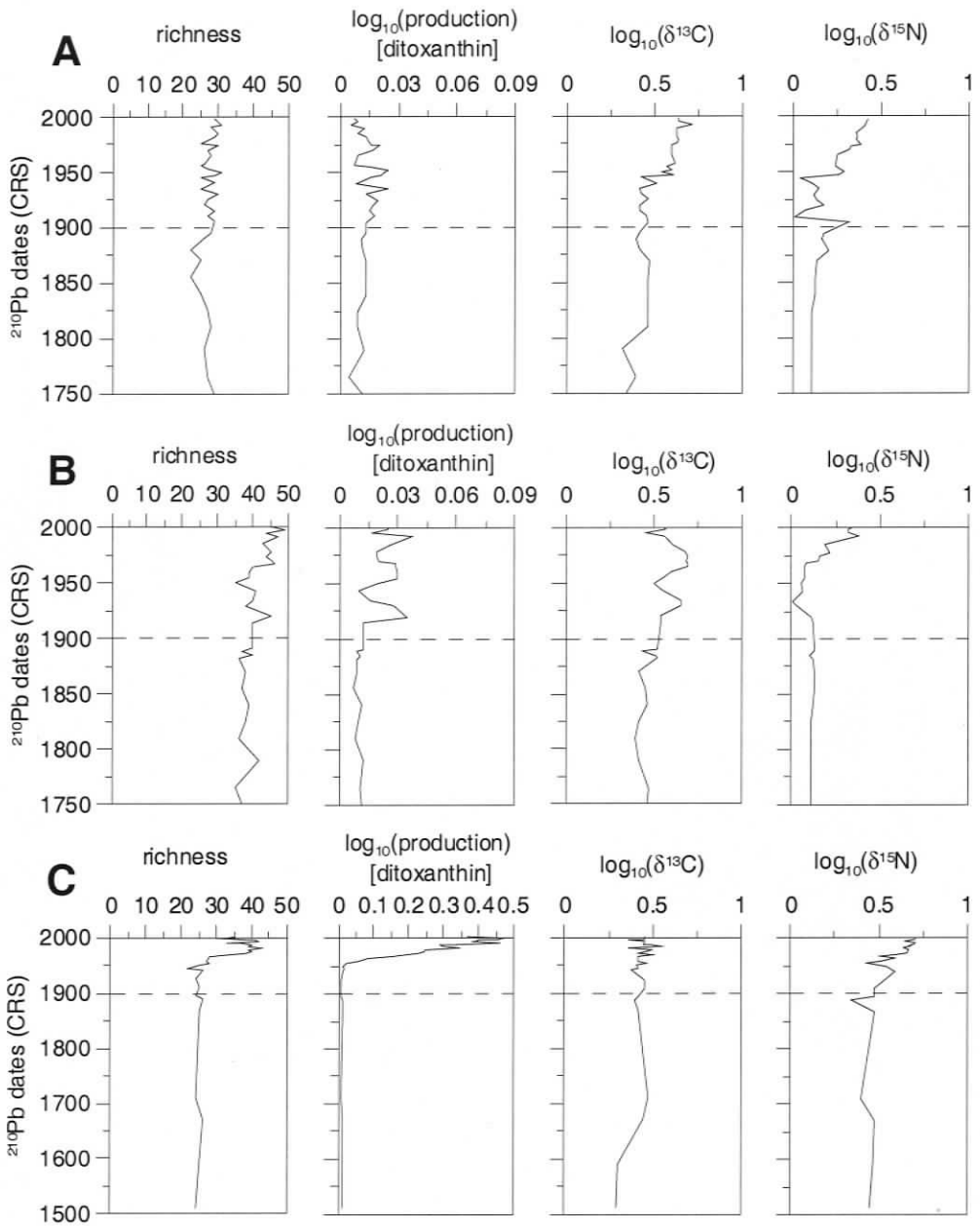

Figure 4.1: Historical profile of diatom species richness, diatom production and $\delta^{13}C$ and $\delta^{15}N$ signatures in the study lakes (A. Sooke Reservoir, B. Shawnigan Lake, C. Elk Lake). Dating records were based on ^{210}Pb activity and using the constant rate supply (CRS) model. Vertical dashed line separates pre- (pre-1900) and post-disturbance (post-1900) regimes.

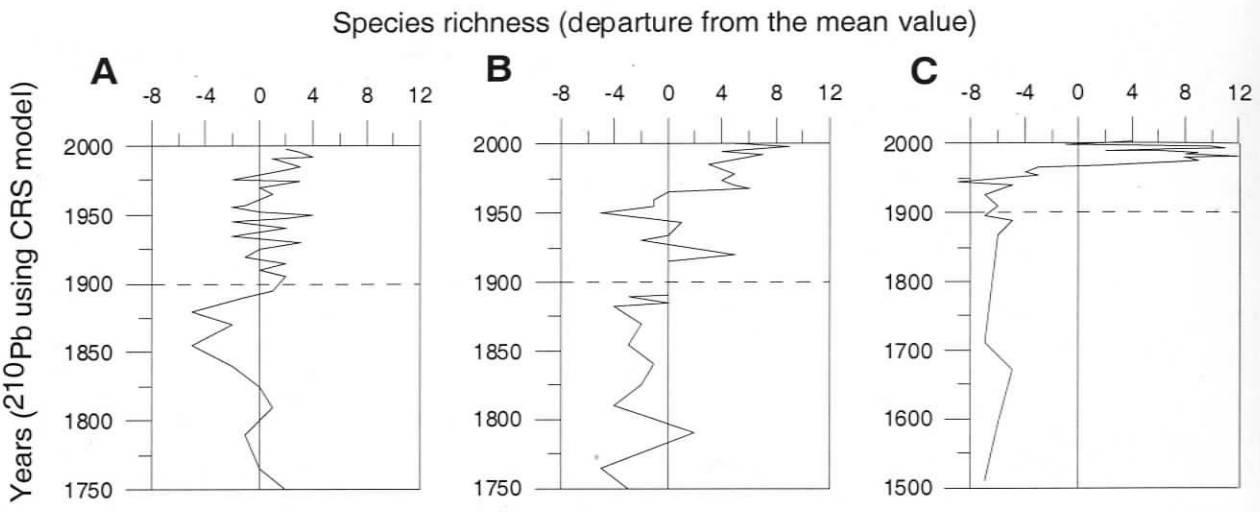

Figure 4.2: Species richness of diatom, plotted as departures from the mean value for each series, for the three study lakes (A. Sooke Reservoir, B. Shawnigan Lake, and C. Elk Lake). Vertical dashed line separates pre- (pre-1900) and post-disturbance (post-1900) regimes.

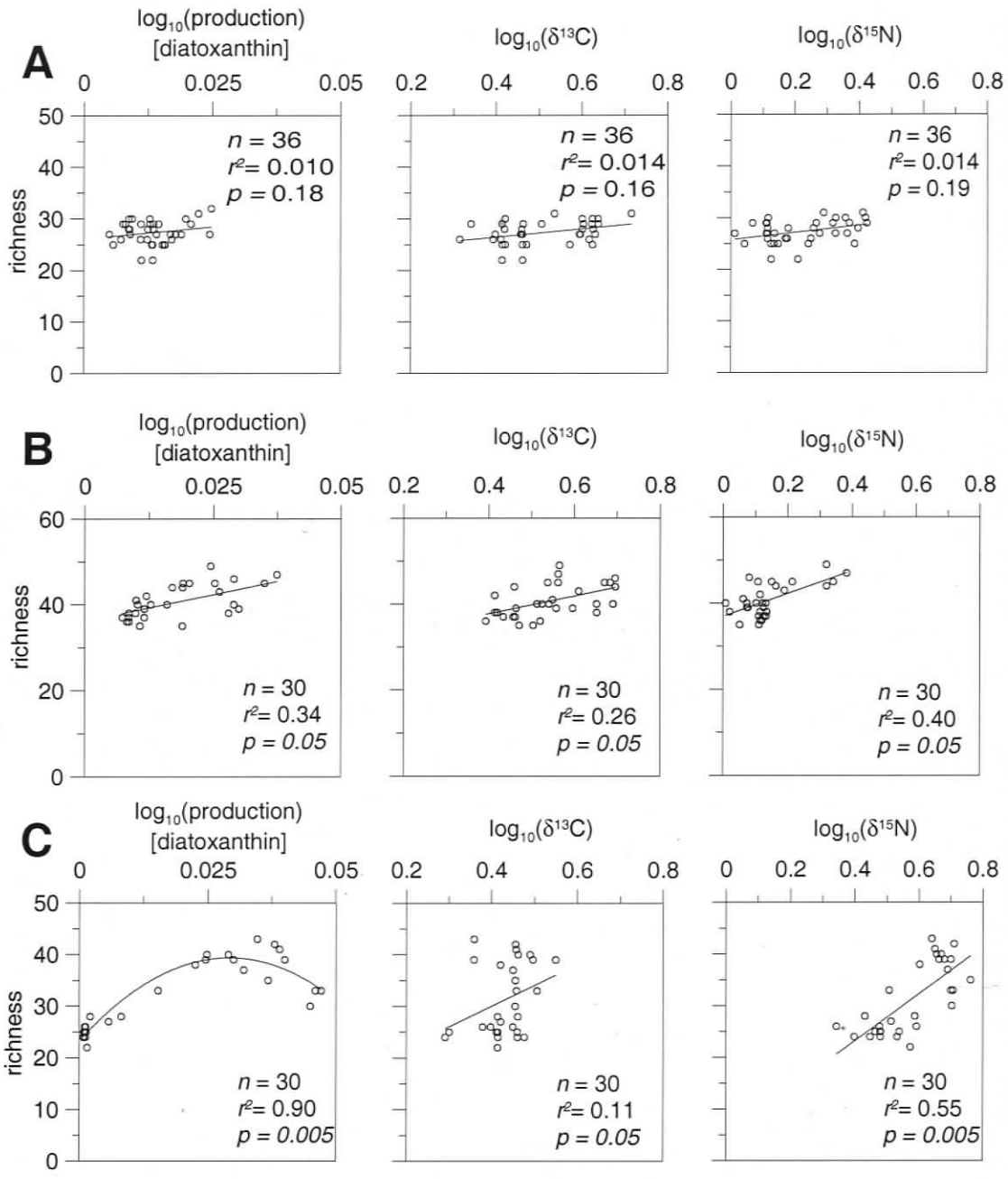

Figure 4.3: A regression analysis of species richness as a function of log (production), log ($\delta^{13}C$) and log ($\delta^{15}N$) for the study lakes (A. Sooke Reservoir, B. Shawnigan Lake, C. Elk Lake).

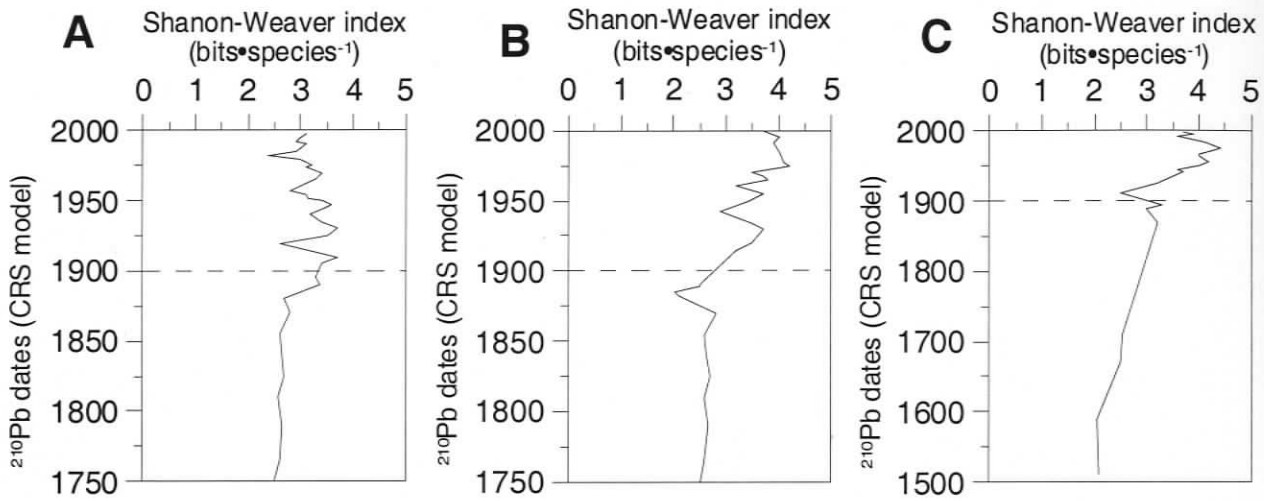

Figure 4.4: Shannon-Weaver diatom diversity estimates over time in the three study lakes (A. Sooke Reservoir, B. Shawnigan Lake, C. Elk Lake). Vertical dashed line separates pre- (pre-1900) and post-disturbance (post-1900) regimes. Years on vertical axis were based on the ^{210}Pb and constant rate supply (CRS) modeled dates.

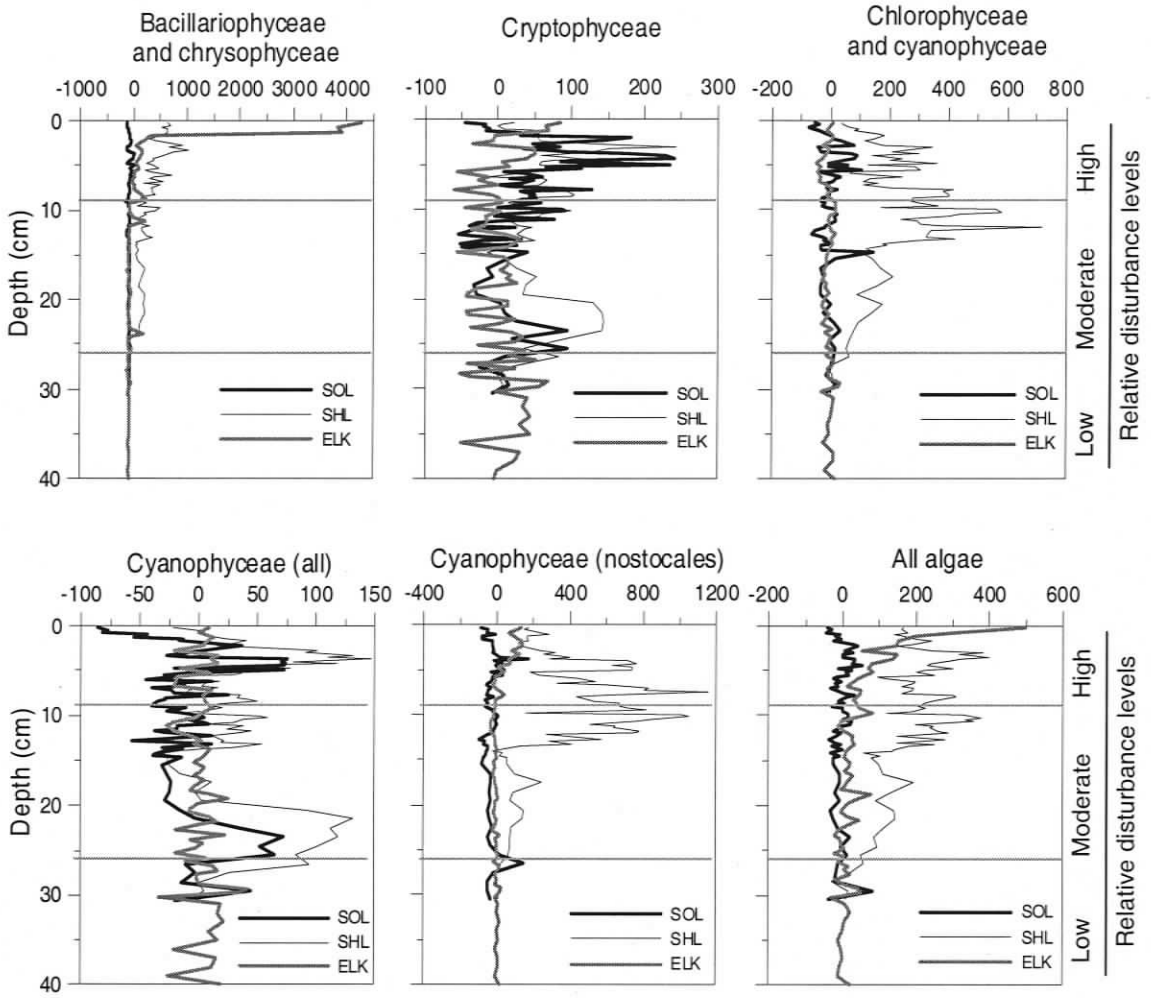

Figure 4.5: Sedimentary profiles of percent change in production of algal functional groups compared with natural background levels in the study lakes (SOL = Sooke Reservoir, SHL = Shawnigan Lake, C. Elk Lake). Natural background levels and relative disturbance levels (low, intermediate and high) were based on the ^{210}Pb modeled dates and major historical events. This figure is a modified version of Figure 2.4 with added information from Elk Lake.

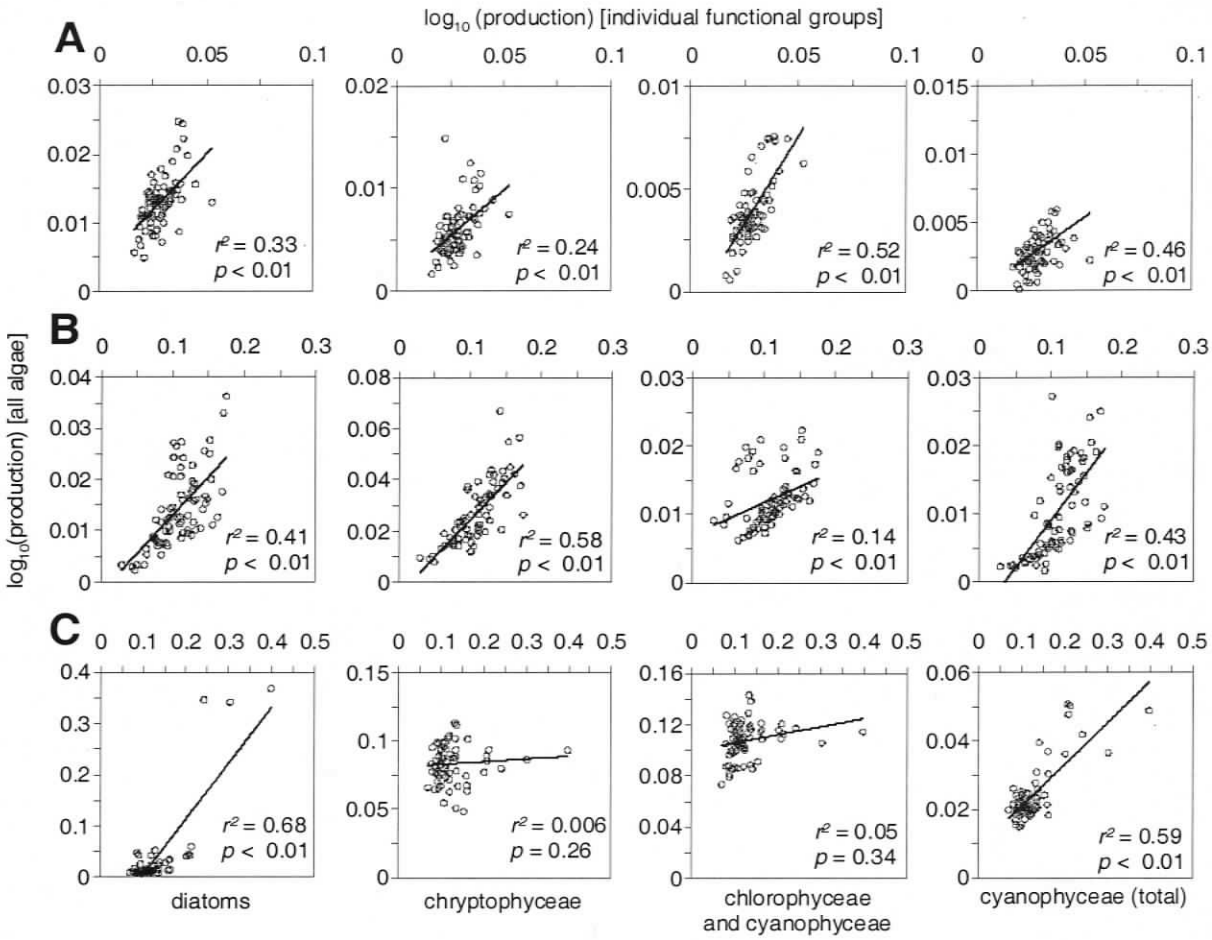

Figure 4.6: A regression analysis of log (overall algal production), inferred from total chlorophyll *a* and all derivatives concentration, as a function of log (production) for individual algal functional groups from studied lake sediment samples (A. Sooke Reservoir, B. Shawnigan Lake, C. Elk Lake).

Chapter 5: An alternative approach to reconstructing organic matter accumulation with contrasting watershed disturbance histories from lake sediments

Abstract

Although, a number of proxies, including carbon to nitrogen ratio (C:N) and stable isotopes ($\delta^{13}C$ and $\delta^{15}N$), have been used to reconstruct organic matter (OM) profiles from lake sediments, these proxies individually or in combination cannot clearly discriminate different sources. Here I present an alternative approach to elucidate this problem from lake sediments as a function of watershed-scale land-use changes. Stable isotope signatures of defined OM sources from the catchment and surface water of the study watersheds, Shawnigan Lake (SHL) and Elk Lake (ELL), were compared with sedimentary proxy records. Results from this study reveal that terrestrial inputs and catchment soil coinciding with the watershed disturbance histories probably contributed to recent trophic enrichment in SHL. In contrast, cultural eutrophication in ELL was partially a result of input from catchment soil (agricultural activities) with significant input from lake primary production as well. Results were consistent in both a source separation program (IsoSource) and discriminant analysis.

Introduction

Organic matter (OM) preserved in lake sediments can provide key information on lacustrine nutrient dynamics as a function of historical watershed scale land use change (Meyers 1994; Meyers et al. 2001). Changes in land use within watersheds, commonly involving the conversion of forest cover to agricultural land or urban areas, result in an increased input of nutrients to aquatic environment (Peterjohn and Correll 1984; Rhodes et al. 2001), which may lead to changes in community structure (Harding et al. 1998; Gergel et al. 1999; Ometo et al. 2000) in the aquatic ecosystem. Additionally, land use influences surface permeability and flow velocity, which are of critical importance for point-source pollution of a watershed in the event of flooding (Roo et al. 2001). With the increasing threat to global freshwater resources it is now crucial to have information on the dominant stressors and changes in OM sources accumulating in water bodies for watershed and water resources management. Long-term monitoring data, which are rare or absent for most lakes, become essential in assessing the rate and magnitude of nutrient enrichment, thus providing a context for proper water-quality management. Paleoecological analyses of sediment cores can generate robust data needed to track historical changes in water quality as a function of land use changes over the time span of decades to centuries (Garrison and Wakeman 2000; Bradbury et al. 2004; O'Reilly et al. 2005).

Despite the potential complexity of variable sources and diagenetic alteration of source signals, including ammonification, nitrification and denitrification (Matson and Brisnon 1990; Thornton and McManus 1994; Cifuentes et al. 1996; Yamamuro

2000; Graham et al. 2001), stable isotopes ($\delta^{13}C$ and $\delta^{15}N$) can provide information on paleoproductivity, trophic structure and food web dynamics associated with land use changes (Brenner et al. 1999; Alin et al. 2002; Lawson et al. 2004; Andrews et al. 1998). Additionally, carbon to nitrogen ratios (C:N) in lake sediments are often used to trace OM sources. Increases in C:N ratio of sedimentary OM relative to the source, over time or with depth in a core, have been interpreted as indicative of preferential loss of nitrogen (N) (Köster et al. 2005; Gälman et al. 2008), while small changes over time suggest that C and N are mineralized or preserved at the same rate. Decreases in C:N ratio, which have also been observed in some lake sediments, have been used to explain the absorption of organic or inorganic N onto silicate clay surfaces (Macko et al. 1993) or the incorporation of N by bacteria in decaying OM (Cifuentes et al. 1996). However, if small changes in C:N are observed between living (sources) and decaying OM pools, then this elemental ratio may be utilized as a tracer of OM sources. Most often the mixed contribution of different OM sources can create a complex situation when defining sources of organic matter. As a result, the previous paleoecological studies on OM source detection have often been limited to discriminating terrestrial from aquatic contributions (Macko et al. 1993; Andrews et al. 1998; Brenner et al. 1999). Consequently, a major constraint of using C:N ratios, $\delta^{13}C$ and $\delta^{15}N$ in OM accumulation reconstruction studies is that these proxies cannot clearly discriminate source changes individually or in combination of multiple indicators.

Recently, it has been demonstrated that the IsoSource mixing model could be an alternative source detection technique and has been applied in contemporary (Philips and Gregg 2003; Hall-Aspland et al. 2005) and paleo-human dietary analyses (Philips et al. 2005) using stable isotopes ($\delta^{13}C$ and $\delta^{15}N$). This study explores whether a similar approach could be applied to paleoecological study in reconstructing changes in OM accumulation pertinent to contrasting disturbance histories from lake sediments. This can be explained by mixing between known and well defined present OM contributing end member sources and by comparing with signatures from sediment archives.

To address this objective, two study lakes with contrasting limnological regimes (oligotrophic and eutrophic) were selected. I conducted a field source detection study to (a) identify and define the OM source end members surrounding each watershed, (b) quantify source signatures for $\delta^{13}C$, $\delta^{15}N$ and C:N ratio, and compare with sample signatures, (c) apply the IsoSource program (a source separation program) and discriminant analysis to define historically dominated OM accumulating sources from the lake sediment samples. In this study, I also tested the hypothesis that historically dominated OM accumulating sources would be pertinent to contrasting watershed land use histories.

Materials and methods

History of study watersheds

Description of the study lakes was given elsewhere (Chapters 2, 3 and 4). Briefly, both Shawnigan Lake (SHL) (48°33′N latitude and 123°42′W longitude) and Elk Lake (ELL) (48°37′N latitude and 123°38′W longitude) are located on southern Vancouver Island, British Columbia, Canada. Before the end of nineteenth century, SHL was an untouched wilderness. The Salish Indians used the area for hunting and fishing, and the watershed was not opened up for development by European settlers until 1862, when the Goldstream trail was created between Victoria and Nanaimo for wagon travel (Gibson 1967). Settlement was fairly limited until 1886 when the first railway was built through the area. Significant watershed disturbance began due to logging in 1891 with the building of SHL's first sawmill. By 1908, the entire shoreline had been logged (Nordin and Mckean 1984). SHL became a popular recreational area soon after. The first permanent human settlement began on the shoreline of SHL around 1910 and since then the population has been increasing steadily. Today there are over 6000 permanent residents in the watershed, and the shoreline is extensively developed.

In the historical records, ELL first appeared on a Hudson Bay Company map published in 1855. The most important developments influencing the lake system were the agricultural activities in the northern part of watershed, construction of the Victoria waterworks between 1873 and 1879 and the Patricia Bay Highway in the 1950's. Catchment vegetation types and climate are similar to SHL. With regards to

the different hydrological changes, 1993's Natural Resource Inventory of Elk/Beaver Lake and Bear Hill Regional Parks contains a comparison of the situations in 1859 and 1982. It concluded that the principal hydrologic features that were dramatically altered since the end of the 19th century were (a) the surface area expanded 21%, from 184 to 223 hectares, (b) the shoreline perimeter increased nearly 19%, from 7920 to 9390 metres, and (c) most notable was also the disappearance of many small streams. The disappearance of small streams can probably partly contributed to the construction of the highway, and the maintenance of the recreational areas and trails around the lake shore (CRD 1983). In 1872, ELL was recommended as Victoria's main domestic water source by Thomas Buckley, the provincial government's chief surveyor (CRD 1983). Between 1873 and 1920 the City of Victoria used the lake system as a source of domestic water. By 1908, the water demand in Victoria was in excess of 9 million L per day and the ELL supply soon became inadequate to meet the needs of the city's population. In 1914, the lake was abandoned as city water supply source, but remained in local use until 1920. In 1942, a pumping and filtering station was established to supply water to the Patricia Bay Air Force Base. The system was turned over to the Municipality of Central Saanich in the late 1950's with the proviso that water be supplied to North Saanich, Sidney and Swartz Bay Ferry Terminal (Oliver 1972). The supply was augmented over this period by wells and, by 1976, ELL supplied only 30-50% of the supply to the north part of the Saanich Peninsula (Brown et al. 1976; Comeau 1976). In 1977 the Greater Victoria Water District extended its pipeline to the north part of the peninsula and ELL ceased to be

used as a water supply (Nordin 1982). For the last 25 years, ELL has primarily functioned as a recreational lake.

Limnological description of study sites

The study lakes lie within the Insular and Coastal Mountain Limnological region of south-eastern Vancouver Island (CRD 1999). SHL is classified as oligotrophic (4.9 $\mu g \cdot L^{-1}$ for TP and 1.3 $\mu g \cdot L^{-1}$ for chlorophyll *a*) with a total catchment area and surface area of 69.4 km^2 and 5.5×10^6 m^2, respectively (Nowlin et al. 2004). It is monomictic in nature, and becomes thermally stratified usually by May. It is fed through the major inflow of Shawnigan Creek and has a moderate residence time (~ 2 yrs). The bedrock of most of the watershed is of Devonian origin with part of the Wark and Coquitz Gneiss Complexes (Barraclough 1995; CRD 1999). The catchments are characterized by Western Hemlock stands interspersed with Coastal Douglas Fir and Western Red Cedar (Barraclough 1995; CRD 1999). The climate in this area is characterized by mild winters and cool summers due to the moderating influence of the ocean.

ELL is a meso-eutrophic lake (14 $\mu g \cdot L^{-1}$ for TP and 4.5 $\mu g \cdot L^{-1}$ for chlorophyll *a*) (McKean 1992) influenced by various anthropogenic activities and is under constant pressure from the recreational activities. It has a total catchment area and surface area of 11.5 km^2 and 2.46×10^6 m^2, respectively with a residence time between 4.4 (McKean 1992) and 7.5 (Nordin 1982) years.

Source end-members

Organic matter source-end-members were selected within each watershed boundary, and includes pooled catchment soil (e.g., agricultural, garden, cattle farm, barren land and forest), terrestrial vegetation (mainly leaves), stream sediment, littoral vegetation and particulate organic matter from the water column (POM > 200 μm). POM was collected every two weeks (April – November, 2005) from the epilimnion and metalimnion using a 6-m section of Tygon tubing and a vertically oriented Niskin sampler, respectively. Samples were filtered at least 20 liters of lake water though a 200-mm Nitex mesh and then backwashed the POM onto precombusted (550°C for 1 h) 25-mm Whatman GF/C filters. Filters were dried overnight at 60°C and packaged in tin cups for isotope analysis. Vegetation samples (living and senescent) were rinsed to remove unnecessary debris. All end-member samples were freeze-dried, ground and homogenized before further processing for stable isotope analysis. Results from individual source signatures from each study watershed were combined together and compared with each sediment profile separately.

Sampling and sediment chronology

Sediment core was taken from the deepest part of the lakes using a modified gravity corer (Kliza and Telmer 2001) and extruded on site. Sampling and dating techniques were described elsewhere (Chapter 2).

Stable isotope characterization

The isotopic compositions ($\delta^{13}C$ and $\delta^{15}N$) of all samples were analyzed using a continuous flow system high temperature elemental analyzer coupled to a DELTA^{plus} Advantage mass spectrometer. A brief description has been given in Chapter 3.

IsoSource: source separation program

IsoSource version 1.2 is a Visual Basic® program created by Robert Gibson (Computer Sciences Corp.) and described in (Philips and Gregg 2003) was used for source separation (http://www.epa.gov/wed/pages/models/isosource/isosource.htm). Briefly, the user needs to input isotopic signatures of the different end member sources and the sediment sample (mixer) along with the desired source increment and the mass balance tolerance. The program is designed to use isotopic signatures to determine the range of feasible source contributions to a mixture when there are too many sources to allow a unique solution (>$n+1$ sources when n isotope signatures are used). I followed the '*a priori source aggregation*' technique as given in (Philips et al. 2005). All source end members were classified into four broad categories: catchment soil (a), terrestrial vegetation (b), littoral vegetation (c), and POM (d). A typical formulation using two isotopic signatures ($\delta^{13}C$ and $\delta^{15}N$) to partition the contribution (f) of four sources (a, b, c, d) to a mixture sample (m) is

$$\delta^{13}C_m = f_a\delta^{13}C_a + f_b\delta^{13}C_b + f_c\delta^{13}C_c + f_d\delta^{13}C_d$$

$$\delta^{15}N_m = f_a\delta^{15}N_a + f_b\delta^{15}N_b + f_c\delta^{15}N_c + f_d\delta^{15}N_d$$

$$\text{and, } 1 = f_a + f_b + f_c + f_d$$

Relative contributions of each source were examined with small increments (1%) and small tolerances (0.1%) as suggested by (Philips and Gregg 2003). For analyses illustration purposes, specific values were selected from the each source contribution frequency in histograms rather than looking at the single value (i.e., mean) (Philips and Gregg 2003). Historical source contributions of each end members were compared with the historical land use records in each watershed.

Discriminant analysis

Discriminant analysis is a classification technique that can be used to place an unknown case into one of the groups. Theoretically, every individual source in the population must have an equal chance of being included in the mixer sample. Discriminant analysis works by creating a new variable that is a combination of the original variables, which is often termed as factors. This is done in such a way that the differences between the predefined groups are maximized. A discriminant analysis was run to re-examine the source contributions comparing pre- (pre-1900) and post-disturbance (post-1900) samples using SYSTAT® for Windows® version 10.2. The placement of the pre- and post-1900 samples were plotted passively over the reference signatures based on their respective composition of $\delta^{13}C$, $\delta^{15}N$ and C:N.

Results

Sediment geochemical signatures

Sedimentary isotopic profiles indicate a distinct separation of $\delta^{13}C$ and $\delta^{15}N$ signatures during pre- and post-disturbance periods in both study lakes (Figure 5.1). In SHL sediment samples, the mean $\delta^{13}C$ and $\delta^{15}N$ signatures increased by 1.3‰ and 0.5‰ in post-1900 periods respectively, when compared to pre-1900 levels. The mean $\delta^{13}C$ and $\delta^{15}N$ signatures increased in ELL samples by 2.3‰ and 1.0 ‰ respectively, during post-disturbance (post-1900) periods compared to pre-disturbance regimes. Consequently, the C:N ratio also differs in pre- and post-1900 periods in both study lake sediment profiles, and was particularly evident in ELL samples.

End member isotopes

All four defined end-member (as mentioned in methods section) $\delta^{13}C$ signatures were plotted with C:N ratio to extract the cluster clouds for each source. The C:N ratio was applied instead of $\delta^{15}N$ signatures (not shown) due to the $\delta^{15}N$ labile nature and because different end member signatures of $\delta^{15}N$ overlapped with each other and it was hard to distinguish each source signature clearly. All source signatures clustered separately as expected (Figure 5.2). All four OM accumulating sources, except terrestrial vegetation, showed considerable spread (~2‰) in $\delta^{13}C$ signatures among source materials.

Sedimentary OM sources

Before defining the individual contributions of each OM source in sediment samples, all samples in each lake were separated into two broad groups, pre- and post-disturbance regimes. Three independent approaches were taken when defining sample OM sources in both study lakes. Firstly, sample signatures ($\delta^{13}C$ and C:N ratio) were compared with that of the raw source signatures (Figure 5.3). Secondly, a source separation program (IsoSource) was used to discriminate different source contributions in the sediment samples (Figure 5.4). Lastly, a statistical analysis (discriminant analysis) was run to compare the source contribution results from other approaches (Figure 5.5).

Although the first approach was able to distinguish the major contributions of the two different sources (pre = littoral vegetation and post = catchment soil) with clusters for pre- and post-disturbance sample groups in ELL sediment samples, it was unable to do the same for SHL samples. In contrast, after the second approach of applying the source separation program (IsoSource), the relative contribution of individual OM sources both in ELL and SHL sediment samples were clearly defined (Figure 5.4). Ranges of all possible combinations of each source contribution (grouped in pre- and post-1900 periods) are shown in Table 5.1. The last approach, using discriminant analysis, resulted in separate clusters for each OM source when factor-1 scores with factor-2 scores were plotted against each other (explanations of factors given in methods section). Additionally, when the sample signatures (factors) were plotted in

source signature clusters, pre- and post-disturbance samples were grouped separately indicating the robustness of the methods in tracking OM sources.

Discussion

For water management decisions it is quite crucial to assess the dominant OM accumulating sources in freshwater systems. In this study it has been demonstrated an alternative approach in paleo-ecological perspective to reconstruct historical OM sources accumulation as a function of watershed-scale land-use change.

The $\delta^{13}C$ and $\delta^{15}N$ records in the SHL uppermost sediments (i.e., post-settlement periods) showed subtle opposite trends (Figure 5.2). This might be due to recent human settlement and land-use changes along the shoreline of SHL resulting in decreased carbon loading and enhanced nitrogen loading, or changes in the sources of nitrogen loading due to anthropogenic activities. In contrast, markedly elevated signatures for both $\delta^{13}C$ and $\delta^{15}N$ were observed in recent samples from the ELL sedimentary profiles. This enrichment of stable isotope signatures might be due to intense watershed disturbances attributable to septic outfalls, agricultural activities, road building or recreational uses. (Arbuckle and Downing 2001).

The results also show that C:N ratio in lake sediments can be used to elucidate a generalized reconstruction of historical accumulating sources (terrestrial *vs.* aquatic) of sedimentary OM (Sollins et al. 1984; Aller 1994; Meyers 1994; Meyers et al. 2001). The C:N ratio in both study lakes indicated that terrestrial sources were the

main contributor of the elemental nutrient inputs into both water bodies (Figure 5.2). Increased nitrogen loading from catchments, due to watershed disturbances in the post-disturbance period, were reflected in the C:N ratios of both lakes (Meyers 1994; Meyers et al. 2001). This is quite evident when comparing sample profiles with the source isotope signatures. Although it is impossible to analyze the limnological response of the ELL system, nutrient inputs from watershed agricultural activities might have played a partial role in the enrichment of primary production, in addition to the higher water residence time, depth of the lake and other factors including natural variability. This is also evident while comparing the sediment isotope signatures in upstream and downstream sediment samples from tributary streams (data not shown). Elevated isotopic signatures in downstream sediment were observed, which indicated that nutrient enrichment was accumulating from the surrounding agricultural activities and cattle farms along with input from lake algal production. In SHL, recent increases in catchment soil inputs and terrestrial vegetation suggest on-going watershed disturbances from human settlement and recreational uses. Fertilizer run-off from the lawns of houses built on the shoreline or adjacent to inflow streams of this lake might also be one of the nutrient contributors into the water body. Nonetheless, neither stable isotope and C:N ratios, nor the results from the comparison with source signatures, can give information on the contributions of each accumulating source in both study lake sediment samples (Figs. 5.1, 5.3 and 5.5). As an alternative approach, the relative contribution of each OM accumulating source was explained by applying IsoSource, a source separation program (Figure 5.4). Results revealed that the primary OM accumulation from

terrestrial vegetation and catchment soils from the watershed that might have contributed partially in recent trophic enrichment in SHL. In contrast, recent elevated nutrient accumulation in ELL might be partially from the input from catchment soil (agricultural activities) with significant input from lake primary production (POM) as well. Results and patterns generated by both IsoSource and discriminant analyses were consistent, illustrating the robustness of the methods developed from this study. Recent reductions in watershed tree cover contributed to the sedimentary organic matter pool concurrent with the historical land-use changes in both watersheds and are particularly evident in ELL sediment samples. Despite the possibility of diagenetic alterations of fossil organic matter and potential loss of some OM sources from the watershed, the end member source detection approach could give important insights into detecting historical OM accumulation and, therefore, into managing lake water quality.

Given the burgeoning problems of land use change and the increasing threat to global freshwater resources, it is critical to trace watershed disturbances and subsequent alterations in accumulation of organic matter and impacts on aquatic ecosystems (Houghton et al. 1999). From the perspective of contrasting land use patterns, elevated nutrient inputs from agricultural and cattle farm activities in the watershed might have played a vital role in the recent trophic enrichment of ELL, where modern agriculture practices are one of the major contributors to water contamination (Van Leeuwen et al. 1999; Arbuckle and Downing 2001). Increasing conversion of land cover for agricultural use (mostly organic farming and livestock) near watersheds has

resulted in increasing nitrogen loading in groundwater and surface water, most notably in the past three decades (Van Herpe et al. 2002). Although point source pollution of watersheds from agriculture can be substantial, non-point source pollution from agriculture is the most significant contributor in nitrate loss to the aquatic environment. The major cause of the increasing nitrate levels in drinking water sources is changes in land-use patterns, including the increased use of nitrogenous fertilizers close to watersheds (Soares 2000). Conversely, human settlement can still lead to minor nutrient enrichment compared to the above-mentioned activities, which can be seen in SHL sedimentary profiles. Collectively, it can be stated that contrasting watershed land uses have divergent effects on OM accumulation in lakes. Conversion of the watershed to agricultural land in ELL has had a greater negative impact on lake water quality following elevated organic matter loadings when compared to human settlement on the shoreline of SHL watershed.

Conclusion

Regardless of the motives for watershed conservation, it is important that watersheds are monitored for water quality and to limit the effects of land use change in the vicinity. The OM source-detection approach that was developed in this paper can be a robust tool in defining dominant OM accumulating sources with contrasting watershed-scale disturbance histories when combined with the IsoSource source separation program and therefore, can be used for watershed management decisions to sustain better water quality.

Tables

Table 5.1: Ranges of all possible combinations of each source contribution (statistical output from IsoSource) grouped in pre- (pre-1900) and post-disturbance (post-1900) samples. Years are based on ^{210}Pb data. Values in parenthesis are the mean with ± standard deviation. (SHL = Shawnigan Lake, ELL = Elk Lake, POM = Particulate organic matter, 41 - 200μ).

Lakes	Sample groups	Catchment soil	Littoral vegetation	Terrestrial vegetation	POM
SHL	Pre-1900	11 – 27%	27 – 36%	15 – 34%	19 – 36%
		(21 ± 3)	(31 ± 5)	(25 ± 5)	(27 ± 5)
	Post-1900	23 – 35%	13 – 27%	15 – 34%	19 – 37%
		(29 ± 4)	(23 ± 5)	(27 ± 3)	(29 ± 5)
ELL	Pre-1900	15 – 17%	32 – 35%	33 – 34%	15 – 19%
		(16 ± 2)	(33 ± 3)	(34 ± 2)	(16 ± 2)
	Post-1900	17 – 37%	15 – 32%	15 – 29%	18 – 34%
		(27 ± 5)	(24 ± 4)	(22 ± 3)	(25 ± 4)

Figures

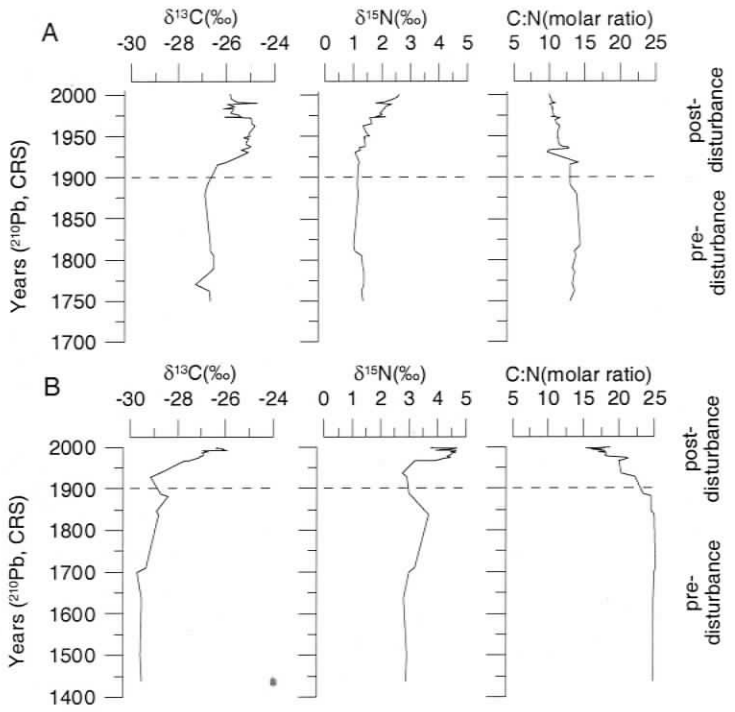

Figure 5.1: Temporal profiles of stable isotopes ($\delta^{13}C$ and $\delta^{15}N$) and molar carbon to nitrogen ratio (C:N) retrieved from the sediment cores of A) Shawnigan Lake, and B) Elk Lake. Years in the Y-axis are based on ^{210}Pb activity and applying the constant rate supply (CRS) model. Horizontal dashed lines separated pre- (pre-1900) and post-disturbance (post-1900) periods in both study lakes.

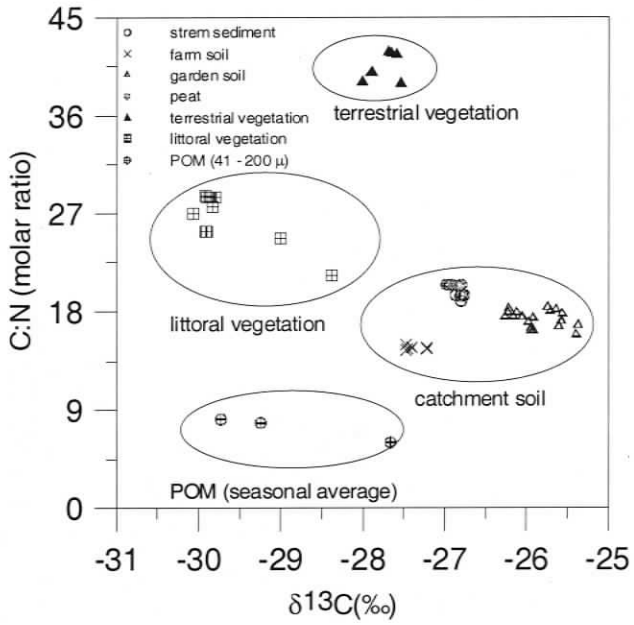

Figure 5.2: Pool of molar carbon to nitrogen ratio (C:N) *vs.* $\delta^{13}C$ of the source end member signatures from both study watersheds.

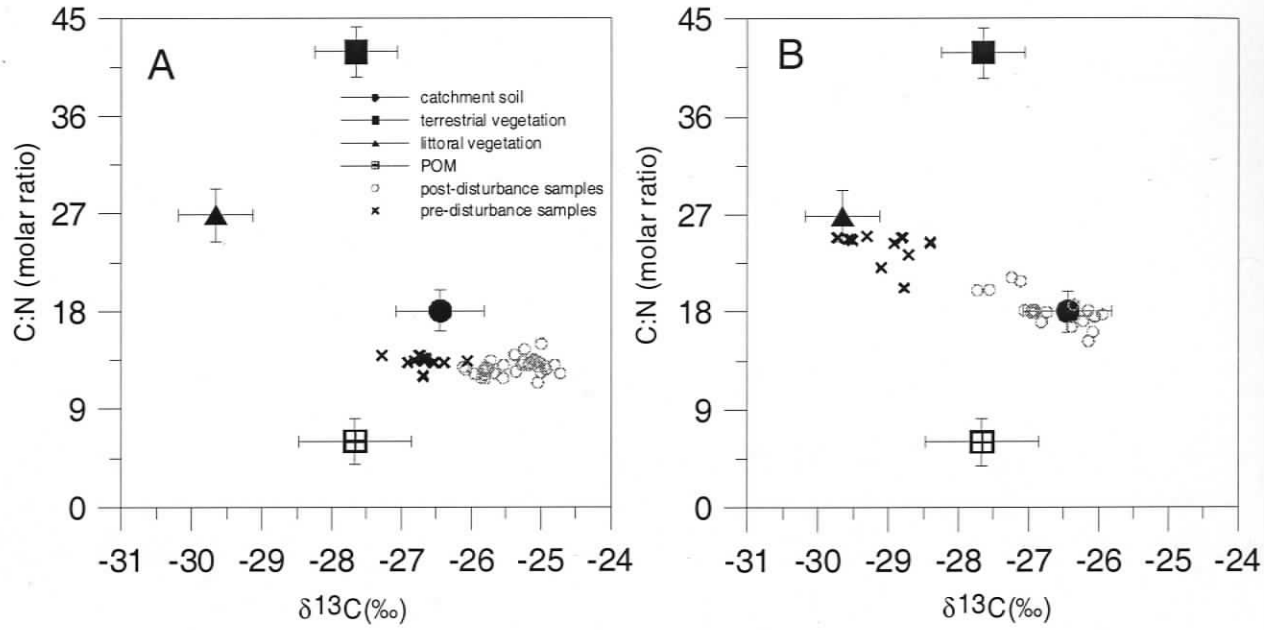

Figure 5.3: Comparison of sample molar carbon to nitrogen ratio (C:N) *vs.* $\delta^{13}C$ with the source signatures. Samples from each study lake (A. Shawnigan Lake, and B. Elk Lake) were broadly grouped into two regimes, pre- (pre-1900) and post-disturbance (post-1900). Vertical and horizontal lines in each source signature indicate error bars.

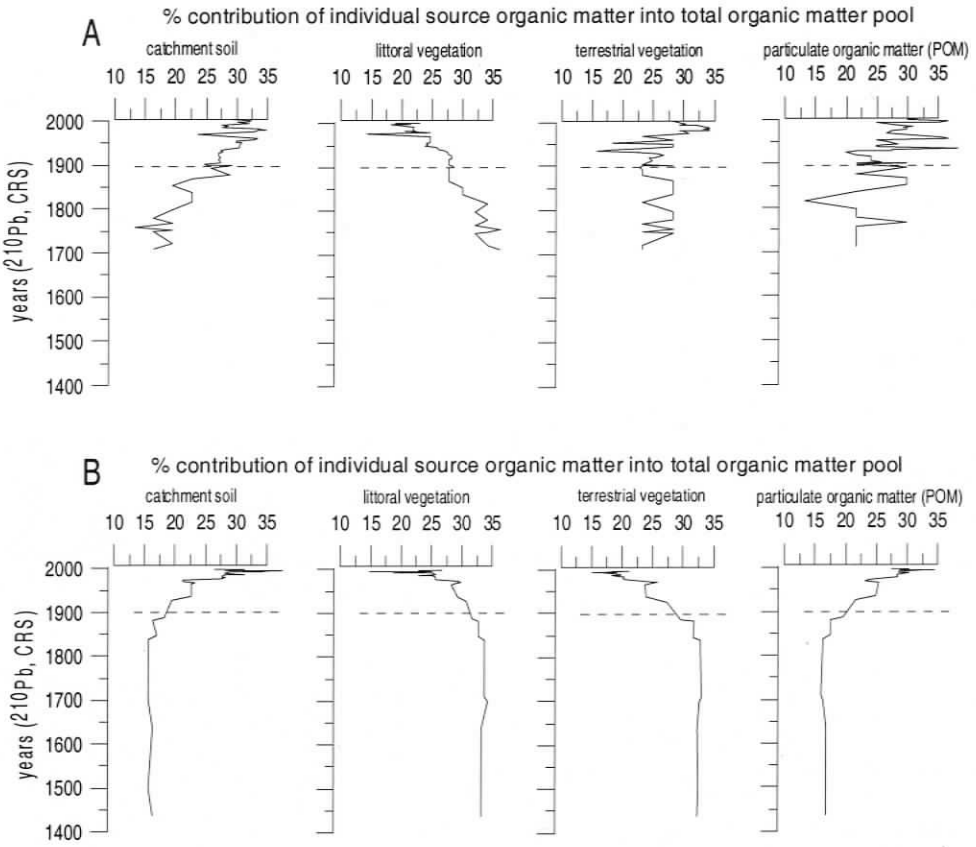

Figure 5.4: Possible contribution of each source organic matter to the sample pool retrieved from the statistical output using IsoSource (a source separation program). Isotopic signatures ($\delta^{13}C$ and $\delta^{15}N$) of four different sources (catchment soils, littoral and terrestrial vegetation, and particulate organic matter) and the sediment sample (mixer) were defined along with a 1% source increment and a 0.1% tolerance. Years in the Y-axis are based on ^{210}Pb activity and applying the constant rate supply (CRS) model. Horizontal dashed lines separated pre- and post-disturbance periods in both study lakes (A = Shawnigan Lake, B = Elk Lake).

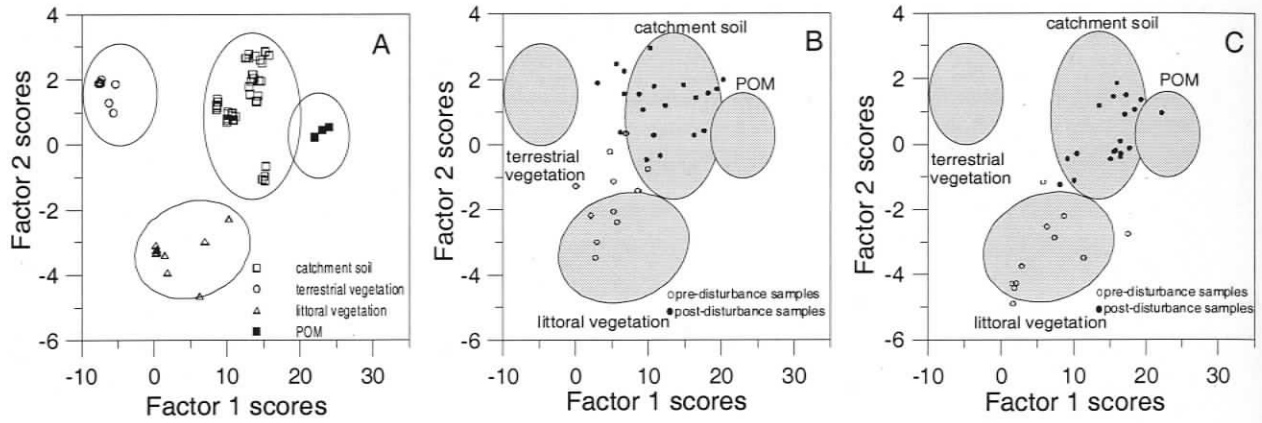

Figure 5.5: Discriminant analysis of (A) organic matter source signatures compared with the sample records from (B) Shawnigan Lake and (C) Elk Lake. Samples were broadly grouped into two separate regimes, pre- (pre-1900) and post-disturbance (post-1900) based on historical land use data.

Chapter 6: Aminopeptidase activity in lake sediments

Abstract

The potential of bacterial enzyme activity in lake sediment as a proxy to infer historical productivity was assessed by comparing with existing traditional indicator variables. A eutrophic lake, Elk Lake (ELL) with divergent watershed land use histories was selected for this feasibility study. The aminopeptidase activity, as inferred by Leu-MCA (L-Leucine-4-methylcoumarinyl-7-amide, Sigma) substrate, was highest in the most recent trophic enrichment periods (topmost samples) and the opposite when the ELL was oligotrophic (deeper samples) concurrent with the results from plate count (colony forming unit, c.f.u.) ($r = 0.91$, $p < 0.01$) and acridine orange total bacterial count ($r = 0.92$, $p < 0.01$). Significant positive correlation with several environmental proxies including total chlorophyll *a* + derivatives ($r = 0.77$, $p < 0.01$), $\delta^{13}C$ ($r = 0.83$, $p < 0.01$), and $\delta^{15}N$ ($r = 0.63$, $p < 0.05$), it is evident that the aminopeptidase activity profile was related to the historical productivity of the lake. Results from this study revealed that aminopeptidase activity in the sediment core is strongly dependent on the historical water column processes and subsequent sedimentation, which corresponded with the degree of lake watershed disturbances. This suggests that enzymatic activity in lake sediments could be a qualitative viable proxy to infer historical productivity.

Introduction

Lake sediments are archives of trace amount of fossil indicators and therefore, often used to infer trophic evolution of lakes. Recent changes in watershed land use might lead to nutrient enrichment, which in turn deteriorate water quality preceded by enhanced primary production. Many paleolimnological indicators have been used to infer the consequences of nutrient enrichment using the sediment record, including siliceous microfossils (diatoms and chrysophyceae), invertebrates, pigments, and geochemistry (Leavitt 1989; Quinlan et al. 2002; Itoh et al. 2003; Das et al. 2005). In earlier studies it has been demonstrated that bacterial production in the water column are positively linearly correlated with algal primary production (Bird and Kalff 1984; Rothfuss et al. 1997; Haglund et al. 2002; Vezzulli et al. 2002; Porter et al. 2004). Much of the organic matter in aquatic ecosystems is composed of relatively high molecular weight compounds. Prior to use by bacteria, these high molecular weight compounds need to be hydrolyzed by extracellular enzymes (Misic et al. 1998; Ogawa et al. 2001). Bacterial biomass in the water column is dynamic and quite sensitive to elevated nutrient loading, which in turn can alter extracellular enzymatic activities (Morgan and Pickup 1993; Burns and Ryder 2001; Prenger and Reddy 2004). Most of the studies documenting enzyme assays were conducted in surface water (Karrasch et al. 2003; Obayashi and Suzuki 2005) and surface sediments, mostly in marine environments (Nilsson and Renberg 1990; Fabiano and Danovaro 1998; Miskin et al. 1998; Coolen and Overmann 2000) and none of them looked at the activities in sediment core samples with the objective to reconstruct historical productivity and hence, water quality. Once deposited from the water column, some

bacteria are able to survive in a dormant state for long periods depending on the environmental conditions (Bird and Kalff 1984). I hypothesize that the lake sediments might preserve bacteria for years and that they could be used as a proxy to infer past limnological changes. Supplying the dormant bacteria, preserved in lake sediments, with artificial substrate might lead them to become metabolically active and that they could be detected from exoenzyme activities, which might reflect respective bacterial abundance.

To test this hypothesis, a eutrophic lake with divergent watershed land-use histories was selected. The aim of this study was to determine the feasibility of bacterial exoenzyme activity in lake sediments as a proxy to infer historical productivity by comparing with the temporal pattern of other traditional proxies. I conducted a field study to (a) reconstruct temporal profiles of bacterial abundance (b) quantify bacterial proteolytic activities in sediment core, and (c) compare and verify the sedimentary temporal profiles in additional proxies [total chlorophyll *a* and derivatives, stable isotopes ($\delta^{13}C$, $\delta^{15}N$) and carbon to nitrogen (C:N) elemental ratio]. Protease enzymes are important in the breakdown of proteins, which are one of the major components of organic matter. Among the protease enzymes, L-Leucine-4-methylcoumarinyl-7-amide is three times higher than other aminopeptidases and therefore, considered to be model proteolytic enzyme.

Materials and methods

Elk Lake (ELL) (48°37′N latitude and 123°38′W longitude) is located on southern Vancouver Island, British Columbia, Canada. ELL is a mesotrophic lake (14 $\mu g \cdot L^{-1}$ for TP and 2.5 $\mu g \cdot L^{-1}$ for chlorophyll *a*) (Mckean 1992) influenced by various anthropogenic activities and is under constant pressure from the recreational activities both on the lake and in the watershed. Sediment cores (50 cm long) were taken from the deepest part (~17 m) of the lake using a modified gravity corer (Kliza and Telmer 2001) and were dated using ^{210}Pb techniques by α-spectroscopy (Appleby and Oldfield 1978). Pigments were analyzed following the methods of Leavitt and Hodgson (2001) using high pressure liquid chromatography (HPLC). All pigment concentrations were normalized to their mass per gram of organic matter ($mg \cdot g^{-1}$ OM) (Heiri et al. 2001). The isotopic compositions ($\delta^{13}C$ and $\delta^{15}N$) of all samples were analyzed using a continuous flow system high temperature elemental analyzer coupled to a DELTA^{plus} Advantage mass spectrometer. Reproducibility of duplicate analyses was ±0.1‰.

Serial dilution of sediment slurries (1:200 dilution was appropriate) were prepared with sterile filtered deionized water, and 5 µL of the slurries was transferred to 9.9 mL of sterile filtered 4% formaldehyde solution. After vortex mixing each sample for 1 min., 0.1 mL of acridine orange staining solution (200 $\mu g \cdot mL^{-1}$) was added and kept for 10 min. in the dark. Care was taken (shape and color) in counting sediment bacteria as the acridine orange could stain other particles in sediments. The stained

sample was filtered with a black polycarbonate filter (0.2 μm pore size, Millipore). Stained bacteria cells were counted by epiflurorescence microscopy (Zeiss, Germany) at a magnification of 1000×. Counts of viable heterotrophic bacteria in sediment samples were performed by the dilution method. Serial dilutions were made in sterile filtered (0.45 μm) hypolimnetic water and 0.1 mL of sediment slurries were plated on trypticase soy agar (TSA) media plates, in duplicate. After 5-7 days incubation at 20 °C, the number of colony forming units (CFU) was determined.

I followed the procedures described in Hoppe et al. (1988) and Talbot and Bianchi (1997) for analysis of extracellular aminopeptidase activity (L-Leucine-4-methylcoumarinyl-7-amide, Sigma, hereafter Leu-MCA). The release of fluorescent dye was determined fluorometrically (380 excitation, 440 emission). Based on Michaelis-Menten kinetics determined in ELL sediments, a final concentration of 250 μmol was chosen for the substrate analogues for all three batches. Velocity (V) was reported as $\mu mol \cdot h^{-1} \cdot g^{-1}$ of sediment. Nonparametric Spearman's rank correlation coefficient (using SPSS 10.0 for Windows) was used to determine relationships between aminopeptidase (Leu-MCA) activity and other environmental variables.

Results and Discussion

Aminopeptidase activity, as inferred by Leu-MCA (L-Leucine-4-methylcoumarinyl-7-amide, Sigma) substrate, was highest in the most recent trophic enrichment periods (topmost sediments) and the lowest when the ELL was oligotrophic (~12 cm; Figure

6.1). The results were concurrent with the results from plate count (colony forming unit, c.f.u; $r = 0.91$, $p < 0.01$) and acridine orange total bacterial count ($r = 0.92$, $p < 0.01$). The aminopeptidase activity profile in lake sediments might reflect either (a) the availability of useable fossil organic matter, or (b) diagenesis. First, if the enzymatic activity was related to the fossil organic matter (i.e., algal remains) then a positive relationship between organic matter and activity would have been expected. A positive correlation between ELL sediment organic matter content ($r = 0.47$, $p < 0.05$) and aminopeptidase activity indicated that enzymatic activity was partially (~22% of variability) governed by the availability of utilizable organic matter. This also was supported from the earlier studies, where it has been demonstrated that the input of organic matter to the water column and sediment should initially lead to an immediate increase in bacterial biomass and hence, exoenzyme activities (Mayer-Reil 1983, Goedkoop et al. 1997, Mallet and Debroas 1999). The relationship also has been reported to be positive in marine environments (Meyer-Reil 1984, Meyer-Reil and Köster 1992, Boetius and Lochte 1994). Additionally, significant positive correlations were observed between the enzyme activity and total chlorophyll *a* + derivatives ($r = 0.77$, $p < 0.01$) suggesting that aminopeptidase activity in lake sediments probably was related to the fossil organic matter content. Secondly, to support the statement that enzymatic profiles retrieved from the ELL sediments might not solely be related to diagenesis, I compared the results with the ratio between primary and degraded chlorophyll, pheophytin *a* (Figure 6.2). The pattern expected, if only diagenetic processes were modulating the down-core distribution of pigments, should have been high pheophytin *a* concentrations in samples of low chlorophyll *a*

concentration. The overall trend between primary chlorophyll *a* and chlorophyll *a*:pheophytin *a* ratio was found to be related linearly (Figure 6.2), which may have reflected a shift in productivity regimes (i.e., higher primary production, higher degraded pigments) and was not related to diagenetic transformation (Hurley and Armstrong 1990, Leavitt and Carpenter 1990).

Additionally, the sediment aminopeptidase activity profile was compared with stable isotope ($\delta^{13}C$ and $\delta^{15}N$) values, and a positive relationship was observed [$\delta^{13}C$ ($r = 0.83$, $p < 0.01$), and $\delta^{15}N$ ($r = 0.63$, $p < 0.05$)]. However, one of the major concerns in interpreting shifts in biological and geochemical variables of organic matter is the possibility of post-depositional decay that may mislead interpretation of sedimentary isotopic profiles (Lehmann et al. 2002). The general hypothesis is that systems with elevated nutrient inputs are enriched with heavier C and N isotopes, resulting in increased $\delta^{13}C$ and/or $\delta^{15}N$ sediment values (Lehmann et al. 2002). No significant linear relationship was found when comparing $\delta^{13}C$ and $\delta^{15}N$ values with %C and %N in ELL sediments respectively, suggesting that the decay of organic carbon was independent of the $\delta^{13}C$ signature. The possibility exists that the lack of dependence was caused by changes in the source of organic carbon that had different isotopic values, suggesting that the $\delta^{13}C$ and $\delta^{15}N$ values reflected changing sources of C and N rather than diagenetic processes (Finney et al. 2000, Teranes and Bernasconi 2000). A significant positive correlation between aminopeptidase activity and other environmental proxies (total chlorophyll *a* + derivatives and stable isotopes, $\delta^{13}C$ and $\delta^{15}N$) therefore suggests that the enzymatic profile may have been related to the fossil

organic matter content and indirectly to paleoproductivity. Collectively, it can be stated that increased aminopeptidase activity in ELL sediments may be a reflection of the elevated fossil organic matter. Historically, algal products might have contributed positively to the development of nutrient-rich regimes that lead to a nutrient-rich zone around them, enhancing attached bacterial growth both in the water column and sediments.

Results from ELL C:N ratios illustrate a trend for historical sources (terrestrial vs. aquatic) of sedimentary organic matter (Aller 1994, Meyers 1994). Increased nitrogen loading from catchments due to watershed disturbances in the post-1900 period were reflected in the C:N ratio in ELL sediment profile (Figure 6.2). The C:N profile could also be supported from the aminopeptidase activity profile. High aminopeptidase levels are evidence of inorganic nitrogen being obtained from organic sources in post-1900 sediments that occurs when inorganic nitrogen availability is low (Sala et al. 2001). Additionally, extracellular protease production in microorganisms is strongly influenced by useable sedimentary components, (e.g., variation in C:N ratio, presence of some easily metabolizable sugars such as glucose (Beg et al. 2002), and metal ions (Varela et al. 1996). Protease synthesis also is affected by rapidly metabolizable nitrogen sources, such as amino acids in the medium. Besides these, other biotic factors including increased algal production and/ or partial diagenesis (Gälman et al. 2008), as well as several other physical factors, such as aeration, bacterial density, pH, temperature and incubation also affect the amount of protease produced (Hameed et al. 1999, Puri et al. 2002). However, the activity reported here may underestimate

the actual activity rates due to sediment dilution and the lack of existence of standardized protocols. Moreover, bacterial and algal communities also could adapt themselves physiologically to unfavorable environmental conditions (Borchardt 1994), but this process is difficult to quantify in sediment cores. Nonetheless, the aminopeptidase activity in ELL sediments reported here was correlated significantly with other traditional paleo-proxies. Future research, therefore, would benefit by studying other exoenzyme activities (i.e., alkaline phosphatase, β-glucoside) in relation to fossil organic matter and bio-chemical composition in sediments. Additionally, exoenzyme activities in lake sediments in relation to changes in microbial community structure and with contrasting historical productivity regimes also could be explored.

Figures

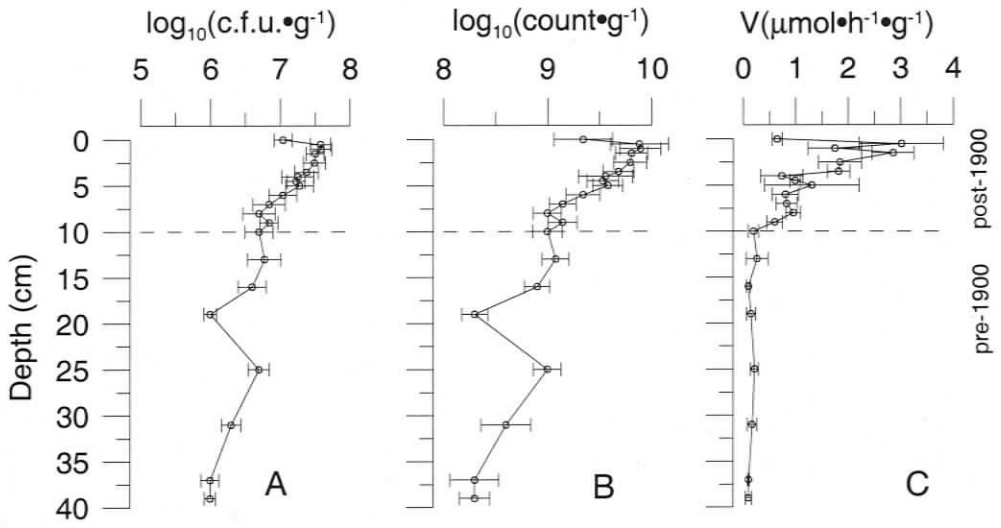

Figure 6.1: Temporal profiles of microbial varaibles (A. colony forming unit, c.f.u., B. acridine orange total bacterial count, C. aminopeptidase activity, V) in Elk Lake sediments. Horizontal dashed lines separate between pre- and post-disturbance periods.

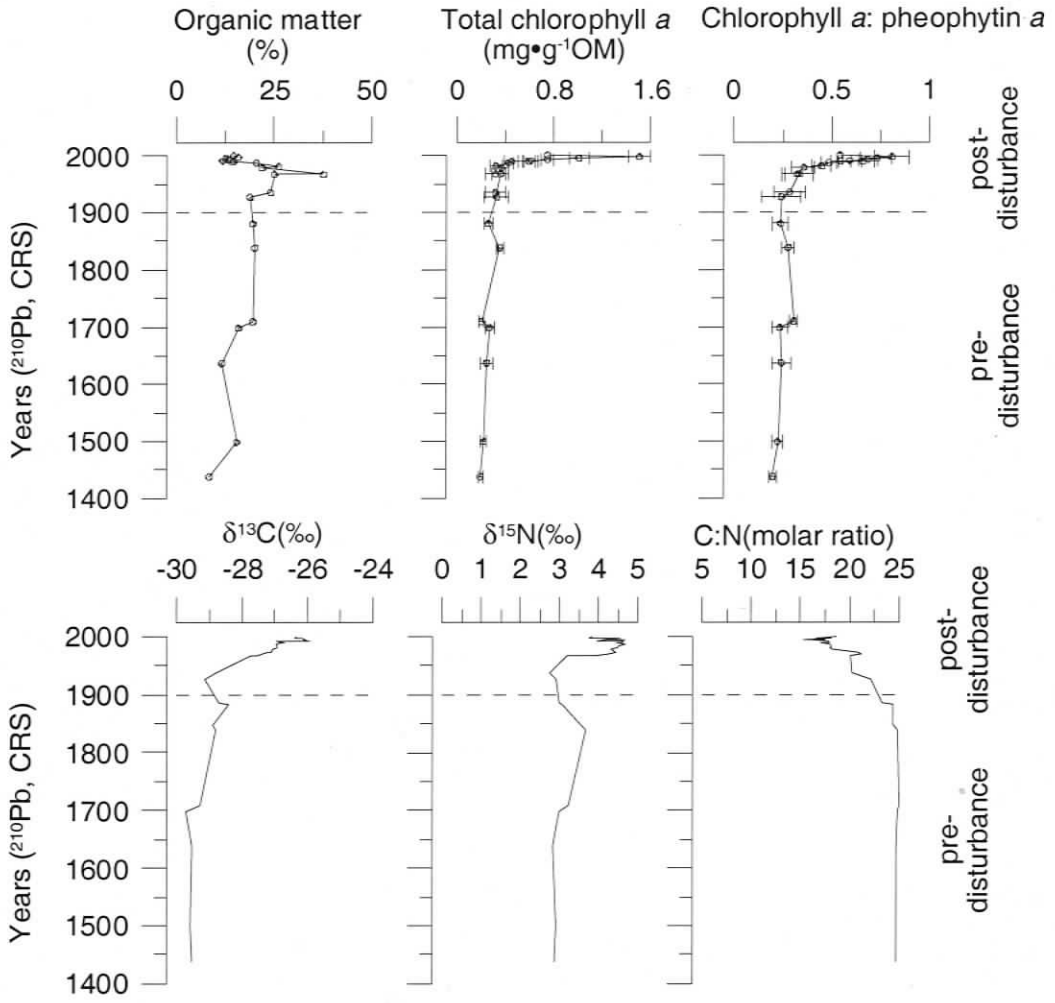

Figure 6.2: Organic matter, pigment stratigraphies, stable isotopes ($\delta^{13}C$ and $\delta^{15}N$) and C:N ratio profiles from Elk Lake sediments. Years on Y-axis are based on ^{210}Pb activity and using constant rate supply (CRS) model. Horizontal dashed lines separate between pre- and post-disturbance periods.

Chapter 7: General Conclusions

General Conclusions

Nutrient enrichment in aquatic ecosystems, whether resulting from watershed disturbance, agricultural effluent, industrial development, or atmospheric deposition, continues to be a significant threat to global freshwater resources (UNEP-IETC, 1999). Proper management of freshwater quality requires long-term data in order to assess when, and by how much, a lake has deteriorated. Paleolimnological techniques can provide these previously unavailable data sets. Many paleolimnological indicators have been used to infer the legacy of nutrient enrichment from the sediment record, including siliceous microfossils (diatoms and chrysophytes), invertebrates, pigments, and geochemistry (Vinebrooke and Leavitt, 1999; Smol, 2002; Quinlan et al., 2002; Itoh et al., 2003; Saros et al., 2003). In this thesis, I have demonstrated that these traditional proxies can be applied in alternative ways. In addition, I have illustrated the development of potentially new proxies to reconstruct lake productivity, in order to enrich our understanding of lake ecosystem processes as well as watershed land-use management options.

Biodiversity of aquatic ecosystems are altered in response to recent modifications and disturbances of the watershed. From fossil pigment analyses, I showed that land-use changes in Shawnigan Lake watershed had a more negative impact on algal productivity and therefore, lake-water quality compared to Sooke Reservoir where water levels are regulated (Chapter 2). Paleolimnological evidence from the analysis illustrate that raising the water levels in Sooke Reservoir affected water residence time and seasonal succession and subtly changed aquatic productivity. In contrast, a

comparison of Shawnigan Lake and Sooke Reservoir using sediment pigment profiles indicated that land use changes in Shawnigan Lake watershed increased lake productivity more than regulating water levels in Sooke Reservoir. This difference occurred as a result of the input of nutrients from diffusive sources. Regardless, of the type of anthropogenic disturbance (i.e., regulated water level or human settlement), irregular aquatic productivity regimes and increased ecosystem variability were observed. Fossil pigment data in lake sediments can provide information on temporal coherence and variability due to natural or anthropogenic disturbances and thus, can be used to guide and manage lake-water quality.

Exploring the anthropogenic impacts on paleoindicator signatures, I found that productivity (as indicated by $\%BSiO_2$) is controlled on a local scale (Chapter 3). There was evidence of regional control for %C, $\delta^{13}C$ and %N. However, variability in these paleoindicators explained by their regional correlations was not conclusive. Process and measurement error could have reduced regional correlation between these paleoindicators (Hilborn and Mangel 1997), but some of the remaining variability may have been due to local processes. The difficulty in interpreting the change in temporal coherence of $\delta^{15}N$ data exemplified one crucial weakness in this method; namely that the expected impacts of the local disturbances on a given ecosystem property must be unique. In this case, I did not measure the impact of wetland inundation in Sooke Lake Reservoir. The effect of this local disturbance may have given a very similar signature to the impact of local watershed development in Shawnigan Lake. When local disturbances have similar impacts, it impedes the ability

to detect the relative importance of local versus regional drivers. I recommend, therefore that this method be used in future studies where local disturbances are expected to have unique impacts, or where one ecosystem is maintained in the reference state (i.e., without disturbance), while the other ecosystem is disturbed.

One of the greatest threats to biodiversity is the loss of habitat due to human activity and habitat destruction is also a major threat to biodiversity in aquatic ecosystems. In Chapter 4, I have demonstrated that changes in biodiversity could differ in contrasting trophic states. I compared results for three different limnological regimes: low (ultra-oligotrophic), mid (oligotrophic to mesotrophic), and mid-to-high (mesotrophic) productive systems. The conclusion of overall historical species richness-production relationships from this study is that a hump shaped or unimodal relationship may be limited to mid-to-high productive systems at high disturbance levels. Additionally, with increased disturbance and primary production, diversity of algal functional groups declined favoring certain diatoms and filamentous cyanobacterial growth suggesting that the functional diversity governed the overall primary production.

Regardless of the motivations for watershed conservation, it is important that watersheds are monitored for water quality and to limit the effects of land-use change in the vicinity. The organic matter (OM) source detection approach that I developed in Chapter 5 can be a robust tool in defining dominant OM accumulating sources with contrasting watershed scale disturbance histories when combined with the IsoSource

source separation program and therefore, could be used for watershed management decisions to sustain water quality.

From the perspective of contrasting land-use patterns, elevated nutrient inputs from agricultural and cattle farm activities in the watershed might have played a key role in the recent trophic enrichment of Elk Lake (ELL). Increasing conversion of land cover for agricultural use (mostly organic farming and livestock) near watersheds has resulted in increased nitrogen loading in groundwater and surface water, most notably in the past three decades (Van Herpe et al., 2002). Although point-source pollution of watersheds from agriculture can be substantial, nonpoint source pollution from agriculture is the most significant contributor in nitrate enrichment of the aquatic environment. One of the possible explanations of the increasing nitrate levels in drinking water sources is changes in land-use patterns including the increased use of nitrogenous fertilizers closer to watersheds (Soares, 2000). Conversely, human settlement can still lead to minor nutrient enrichment compared to the above-mentioned activities. This can be seen in SHL sedimentary profiles. Collectively, it can be stated that contrasting watershed land uses have divergent effects on OM accumulation in lakes. Conversion to agricultural land in ELL watershed has had a more negative impact on lake-water quality based on elevated organic matter loadings when compared to human settlement on the shoreline of SHL watershed.

Bacterial production in the water column are positively correlated with algal primary production (Bird and Kalff, 1984; Rothfuss et al., 1997; Haglund et al., 2002;

Vezzulli et al., 2002; Porter et al., 2004). Some unresolved issues in microbial ecology are: 1) whether the bacterial abundance in the water column is related to their abundance in surface sediments with contrasting trophic state and if any, 2) whether there is any close relationship between bacterial abundance and historical productivity. Whereas it may be possible to relate bacterial abundance with varying trophic status, it is still important to determine how many of these microbial communities are metabolically active to relate it to organic matter. In Chapter 6, I showed the temporal distribution of aminopeptidase activity in lake sediment with the objective of developing an alternate proxy to reconstructing historical productivity. The weak relationship between ELL sediment organic matter content and the aminopeptidase activity indicated that the enzymatic activity was not governed by the availability of useable organic matter, which is consistent with other microbial ecological studies (Mayer-Reil 1983; Goedkoop et al. 1997; Mallet and Debroas 1999). Changes in bacterial exo-enzyme activities in lake sediments may be reflective of diagenetic processes. To explore this possibility, I compared the enzymatic profiles with fossil pigment results. The expected pattern, if diagenetic processes were modulating the down-core distribution of pigments, high pheophytin *a* with low chlorophyll *a* concentrations would be present. The overall trend between primary chlorophyll *a* and chlorophyll *a*:pheophytin *a* ratio was shown to be linearly related, which may be reflective of a shift in the productivity regimes (i.e., higher primary production, higher degraded pigments) and are not related to diagenetic transformation (Hurley and Armstrong1990; Leavitt and Carpenter 1990a, 1990b). The general hypothesis is that systems with elevated nutrient inputs are enriched with

heavier C and N isotopes, resulting in higher $\delta^{13}C$ and/or $\delta^{15}N$ sediment values (Lehmann et al. 2002). No significant linear relationship was found when comparing $\delta^{13}C$ and $\delta^{15}N$ values against %C and %N in ELL sediments respectively, suggesting that the decay of organic carbon is independent of the $\delta^{13}C$ signature. The possibility exists that this lack of dependence is caused by changes in the source of organic carbon which have different isotopic values, suggesting that the $\delta^{13}C$ and $\delta^{15}N$ reflects the changing sources of C and N rather than diagenetic processes (Finney et al. 2000; Teranes and Bernasconi 2000). Therefore, the significant relationship between aminopeptidase activity and other environmental proxies (total chlorophyll *a* + derivatives and stable isotopes, $\delta^{13}C$ and $\delta^{15}N$) indicated that the enzymatic profile was related to the paleoproductivity.

Future research

Ecosystem experimenters contend that only substantial replication will reveal the response potential of lakes (Kitchell et al. 1988). Nevertheless, more subtle responses of lakes are of potential theoretical and practical interest (Schindler 1987, Crowder et al. 1988). Large scale and replicated and hence extremely expensive experiments are often avoided in Paleolimnology. Future research should focus on the replication of different land-use types and the subsequent response of different paleoindicators.

I found that variability in the paleoindicators was uniquely affected by the local disturbances. The only exception to this finding was that there was a uniquely

significant effect for $\delta^{13}C$ in SOL, for which there was evidence of regional control, but the same relationship was not statistically significant in the other lake. Lakes are particularly good study systems for this type of analysis because the 'local' and 'regional' scales are clearly defined. However, I posit that this method could be applied in any system where the local scale can be shown to be relatively discrete, giving independence of the local units on the regional scale. Future studies using this technique in other systems and with other paleoindicators should be done, to explore the extent at which wider arrays of ecosystem properties are regulated. This work would be valuable to ecologists and natural resource managers alike.

Enzyme activity in natural sediments may provide an important measures of historical primary production and hence, paleo-water quality. However, the results reported here might underestimate the actual activity rates due to sediment dilution and the lack of existence of any standardized protocol. Moreover, in addition to other variables, bacterial and algal communities may also adapt themselves physiologically to altered and unfavourable environmental conditions (Borchardt 1994; Pusch et al. 1998), but this process is difficult to quantify in sediment cores. Nonetheless, the aminopeptidase activity in ELL sediments reported here was significantly correlated with other traditional paleo-proxies suggesting that enzymatic activity in lake sediments could be a qualitative viable proxy to infer historical productivity. Moreover, the study of exoenzyme activities in lake sediments is relatively rapid (once optimized) and inexpensive compared to other existing methods used to reconstruct historical productivity. Future research on other exoenzymes need to be

explored, such as alkaline phosphatase, glucosidase activity in sediments in order to relate to historical productivity. In addition, future work could explore different exoenzyme activities in lake sediments in relation to changes in microbial community structure, along with contrasting historical productivity regimes.

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