#### Paleolimnological Analysis of Sediments from Killarney Lake, Manitoba

By

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A Thesis Submitted to the Faculty of Graduate Studies in Partial Fulfillment of the

Requirements for the Degree of Master of Science

Department of Botany

University of Manitoba

Winnipeg, Manitoba

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#### PALEOLIMHOLOGICAL ANALYSIS OF SEDIMENTS PROM KILLARNEY LAKE, MANITOBA

by

#### KELLY-ANNE RICEMOND

A Thesis/Practicum submitted to the Faculty of Graduate Studies of The University

of Manitoba in partial fulfillment of the requirements of the degree

MASTER of SCIENCE

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#### Acknowledgments

I would foremost like to thank my advisor, Dr. L.G. Goldsborough, for his guidance on this project. He has been an excellent teacher and a lot of fun to work with over the years. Even though Brandon, MB was not the "bright lights, big city" he had promised, I will fondly remember the wonderful hospitality he and Maria extended to me during my time there. While in Brandon I also benefited from numerous academic discussions with Rhonda McDougal, and just as many nonacademic pizza/movie nights with the McDougal family. The faculty and staff of Brandon University were also very generous with advice and the use of their laboratory equipment.

I would like to thank those people who helped in the field and lab, and made time spent in each location less arduous. Mike Forster, Scott Gadsby, Hugh Kiffen, Ryan McGregor, Pauline Morton, Maria Zbigniewicz, Bob Vance, Don Lemmen, and Debbie Hysop assisted with core collection. Iain Pimlott, Tom Henderson and Rhonda McDougal helped with core analyses. Tom Henderson graciously drew the diagrams of the coring equipment in Figures 5 and 6. Dennis Brown of the Manitoba Environment provided the metal analysis of core K5. Hedy Kling assisted in SEM identification of difficult diatom taxa. Dr. N. Kenkel kindly performed the diatom cluster analysis.

I gratefully acknowledge financial support from the Manitoba Environmental Innovations Fund, the Town of Killarney, the Rural Municipality of Turtle Mountain, the Geological Survey of Canada Global Change Program, an NSERC Operating Grant to L.G.G., a University of Manitoba Fellowship and Manitoba Naturalists Society Scholarship to K.A.R..

I thank my wonderful parents for their endless support. And last but not least, I thank my husband Richard, for being my best friend and for never failing to turn my frowns into smiles.

#### Abstract

Sediment stratigraphic analyses of plant pigments, fossil diatoms, and selected chemical parameters were used to infer postglacial trends in primary production in Killarney Lake (southwestern Manitoba). Three 2.7 to 2.8 meter long cores and three surficial (top 30 cm) cores were collected from the lake during 1992 and 1993. The cores were predominantly organic, dark olive grey silt, although the bottom of one long core contained coarse sand and gravel; a radiocarbon dated stratum immediately above this layer indicates the lake basin is at least 4,700 years old. The stratigraphic profiles of organic matter, phosphorus, chlorophyll, carotenoid, and diatom concentrations indicate that initially the lake was shallow with low primary production. Water levels and primary production began to rise in Killarney Lake likely in response to a cooler and wetter climate about 3,900 years BP. By about 2,100 years BP a deep lake with low primary production existed. A change in the climate about 1,200 years BP again caused low water levels and increased primary production. Water levels increased again about 500 years BP but did not reach the level of the previous deep water stand (2,100 years BP). Primary production was low at this time but showed a trend toward increasing production during the last 100 years. The most recent phase in the history of Killarney Lake, which began about 1940 AD, was indicative of stable conditions relative to earlier periods, during which time only minor fluctuations were observed in sediment chemistry and pigments. In an effort to reduce chronic cyanobacterial blooms, the Town of Killarney's long history of copper sulphate use has resulted in very high surface sediment (top 2 cm) copper levels. Collectively, these analyses indicate that Killarney Lake has been naturally productive for at least the last five millennia.

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#### **1.0 Introduction**

"[Killarney] Lake is a beautiful sheet of water, clear as crystal and abounding with fish and foul. I think we would travel the world over before we would hit another spot to equal Manitoba and this locality in particular."

Captain John Rigby, July 23, 1882 (Garland, 1967)

The residents of the Town of Killarney, in southwestern Manitoba, no longer experience the pristine lake that Captain John Rigby first described in the early settling days of this area. Killarney Lake has a long history (>50 years) of manipulation in an effort to reduce the frequent occurrence of cyanobacterial (blue-green algal) blooms. The rapid growth of algae gives rise to numerous undesirable effects on treatment of potable water, fisheries, bathing sanitation, and recreation (tourism). There are few data on changes in lake water quality since 1879, when intensive agricultural land use began in the watershed. In the absence of long-term historical data collected from the water column, a study of Killarney's paleorecord will provide a means to infer historical lake production as well as past environmental conditions.

Analysis of vertical sediment cores for constituent chemical, physical and biological parameters is a powerful technique for studying historical changes in lake primary production due to changes in global and regional climate, hydrologic patterns, nutrient loading, and other environmental factors. Materials produced within the lake (algae, aquatic plants, invertebrates, and fish), as well as those arising from the surrounding watershed (particulates and litter), are deposited on the lake bottom. Depending on their chemical composition and the environmental conditions at the sediment/water interface, these materials may persist, preserving a record of conditions in and around the lake at the time of deposition. The task of paleolimnology is to decipher and interpret past conditions from the nature of the lake sediments by applying an understanding of modern limnology to the past. In turn, knowledge of a lake's historical responses to environmental change can be used to predict future changes. The purpose of my study is to infer, based on stratigraphic profiles of sedimentary plant pigments, diatoms and selected chemical parameters, trends in Killarney Lake's primary production during the postglacial period. The data collected may provide a reference for future changes occurring in lakes in this region, for example, as a result of hypothesized climatic warming.

#### 2.0 Literature Review

#### 2.1 Lake Trophic Status and Eutrophication

The concept of lake trophic state was first introduced by Naumann (1919) who distinguished between oligotrophy and eutrophy on the basis of phytoplankton populations. Simply, if the supply of nutrients is high, the lake is eutrophic. If nutrients are in short supply, the lake is considered oligotrophic. Eutrophic lakes are usually productive, turbid, shallow water bodies rich in algae and with considerable fluctuations in surface and benthic oxygen levels (Horne & Goldman, 1994). The opposite is true of oligotrophic lakes which are typically unproductive, often deep, with very transparent waters that are fully saturated with dissolved oxygen (Horne & Goldman, 1994). Between these two extremes are mesotrophic lakes, which are moderately fertile.

A postglacial lake is typically oligotrophic and contains few nutrients. Natural processes, such as wind erosion or leaching by rainwater, add nutrients to the water which encourage plant and animal life. The increasing fertility of lakes as they age is a natural phenomenon and proceeds gradually throughout their lifetime. This process of eutrophication normally takes centuries, though in some lakes a dramatic increase in this rate can create eutrophic conditions within decades or less. This accelerated or 'cultural' eutrophication is caused largely by an increase in phosphorus and nitrogen exports from land to water bodies arising from human activities in their catchment. Agricultural intensification (increasing use of nitrogen and phosphorus-based fertilizers) and urbanization processes (especially with respect to the discharge of treated wastewater to water bodies) have been implicated as the main sources of this nutrient export (Henderson-Sellers & Markland, 1987). Elevated nutrient levels in lake water allow algal biomass and aquatic plant production to increase dramatically which leads to water quality deterioration, reducing its amenity and aesthetic values.

Such deterioration can be reduced, stopped and even reversed by the use of suitable rehabilitation techniques that can be either preventive or curative. Preventative methods should be

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regarded as the most ecologically acceptable because they operate by reducing the input of nutrients to the lake water. Therefore they tackle the problem at its source and give permanent results. Preventive methods can be replaced or supplemented by curative methods. These operate by removing nutrients from the water and so show results almost immediately. However, as they do not tackle the source of the problem, their effective duration is limited and they must be maintained indefinitely.

Copper administered as copper sulphate (CuSO<sub>1</sub>) has long been the most commonly used algicide in Canada (S.E.P.S., 1989). The use of copper sulphate may result in a quick and effective increase in perceived water quality (for example, by recreation-based users) but it is likely to be only temporary since the dead organic matter resulting from its use tends to remain in the lake and is thus available for future assimilation. Repeated dosing can also lead to the development of physiological tolerance in the algae or to the replacement of cyanobacteria by copper-tolerant green algae (Henderson-Sellers & Markland, 1987). This was found to be the case in a study of 58 years of copper sulphate use in the Fairmont Lakes of Minnesota (Hanson & Stefan, 1984). Over short periods Hanson and Stefan (1984) noted that oxygen depletion occurred due to the biological oxygen demand (BOD) of the dead decaying algae, leading to accelerated recycling of nutrients (especially phosphorus) from the sediments. This new availability of phosphorus in many cases led to the re-establishment of the algal population some 7 to 21 days after the treatment. Almost all of the copper introduced during aquatic nuisance control efforts eventually moves from the aqueous phase to the sediments where it generally persists indefinitely. Furthermore, due to the elemental nature of copper and its ability to form stable complexes with organic matter and mineral salts, total copper concentrations in sediments tend to be cumulative (S.E.P.S., 1989). Over the long-term the accumulation of copper in the sediments may cause shifts of both algal and fish populations, physiological tolerance in the algae, disappearance of macrophytes and reduced numbers of benthic macroinvertebrates (Henderson-Sellers & Markland, 1987).

#### 2.2 Paleolimnology

The task of paleolimnology is to reconstruct limnological history by analyzing the physical, chemical and biological information contained in lake sediments. Lake sediments can record a nearly continuous record of what has occurred in the lake water and catchment (watershed and airshed) extending back thousands of years. While paleolimnological reconstructions lack the accuracy of properly taken direct readings, they can circumvent the problem of direct sampling of short-term variation in environmental variables by integrating daily, seasonal and annual variation in single sediment samples encompassing an entire year or a number of years (Davis & Anderson, 1985). Moreover, for a particular site or region without historical data, it becomes possible to characterize "background" or "reference conditions" with which current conditions can be compared (Dixit *et al.*, 1992a). For many systems in which it is suspected that a lake's productivity has been altered by nutrient inputs, the only clear evidence can be derived from core studies because the major changes in primary production will usually have occurred prior to the start of a sampling program. In addition, monitoring programs once in place must continue for many years before meaningful environmental trends can be detected.

Paleolimnology reveals historical trends best when a number of parameters (e.g. geochemistry, absolute dating, biochemical markers, and fossils such as diatoms) are examined together. As each stratigraphic parameter is added, the number of hypotheses that can account for the data is reduced until the history of a lake can be reconstructed with reasonable certainty (Swain, 1985).

#### 2.2.1 Chemical Parameters

The chemical composition of lake sediments is a reflection of the substances that have accumulated, their transformation by biological and purely chemical processes at the sediment surface, and the exchange of substances between the sediment and the water. The matrix for all fossil components usually constitutes the bulk of lake sediment and includes organic materials that cannot be recognized as specific fossils, along with a fine-grained inorganic component that likewise cannot be easily distinguished as to mineral species (Engstrom & Wright, 1984).

Sources of the organic component include both the autochthonous production of algae, aquatic macrophytes, aquatic vertebrates and invertebrates, and the allochthonous detritus from terrestrial or littoral vegetation and surrounding soils. Separation of allochthonous from autochthonous sources of organic matter is difficult to determine. The assumption made is that autochthonous detritus, with a shorter transit time through the water column to the lake bottom, tends to be better preserved in the sediments (Sanger, 1988). Therefore, measurement of the change in organic matter content of sediment strata should generally reflect past levels of primary production in lakes.

Sedimentary carbonate may originate from a variety of sources, including the weathering of limestone rocks, biological production by invertebrates, and the precipitation of calcium carbonate by algae and macrophytes during photosynthesis (Wetzel, 1983). Increases in primary production shift the carbonate equilibrium through greater carbon dioxide uptake and enhance the midsummer precipitation of calcium carbonate (Engstrom & Swain, 1986). This calcium carbonate, or marl, can remain in the sediment as evidence of periods of high primary production. While a measure of total carbonates includes other sources of carbonates besides marl, the total carbonate profile with depth in a sediment core can provide an indication of the trend in primary production.

Stratigraphic phosphorus analysis of the sediment matrix has also been used as an indicator of primary production (Engstrom & Wright, 1984). Phosphorus is often the least abundant macronutrient in the ecosystem and thus is commonly responsible for limiting biological production (Wetzel, 1983). Phosphorus occurs in lake sediments in both authigenic and allogenic materials. The sedimentation of authigenic phosphorus occurs through the biological uptake of dissolved inorganic phosphorus and its subsequent deposition as particulate organic phosphorus (Engstrom & Wright, 1984). Allogenic phosphorus does not contribute to primary production (Engstrom & Wright, 1984). Dissolved phosphorus may also be transported to the bottom sediments via sorption of humic complexes and iron oxides, precipitation as iron phosphates, and possibly via coprecipitation with carbonates. Some of the particulate organic phosphorus that rains to the bottom is incorporated directly into the sediments, whereas more labile materials are degraded either in the hypolimnion or in the surface sediments through microbial activity that liberates orthophosphate and soluble organic

compounds (Engstrom & Wright, 1984). These in turn may become fixed in the sediments primarily by sorption to hydrated ferric oxides or by complexation with refractory organic materials such as humic and fulvic acids (Engstrom & Wright, 1984). Inorganic phosphorus in most sediments occurs primarily as sorbed components of amorphous iron oxides. According to Engstrom and Wright (1984), this iron complex is largely responsible for the exchange of dissolved phosphorus in interstitial waters and ultimately for the levels of phosphorus that accumulate in the sediments.

#### 2.2.2 Plant pigments

Primary producers in lake systems do not always leave morphological traces in lake sediments but may contribute to the fossil pigment record (Battarbee, 1991a). For many years, fossil carotenoids and chlorophylls have been proposed as valuable paleolimnological indicators of algal populations (Swain, 1985; Sanger, 1988). According to Hurley and Armstrong (1991), information gained from sedimentary plant pigments has paralleled developments in analytical techniques. Vallentyne (1955, 1956) and Gorham (1960, 1961) noted the universal presence of chlorophyll derivatives and carotenoids in lake sediments and related them to lake trophic status using extraction and spectrophotometric techniques. Subsequently, others (Guilizzoni *et al.*, 1983; Swain, 1985) have used sedimentary chlorophyll degradation products (SCDP) as a measure of eutrophy. Liquidliquid extraction and column chromatography were used to separate carotenoids into hypophasic and epiphasic fractions (Gorham *et al.*, 1974) and to isolate the cyanobacterial pigments myxoxanthophyll and oscillaxanthin (Swain, 1985). Specific chlorophylls and carotenoids are now being identified with the use of thin-layer chromatography (Zullig, 1981) and high pressure liquid chromatography (HPLC) (Mantoura & Llewellyn, 1983; Leavitt & Findlay, 1994).

Chlorophyll*a* is present in all groups of photosynthetic organisms except some bacteria (Moss, 1968). It is the most abundant chlorophyll in living organisms and is also the most abundant form in lake sediments as pheophytin *a*, pheophorbide *a*, chlorophyllide *a*, or in the isomerized or allomerized form (Daley*et al.*, 1977). Swain (1985) found that undecomposed (native) chlorophyll is less common in lake sediments and if present is usually reported from very recent sediments.

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Carotenoids are found in all photosynthetic plants including algae, cyanophytes and other photosynthetic bacteria (Sanger, 1988). Carotenoids that are commonly present in the sediments can be categorized as hydrocarbon carotenes (epiphasic) and oxygenated xanthophylls (hypophasic). The principal carotene in green plants and in sediments is  $\beta$ -carotene;  $\alpha$ -carotene is common, but in much lower concentrations (Sanger, 1988). The most abundant xanthophylls in higher plants and sediments are lutein, violaxanthin, nioxanthin, cryptoxanthin and zeaxanthin (Sanger, 1988). In the algae and cyanobacteria both  $\beta$ -carotene and lutein are abundant, but in addition there are several common group-specific xanthophylls including fucoxanthin, myxoxanthophyll, oscillaxanthin, echinenone and others (Sanger, 1988).

Carotenoids that are unique to prokaryotes and preserved in sediments can provide important sedimentary evidence for cyanophycean dominated plankton. One of the first of these cyanophycean pigments to be noted and measured in lake sediments was oscillaxanthin, which is highly specific to only two genera in the family Oscillatoriaceae (Sanger, 1988). One genus, *Oscillatoria*, is often among the first genera of cyanobacteria to dominate lakes as they become eutrophic (Zullig, 1981; Griffiths *et al.*, 1969; Engstrom *et al.*, 1985); therefore, oscillaxanthin stratigraphy can reveal trophic shifts. Myxoxanthophyll, an indicator for cyanobacteria in general, can also provide important sedimentary evidence. Griffiths *et al.* (1969) found myxoxanthophyll and oscillaxanthin increased dramatically in response to increased numbers of cyanobacteria that thrive on nutrients derived from expanding human settlements, forest clearance, and agricultural fertilization. The concomitant rise in these pigments with cultural eutrophication may be used to date the onset of anthropogenic disturbances in the lake catchment.

Plant pigments in the water column are derived from *in situ* production, littoral plant material and sediment resuspension (Leavitt, 1993). Once in the water column pigments can be digested by herbivores and may be incorporated into body tissue, modified, or passed through the gut unharmed (Leavitt, 1993). During sinking pigments may be further degraded by the bleaching effects of sunlight, chemically-oxidized, or destroyed by microbial processes (Leavitt, 1993). Degradation or derivative formation can continue after deposition. Rapid oxidation in the water column can take place over days, slower post-depositional losses in surface sediments may take years, and very slow loss of double bonds in deep sediments likely takes place over centuries.

Over the widest range of production, pigment deposition and fossil concentration are proportional to algal standing crop (Leavitt, 1993). In the English Lake District, U.K., Gorham *et al.* (1974) found high correlations between production and sedimentary carotenoids and sedimentary chlorophylls. Linear correlations between sedimentary carotenoids and algal standing crop were excellent (r=0.90), as were log-log relations between algal standing crop and sedimentary bulk chlorophylls (r=0.83) and between epilimnetic and fossil chlorophylls (r=0.74) (Leavitt, 1993). Guilizzoni *et al.* (1983) also found a statistically significant correlation between sedimentary plant pigments and contemporary algal primary production in a study of the recent trophic evolution of twelve Italian lakes. Despite losses during deposition, fossil and algal abundance remain correlated through time, so long as there is no change in basin morphometry, light penetration, stratification or deep water oxygen content (Leavitt, 1993).

Swain (1985) states there is no obvious reason why a eutrophic lake should produce more pigment per gram organic matter than should an oligotrophic lake. However, factors believed to promote pigment preservation, including low oxygen concentration, temperature, light penetration and sediment resuspension; high sedimentation rates, and absence of benthic organisms in sediments, tend to produce higher sedimentary pigment concentrations in eutrophic lakes. Reduced light availability may also contribute to "shade" adaptation in the algal cells, whereby more pigment per gram organic matter is produced by the algal cells. Productive lakes are often shallow and have high sedimentation rates that may result in rapid burial and preservation of pigmented detritus. Preservation is enhanced by only minimal aerobic decay in the water column and on the surface muds (Sanger, 1988). In contrast, oligotrophic lakes tend to have much less pigment preserved in the sedimentary organic matter because primary production is less and there is less sedimenting organic matter. Photo oxidation is also perhaps more of a concern in oligotrophic lakes as these lakes tend to be deeper and pigments are more likely to degrade as they fall through the longer water columns.

Swain (1985) suggests that the proportion of sedimentary chlorophyll not degraded to pheopigments may provide an independent measure of pigment preservation that can be used to distinguish increased pigment production from enhanced preservation. Chlorophyll degrades at about the same rate as total carotenoids, and oscillaxanthin degrades at about the same rate as myxoxanthophyll (Swain, 1985). Therefore, both the ratio of chlorophyll to carotenoids (CD:TC) and the ratio of oscillaxanthin to myxoxanthophyll (OSC:MYX) are mostly determined by the quality of autochthonous production rather than by preservation conditions (Swain, 1985). These ratios may be useful in stratigraphic studies where shifts indicate a qualitative change in the flora. If a lake is largely dominated by phytoplankton, then there will be a predominance of carotenoids (Gorham & Sanger, 1976). Lakes dominated by cyanobacteria other than Oscillatoria will have low OSC:MYX ratios. Relatively high OSC:MYX values indicate that Oscillatoria is the dominant cyanobacteria, but not that the lake is necessarily dominated by Oscillatoria.

#### 2.2.3 Diatoms

Diatoms belong to the algal class Bacillariophyceae and feature a distinctive highly ornamented cell wall composed primarily of silica. They have been especially useful in paleoenvironmental studies because their species distributions are greatly influenced by lake chemistry and nutrient supply, and their remains are well preserved and abundant in the lake sediments (Dixit *et al.*, 1992a). Fossil diatoms have been used qualitatively in many studies to infer lake eutrophication resulting from point-source sewage inputs, the effects of land use activities such as agriculture, road construction, and cottage and municipal land development as well as to document recovery trends in eutrophic lakes following, for example, sewage treatment (Dixit *et al.*, 1992b).

Lake trophic status can be inferred from sedimentary diatom fossils by employing specific diatom indicator species, calculating ratios of selected taxonomic groups, or by the use of simple or multiple regression techniques. The development of weighted averaging regression and calibration has made it possible, theoretically, to determine quantitatively the relationship of a species to a given nutrient (e.g. total phosphorus), and then use these relationships to infer past changes in the

chosen parameter from down-core changes in diatom assemblages in lake sediments (Anderson, 1993). However, there are only a few transfer functions developed thus far that deal with trophic variables (e.g. Hall & Smol, 1992), and they are not regionally applicable. Birks (1994) feels that this approach is also limited by the quality of the available modern training sets, a lack of any consistent and detailed taxonomy, variable sample quality and methodology, and different sedimentary environments of each sample.

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Since patterns of diatom distribution with respect to lake trophic status are not apparent at the family or class levels, reconstruction methods based on ratios of taxonomic groups such as the centric:pennate ratio (Nygaard, 1949) and araphid:centric ratio (Stockner & Benson, 1967) are not as appealing in either theory or practice as those based on the autecology of individual diatom species (Yang & Dickman, 1993). Most diatom-based environmental assessments of trophic state changes are based on the ecological interpretation of shifts in the abundance of individual species in sediment cores. Such studies often use autecological data which are taken from the literature (e.g. Lowe, 1974; Beaver, 1981). For example, the diatom record in lake sediments can been interpreted subjectively using criteria such as phosphorus-rich (eutrophic) lakes are dominated by *Stephanodiscus* and phosphorus-poor (oligotrophic) lakes are dominated by *Cyclotella* (Anderson, 1993). Battarbee (1986) suggests that because some taxa have wider ranges than supposed or because trophic categories have been differently defined by the various authors, it is sometimes necessary to base interpretations on the behaviour of groups of taxa rather than on individual species. *Asterionella formosa* for example, possesses ecotypes, some characteristic of oligotrophic conditions and others characteristic of eutrophic conditions.

According to Battarbee (1991b), diatom concentrations and diatom accumulation rates are especially suited to eutrophication studies where it can be argued that production increases in lakes should cause an increase in the annual flux of diatoms to the sediment. Many factors influence diatom accumulation rates, but in circumstances where preservation is good and sediment accumulation is continuous the most important factor is the level of diatom production in the water column (Battarbee, 1986). Their concentration should reflect past levels of algal standing crop and limnetic chlorophyll*a* (Whitmore, 1991). However, Battarbee (1986) cautions that the diatom response to nutrient changes may be non-linear, especially at high levels of production where silica is a limiting nutrient, and increased production is accounted for by cyanobacteria.

While it is often difficult to subdivide diatom taxa in sediment assemblages into detailed lifeform groups, a general distinction between planktonic species and benthic species can usually be made. Changes in the ratio of planktonic to benthic taxa can be interpreted in two main ways: either as due to a change in the morphology of the lake basin as a lake fills in, and/or to a change in production (Battarbee, 1986). The ratio is more useful in indicating production changes associated with cultural eutrophication than production changes associated with postglacial lake development since, over a long period of time, the ratio is also likely to be sensitive to morphometric changes as the lake fills in (Battarbee, 1986). The diatom record can also be used to reconstruct lake water level and regional climate especially well in closed basin lakes where the water level and lake water chemistry are more sensitive to changes in precipitation and evaporation. The diatom record may indicate water level changes where there is any shift in the proportion of open water habitat to littoral habitat by the planktonic to benthic ratio or an increase in the concentration of benthic microfossils (Battarbee, 1991b).

Anderson et al. (1990) found that a sediment core from Lough Augher, Northern Ireland, showed an unambiguous record of the diatom response to eutrophication; the species succession represented a clear eutrophication gradient, with a shift from mesotrophic planktonic forms (Aulacoseira ambigua, Asterionella formosa, Fragilaria crotonensis, Diatoma tenue var. elongatum) to a variety of small Stephanodiscus spp. typical of very eutrophic conditions (S. parvus, S. hantzschii). They found that interpretations of diatom plankton records based on indicator species and their commonly found associations, could be applied to eutrophication and responses to nutrient reduction. Similarly, Stoermer et al. (1990) found that diatoms from the sediments of McLeod Bay in Great Slave Lake, Northwest Territories showed increased abundance and modified species composition in more recent sediments. Although the Bay remains highly oligotrophic, increased microfossil flux and changes in species composition indicated increasing

nutrient supply (Stoermer et al., 1990).

Rees *et al.* (1991) studied the sediment record from the Bosherston Lakes in Dyfed, South West Wales to determine the record of trophic status. A high external phosphorus loading which includes phosphorus-rich effluent from a sewage treatment works in the catchment of the lakes had produced progressive eutrophication of the lake system. They found that organic carbon, nitrogen and phosphorus concentrations in the surface sediment layer generally correlated directly with trophic status and reflected the distance from the point source of phosphorus input. At one site, the diatom stratigraphy and sediment geochemistry suggested an increase in trophic status most likely due to an influx of nutrient-rich water. Rees *et al.* (1991) found that the sedimentary diatom record went from a mixed flora deposited in the early history of the system, to one in which epiphytic species of *Fragilaria* were abundant. Just below the sediment surface, members of the genus *Stephanodiscus* increased in frequency, indicating to the researchers the onset of advanced eutrophication.

Rawlence and Senior (1988) presented a late-glacial diatom and pigment history of Little Lake, New Brunswick. The occurrence of benthic alkaliphilic diatoms, predominately *Fragilaria* spp., coincident with distinct changes in sediments, organic matter, pollen types and influx rates were utilized in identifying the possible existence of the younger Dryas cool interval (ca. 11,000 to 10,000 years BP). They found that trends in organic matter and pigment values were consistent with a gradual increase in biomass. As well, diatom growth was determined to be indicative of increasing littoral and benthic growth with time, but there was no indication that Little Lake was ever eutrophic (Rawlence & Senior, 1988).

#### 2.2.4 Sediment Chronology

In order to place environmental inferences on a quantitative temporal basis it is necessary to establish a chronology in the lake sediments. Radiometric dating methods are based on the radioactive properties of certain unstable chemical elements, from which atomic particles are emitted in order to achieve a more stable atomic form (Lowe & Walker, 1984). Radioactive decay (atomic transformation) is time-dependent, ranging from days or even seconds for some elements to millions of years for others. If the rate of decay is known, the age of the sediments can be established.

In long core studies, radiocarbon (<sup>4</sup>C) dating has probably been the most widely used method for dating lake sediments. Libby (1955) established the principles of this method which relies on the fact that a radioactive carbon isotope, <sup>14</sup>C, is assimilated into the molecular structure of living organisms. When an organism is isolated from the global system, by death and burial in the sediments, no more <sup>14</sup>C is added to it and the initial activity begins to decrease at a regular rate. The half-life, or rate of decay, of <sup>14</sup>C is about 5,700 years. By knowing the original amount of <sup>14</sup>C in a sample, it is possible to calculate the age of the sample by determining the number of half-lives that must have elapsed in order to account for the sample's residual level of <sup>14</sup>C activity.

The time scale of short core studies (last 200 years) can be determined by identifying the increase of pollen from crop plants or agriculture weeds, by the increase in cesium-137 (<sup>137</sup>Cs) or by lead-210 (<sup>210</sup>Pb) dating (Engstrom & Wright, 1984). The isotope <sup>137</sup>Cs, produced artificially as a consequence of nuclear weapon tests, can be used as a marker horizon which can be traced in lake sediments. It has a half-life of 30 years and has been detectable since 1945. The peak radionuclide fallout produced by nuclear tests occurred during 1962 to 1964 and a lower peak occurred during 1958 to 1959 (Jaakkola*et al.*, 1983). Negligible amounts were deposited before 1954. Radioactive lead (<sup>210</sup>Pb) is a member of the uranium-238 (<sup>234</sup>U) decay series with a half-life of only 22 years (Lowe & Walker, 1984). It is based on the escape of radon from the Earth, and the subsequent decay of this radioactive gas to the isotope <sup>210</sup>Pb. <sup>210</sup>Pb is eventually removed from the atmosphere by precipitation or fall-out and is incorporated into lake sediments. This is known as unsupported <sup>210</sup>Pb. Supported <sup>210</sup>Pb is produced within the sediments, and it is assessed by measuring its radium-226 (<sup>220</sup>Ra) grandparent. The excess <sup>210</sup>Pb over the expected <sup>210</sup>Pb gives the amount of unsupported <sup>210</sup>Pb. Measurement of <sup>210</sup>Pb content can be used to establish rates of sedimentation in lakes over a time-scale of 100 to 150 years (Lowe & Walker, 1984).

#### 2.3 Paleolimnological Studies of Lake Trophic Status

During the last decade, several integrated paleolimnological studies have been carried out to reconstruct and interpret past environmental conditions from the physical, chemical, and biological information contained in sedimentary profiles. Several authors including Tolonen and Meriläinen (1983), Engstrom *et al.* (1985), Fritz (1989) and Hickman and Schweger (1991) have utilized chemistry, sedimentary plant pigments, and diatom microfossils to reconstruct lake histories.

Macro nutrients (e.g. N, P), heavy metals (e.g. Cu, Fe, Mn), sedimentary plant pigments, pH and redox potential are among the many parameters that Tolonen and Meriläinen (1983) analyzed from a sediment core representing a 7,000 year long history of Gallträsk Lake, Finland. In the surface sediments the influence of sewage pollution was clearly reflected by increases in pH and sedimentary plant pigments including myxoxanthophyll (Tolonen & Meriläinen, 1983). Nickel, copper, and manganese only slightly increased in the recent sediments, while other heavy metals (especially Cr and Zn), sulphur, phosphorus, nitrogen, and total organic matter were heavily concentrated in the polluted surface sediment (Tolonen & Meriläinen, 1983).

Engstrom *et al.* (1985) reconstructed a 1,000 year limnological history of Harvey's Lake, Vermont based on stratigraphic analyses of inorganic geochemistry, plant pigments and fossil diatoms in a 0.7 m core of profundal sediments. They obtained an accurate sediment chronology from <sup>210</sup>Pb, <sup>137</sup>Cs, and <sup>14</sup>C dating and from the stratigraphy of pollen and sawmill wastes. It was determined that primary production increased in Harvey's Lake in 1780 following European settlement and again after 1945, as shown by greater accumulation of sedimentary plant pigments and diatom frustules, and changes in fossil algal assemblages (Engstrom*et al.*, 1985). Cyanobacteria first appeared in abundance about 1945 as indicated by the presence of oscillaxanthin and myxoxanthophyll in the sediments. Two episodes of increased sedimentary anoxia (1820 to 1920 and 1945 to present) were marked in the sedimentary record by enhanced pigment preservation, changes in authigenic iron and manganese stratigraphy, and the development of laminated sediments (Engstrom*et al.*, 1985).

Fritz (1989) reconstructed the history of Diss Mere, Norfolk, U.K. from diatom and pigment

analysis of a 17 m sediment core. Large variations in diatom concentrations and distinct lithological changes suggested fluctuating lake levels and a mesotrophic nutrient status early in the lake's history. Increased concentrations of the cyanobacterial pigment oscillaxanthin indicated the expansion of *Oscillatoria* about 6,000 years BP, probably in response to increased stabilization of the water column (Fritz, 1989). Subsequent laminated sediments and extremely high pigment concentrations indicated a long period of moderate water levels and seasonal hypolimnetic oxygen depletion. The diatom taxa were found to shift to those characteristic of moderately enriched lakes. There was a transition from a *Cyclotella*-dominated diatom assemblage to one dominated by *Stephanodiscus* spp. Fritz (1989) attributed the rapid and sustained eutrophication of the mere to increased nutrient inputs caused by forest clearance and agricultural practices in the catchment.

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A 13,200 year history of Fairfax Lake, Alberta was described by Hickman and Schweger (1991) based on the analyses of diatoms, chrysophyte stomatocysts, pollen and sedimentary plant pigments, including myxoxanthophyll and oscillaxanthin in a 10 m core. A maximum in oscillaxanthin and myxoxanthophyll concentrations, hence the largest cyanobacterial populations, occurred in the region ca. 13,200 to 11,600 years BP. Diatoms were not found until ca. 11,255 years BP. Benthic taxa initially dominated, but by ca. 10,100 years BP planktonic taxa had become more prominent indicating a rise in the lake water level and probably increased water transparency. Maximum chlorophyll and total carotenoid concentrations occurred ca. 11,255 to ca. 7,000 years BP corresponding to the warm early- to mid-Holocene period (Hickman & Schweger, 1991). Lake nutrient levels were interpreted to have been higher prior to ca. 7,000 years BP. In contrast to most studies of trophic status, the reconstructed history indicates that the lake has changed from being eutrophic during the early Holocene, to its present status as an oligotrophic to mesotrophic lake.

#### 3.0 Study Site Description

Killarney Lake (49°11'N, 98°42'W) is situated within the Pembina River Plain of southwestern Manitoba (Figure 1), occurring just above the Turtle Mountain Uplands in the south and the Pelican-Rock Lakes and Pembina channel in the north. It is an elongate shallow (maximum depth = 6.0 m, surface area = 163.6 ha) lake with its widest and largest open water portion nearest the town of Killarney (Figure 2). Killarney Lake has essentially no permanent overland inflow or outflow. The lake lies to the north of the Long River (formerly known as Whitemud Creek). There is an artificial channel connecting the river to the lake which serves as the only inlet to the lake. A dam constructed by the Prairie Farm Rehabilitation Administration in 1956 allows water to flow into the lake when the water level upstream of the dam becomes high. Conversely, when the water level upstream of the dam decreases below the actual lake level, water flows out of the lake. According to Kelln (1979) the amount of lake inflow and outflow is small compared to the total volume that flows in the Long River past Killarney indicating that this structure has not been effective in diverting water to the lake.

The physiography in the Killarney area is the result of glacial processes (Michalyna & Holstrom, 1980). A reconstruction of glacial history in Manitoba is provided by Fenton et al. (1983). The Western Interior of Canada was entirely covered by the Wisconsinan glacier; ice disappeared first from the southwest corner of Manitoba roughly 11,500 years BP. The early phases of glacial Lake Agassiz, with southern drainage, were formed at this time. By about 11,000 years BP the ice front intersected the Precambrian Shield area, in the northeast corner of Manitoba, and glacial Lake Agassiz was discharging by an eastern outlet. The ice readvanced in northwestern Ontario, closing the lower eastern outlets. The entire area was probably ice-free by 9,500 years BP and the final stage of draining of glacial Lake Agassiz into the Lake Superior basin by way of the eastern outlets was between 8,000 and 9,000 years BP.

During the recession and waning of the Laurentide continental ice mass from the south, the ice







Figure 2. Bathymetric map of Killarney Lake, showing depth contours in meters and the locations of the sediment coring sites. Cores K1, K2, K4, and K5 were collected at site 1 and cores K3 and K6 were collected at site 2. A black box marks the location of the dam on the Long River.

front remained stationary for a period of time in the area immediately to the north of the present lake basin (Killarney Phase). Waters from the melting ice and surface runoff from the east side of Turtle Mountain flowed easterly toward the Pembina River. Killarney Lake was formed as a result of corrasion beneath a great mass of continental ice. Sediments brought into the area modified the land south of the lake to a gently undulating landscape while the area to the north of the lake remained hummocky in nature, untouched by the modifying effects of glacial meltwater. The underlying bedrock in the area consists of Cretaceous shales of the Riding Mountain Formation at depths of 25 to 30 meters below the surface. The dominant unconsolidated deposit overlying the Cretaceous shales is strongly calcareous, loamy textured glacial till containing thin, sandy and gravely layers (Michalyna & Holstrom, 1980).

Primary land use around the lake is agricultural with a small acreage in recreation and residential associated with the Town of Killarney (incorporated in 1903). The town has a population of 2,200 people and a zero rate of population growth (Mr. H. A. Lamb, Secretary Treasurer, Town of Killarney; personal communication, 1994). Aerial photographs taken in 1948 (Figure 3) and 1992 (Figure 4) show that extensive shoreline development has occurred around the lake. Additional aerial photographs (not included) show that most shoreline development has rapidly taken place over the last 25 years. There are presently approximately 80 homes and 70 cottages on the lake shore. The lake is used extensively by tourists for boating, swimming and fishing (summer and winter).

In the extreme eastern end of the lake a variety of uses including picnic-swimming area, sports fields, cottage areas and residential lots lie adjacent to the lake. Along the southern shore of this eastern end of the lake cottages and tourist camps run parallel to the shoreline. Further west of this intensively developed area, cottages and rural residential lots have been more recently developed. On the north shore of the central portion of the lake a golf course, picnic site, campground, cottages and boat launch have been developed by a private individual. Along the remaining western shoreline pasture land and croplands predominate. Cattle graze in a pasture adjacent to the lake.

Killarney Lake also serves as the source of the town's drinking water. Town drinking water is



Figure 3. Aerial photograph (A11400-198, Energy, Mines and Resources Canada) of Killarney Lake taken during 1948.



Figure 4. Aerial photograph (MB92008-157, Province of Manitoba) of Killarney Lake taken during 1992 (04/05/92).

pumped from the lake to the water treatment plant where it undergoes coagulation treatment. Sewage disposal is via an aerated wastewater holding pond. The Town's storm drains discharge into the main lake basin and the bay to the east of the bridge.

Killarney Lake occurs within the Moderately Cool Boreal, Subhumid Continental Region (C.D.A., 1972). It lies within the transition between the mixed grass prairie and predominantly grassland with scattered groves of willow and aspen (Weir, 1983). According to a biological survey of Killarney Lake conducted by the Provincial Fisheries Branch (Arnason, 1956) the native vegetation consists of mixed short and tall prairie grasses with associated herbaceous plants. Along the north shoreline large clumps of bur oak (*Quercus macrocarpa*) are present. On the south shore trembling aspen (*Populus tremuloides*), green ash (*Fraxinus pennsylvanica*) and willows (*Salix* spp.) occur. Cultivated fields touch the shores in many places or are only cut off by a narrow belt of trees. The margin of Killarney Lake shows both emergent and submerged vegetation. Emergent vegetation consists chiefly of rushes (Juncaceae), sedges (Cyperaceae) and grasses (Gramineae). Other emergent vegetation includes pondweed (*Potamogeton* sp.), duckweed (*Lemna* sp.), and crowfoot (*Ranunculus* sp.) (Arnason, 1956).

Throughout the years 1917 to 1956 an almost continuous series of fish stockings had been made by the Provincial Fisheries Branch (Arnason, 1956). The lake has been stocked over the years with pickerel (*Stizostedion vitreum*), pike (*Esox lucius*), largemouth bass (*Micropter us salmoides*) and yellow perch (*Perca sp.*). Since Killarney Lake experiences severe winter kill in most winters no breeding population of game fish has been able to maintain itself (Arnason, 1956). In recent years the lake has not been fish stocked (Mr. H.A. Lamb, Secretary Treasurer, Town of Killarney; personal communication, 1994).

Killarney Lake is hyper-eutrophic (summer mean phytoplankton biomass 11 to 32  $\mu$ g l<sup>-1</sup> chlorophyll; total phosphorus 30 to 200  $\mu$ g l<sup>-1</sup>; Dr. L.G. Goldsborough, University of Manitoba; unpublished data) with the phytoplankton dominated throughout much of the summer by cyanobacteria (blue-green algae). The frequency of algal blooms and the amount of aquatic weeds may have increased with the amount of agricultural fertilizers applied within the lake's drainage

system. The rapid growth of algae gives rise to numerous undesirable effects on treatment of drinking water, bathing sanitation and recreation (tourism). Toxins are released by many algae and when ingested by humans or other animals can cause detrimental or even lethal effects. Massive growths of algae can physically impede waterways and clog filters at water treatment facilities. Associated with an increase in production is the expanded problem of winter kill resulting from a greater depletion of oxygen in the lake. Decaying algal blooms can produce unpleasant foul smelling masses floating along shorelines.

Killarney Lake has a long history (>50 years) of manipulation in an effort to reduce chronic algal blooms. Efforts to control nuisance algal blooms have been made through regular additions of copper sulphate (for example, about eight tonnes in 1991) to the epilimnion. The copper sulphate is applied by spreading the chemical on the lake surface from a boat. This practice of adding copper sulphate or "bluestoning" may have begun as early as the 1920's. Mrs. B. Blixhavn, a long time resident of Killarney, remembers swimming at the "girl's beach" (the southernmost section of the present public beach) in 1924 when someone was applying a blue-colored substance. She recalls the rocks turning blue and being told to wait to go swimming. Mrs. D. Hysop, also a Killarney resident, cites an anecdotal report from 1943 where town resident Mr. N. Waldon says, "The bay was a stinking mess and town resident Mr. F. Kent bluestoned it; people said he was a fool and that it wouldn't work." This could suggest that bluestoning was a new thing that year. Mrs. B. Wood, another long-time resident of Killarney, recollects her husband bluestoned the bay from a rowboat in 1947. Mr. H. Kiffen also of Killarney began working for the town in 1957 and they were already bluestoning.

There are few data on changes in lake water quality since 1879, when intensive agricultural land use began in the watershed. A surface water sampling program was conducted throughout the ice-free season in 1991 and 1992 by Dr. L.G Goldsborough (University of Manitoba) in partnership with the Manitoba Provincial Water Quality Branch. Select surface water chemistry parameters from these two years and one sampling day in 1993 are illustrated in Table 1. These chemical parameters are compared with other lakes located in southwestern Manitoba in Table 2.

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Parameter	Mean	Range	Mean	Range	Mean	Range
Total alkalinity (mg l <sup>-1</sup> )	ı	ı	193	176-206	199	193-201
hq	r	ı	8.26	8.01-8.57	8.22	8,11-8.43
Specific conductivity (µmhos cm <sup>-1</sup> )	•	·	836	695-958	753	717-764
Dissolved oxygen (mg l <sup>1</sup> )	0.0	8.4-9.3	ı	•	7.6	6.4-8.1
Chlorophyll a (µg l <sup>-1</sup> )	20.9	11.4-31.9	21.6	11.2-37.0	1.8	1.0-3.5
Total phosphorus-P (mg l <sup>-1</sup> )	·	ſ	0.192	0.070-0.236	0.275	0.159-0.236
Secchi depth (m)	1.43	0.86-2.15	•		2.08	1.53-2.85

Table 2. Comparison of selected surface water chemistry parameters (Dr. L.G. Goldsborough (University of Manitoba) & Provincial Water Quality Branch, unpublished data) collected during August 1993 for Killarney Lake compared with other lakes located in southwestern Manitoba (see Figure 1 for locations).

Parameter	Killarney Lake	Pelican Lake	Rock Lake	Crawford Lake	Max Lake
Total alkalinity (mg l <sup>-1</sup> )	199	353	212	450	270
pН	8.22	8.68	8.17	9.03	8.71
Specific conductivity (umhos cm <sup>-1</sup> )	753	1568	749	2643	517
Dissolved oxygen (mg l <sup>-1</sup> )	7.6	7.8	7.0	9.8	7.7
Chlorophyll a (µg l <sup>-1</sup> )	1.8	35.0	1.0	1.2	19.0
Total phosphorus-P (mg l <sup>-1</sup> )	0.275	0.210	0.150	0.039	0.053
Secchi depth (m)	2.08	0.52	1.50	5,55	0.79
Comparisons between lakes listed in Table 2 should be interpreted cautiously because the values given are for only one day of sampling. The total alkalinity, pH, and dissolved oxygen values are lower for Killarney Lake than for the other lakes in the area. The chlorophyll *a* value is low compared to values for Pelican Lake and Max Lake. It is likely that this low chlorophyll*a* value is not representative of typical chorophyll*a* values in the lake given its eutrophic nature. Killarney lake has the highest level of total phosphorus out of the five lakes and lower water transparency as indicated by the Secchi depth.

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# 4.0 Materials and Methods

# 4.1 Coring

Six sediment cores were collected from two sites representative of the deepest portions of the lake during March of 1992 and 1993 (Table 3, Figure 2). A Reasoner percussion corer (Reasoner, 1986) was used to obtain three long cores (K1, K2, & K3) to study the postglacial record of the lake. The coring system consisted of a 7.6 cm diameter 4 m plus long core barrel, a weighted core head, and a core driver (Figure 5). It is designed for winter operation, is simple to operate and inexpensive to assemble.

Coring was conducted from the surface of the ice pack. After a hole was made in the ice pack, the core barrel, core head and driver were lowered through the water column and allowed to settle slowly into the surficial sediments (Reasoner, 1986). The driver was raised and dropped repeatedly in order to drive the core barrel into the sediment. Upon completion of the driving process (when the coring device vibrated upon impact with the driver), the driver was raised and removed from the main line. The core was retrieved using a pulley system attached to the ice pack. A core catcher consisting of a ring of five aluminum fingers attached to the inside base of the core barrel prevented the loss of sediment while retrieving the core. The core barrel was cut to the sediment/water interface and sealed with solvent cement and plastic end caps; the lower end of the barrel was also sealed. The cores were transported to the laboratory and kept at 4°C until analyzed.

The cores were opened by making diametric lengthwise cuts in the wall of the core barrel with a radial saw. A nylon monofilament passed between the two cuts was drawn along the core length, slicing it into two halves. Subsampling of these cores was performed within a 1 cm band at 5 cm intervals. A modified 5 ml syringe was used to obtain approximately 1.9 cm<sup>3</sup> of wet sediment for determining water content, organic matter, and total carbonates; total phosphorus; total chlorophyll; and diatoms at each sampling interval. Approximately 10 g of wet sediment was collected for carotenoid pigment analyses. Additional bulk sediment samples were collected for radiocarbon

Sediment	Collection Date	Corer	Water	Core	Sampling
Core		Туре	Depth (m)	Length (cm)	Interval (cm)
K1	March 15, 1992	Reasoner	6.85	205	5
K2	March 15, 1992	Reasoner	6.85	270	5
K3	March 15, 1992	Reasoner	6.17	280	5
K4	March 21, 1993	Glew	5.82	25	1
K5	March 14, 1993	Glew	5.82	26	1
<b>K</b> 6	March 14, 1993	Glew	5.50	20	1

Table 3. A summary of the sediment cores collected from Killarney Lake.

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Figure 5. Schematic diagram of a modified Reasoner (1986) percussion coring system.

dating (see *Dating*). Care was used to avoid subsampling sediment adjacent to the core barrel to prevent possible contamination from younger material as the core barrel passed through the sediment.

To examine modern changes in lake primary production two short (top 30 cm) sediment cores (K5 & K6) were collected using a Glew modified K-B gravity corer (Glew, 1988, 1991). A third short sediment core (K4) was collected for<sup>210</sup>Pb dating of the recent sediments (see *Dating*). The gravity corer consisted of a lower cylinder, the sleeve and clamping device to secure the core tube; and an upper part that housed the closing piston, release mechanism, and captive float (Figure 6). An acrylic core tube with an inside diameter of 63 mm was used for core collection.

Coring was conducted from the surface of the ice pack through a hole made in the ice. The gravity corer was lowered through the water column and allowed to settle slowly into the surficial bottom sediments. A guided messenger triggered the closure of the top of the core tube and the gravity corer was raised slowly to the surface. The bottom of the core tube was stoppered. The cores were sectioned at 1 cm intervals in the field using a vertical extrusion device for close interval sectioning (Glew, 1988). The bagged samples were transported to the laboratory and kept at 4°C until analyzed.

Subsampling was performed as with the long cores. Approximately 1.9 cm<sup>3</sup> of wet sediment was collected for determining water content, organic matter, and total carbonates; total phosphorus; total chlorophyll; and diatoms at each sampling interval. Approximately 10 g of wet sediment was collected for carotenoid pigment analyses. The remaining sediment of core K5 was sent to the W.M. Ward Technical Services Laboratory (Province of Manitoba, Winnipeg) for analyses of heavy metal content (Cu, Pb, Hg, Cd, Mn, & Fe) at 1 cm intervals.

### 4.2 Composition

Sediment core subsamples were described qualitatively in terms of color (using Munsell soil color charts) and texture. Water content, organic matter, and total carbonates were determined by loss on ignition. Water content (%) was measured as weight loss after drying to constant weight at 105°C for 24 hours, organic matter (% dw) after ignition at 550°C for one hour, and total carbonates



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(% dw) after further ignition at 950°C for three hours (Wetzel, 1970).

An ignition method was also used to determine the total phosphorus in the lake sediments following the methods of Andersen (1976) and Stainton *et al.* (1977). Total extractable phosphorus was determined by combusting samples at 550°C for one hour to destroy organic matter, then boiling the residue in 1 N HCl which extracts the phosphorus and converts it to orthophosphate. The total phosphorus content of the original sediment sample was determined as orthophosphate by the molybdate-ascorbic acid method (Stainton *et al.*, 1977). Color development (blue) proportional to the amount of orthophosphate present in the sample occurs upon the addition of molybdate-ascorbic acid reagent to the samples. The absorbance of samples was measured at 885 nm in a Spectronic 601 (Milton Roy, Rochester, N.Y.) spectrophotometer. Total phosphorus ( $\mu$ g gdw<sup>-1</sup>) was determined by comparing measured sample absorbance to a standard phosphorus (range 50 to 1,400  $\mu$ l) curve.

## 4.3 Plant pigments

Plant pigments were extracted in 90% methanol for 24 hours in the dark. The samples were then centrifuged to remove suspended particles. The extract absorbance was determined at 665 nm and 750 nm in the spectrophotometer before and after acidification with 10<sup>-3</sup> N HCl. Total chlorophyll (µg gdw<sup>-1</sup>) was determined following standard spectrophotometric methods described by Lorenzen (1967) and Marker *et al.* (1980).

Total carotenoid pigments, myxoxanthophyll, and oscillaxanthin were determined following the methods of Sanger & Gorham (1972) and Swain (1985). These pigments were extracted in 90% acetone for 24 hours in the dark. The extract was decanted and centrifuged to remove suspended particles. The clarified sample was collected into a 100 ml graduated cylinder and made to volume. Total carotenoids were measured by first saponifying a 30 ml acetone aliquot via the addition of 15 ml of 20% KOH in methanol (w:v). This mixture was refrigerated for two hours and then the carotenoids were extracted into 30 ml petroleum ether (30 to 60°C BP) in a separatory funnel. The hypophase was drained through anhydrous sodium sulphate and the extract absorbance was read at 448 nm against a petroleum ether blank. The epiphase was washed with 50 ml distilled water (the hypophase was discarded), drained through anhydrous sodium sulphate, and the extract absorbance was read at 448 nm against a 2:1 acetone/methanol blank. Total carotenoids ( $\mu g$  gdw<sup>-1</sup>) were calculated as in Swain (1985).

Myxoxanthophyll and oscillaxanthin were determined from the remaining 70 ml acetone aliquot by adding 40 ml petroleum ether in a separatory funnel. Myxoxanthophyll and oscillaxanthin are highly polar and are completely held in the acetone-water hypophase, which was removed and dried under an air stream. The dry pigments were redissolved in absolute ethanol and the concentration of these two pigments was determined by the trichromatic method (Swain, 1985). This method consists of measuring the absorbance of the ethanol solution at 412 nm, 504 nm and 529 nm, the absorbance peaks for the contaminating pigment phorbin, oscillaxanthin, and myxoxanthophyll, respectively. The concentration of myxoxanthophyll and oscillaxanthin ( $\mu$ g gdw<sup>-1</sup>) was then calculated as in Swain (1985).

#### 4.4 Diatoms

Diatom valves were separated from the sediment matrix using a series of water washings. Distilled water was added to a 1 cm<sup>3</sup> wet sediment sample and the sample was sonicated for approximately 16 minutes. A 0.5 ml subsample was diluted to 100 ml; 40 ml of this solution was removed for washing. To remove clay particles the samples were initially washed three times with 1% Calgon<sup>®</sup> water softener in distilled water (weight:volume). This was followed by at least six distilled water washes. Settling time between washings was three hours as determined following the equation for particle settling time from Folk (1965). Empirical studies showed three hours was adequate to permit separation of larger, rapidly sedimenting diatoms from smaller, more buoyant clay particles.

A measured volume of a well agitated suspension of diatom valves was poured into evaporation

trays (modified from Battarbee, 1973) and left to evaporate in an undisturbed room. This method allowed for a random distribution of diatoms over the floor of the tray. Once dry the coverslips were removed from the trays, combusted at 550°C for six minutes and mounted on slides using Naphrax (Northern Biological Supply, Martlesham, Ipswich) high resolution diatom mountant. A minimum of 500 diatom valves were identified and enumerated from each sample under high magnification (1000x) light microscopy using a Leitz Diaplan (Germany) microscope with phasecontrast optics. Taxonomically challenging specimens were studied further using scanning electron microscopy. Species identification is mainly based on keys by Patrick and Reimer (1966, 1975), Germain (1981), and Krammer and Lange-Bertalot (1986, 1988, 1991a, 1991b). Diatom zonation was based on cluster analysis employing Euclidean distance and sum of squares distance method on log transformed diatom concentration data (Carney, 1982; Wolin, 1996).

#### 4.5 Sediment Chronology

Sediment samples were collected at five positions in each long core for radiocarbon dating. Samples were removed, dried, wrapped in aluminum foil and stored at 4°C. Three samples from K2 (23 to 35, 140 to 150, & 264 to 270 cm) and K3 (25 to 37, 140 to 150, & 270 to 281 cm) were analyzed at the Environmental Isotopes Lab, Alberta Environmental Centre, Vegreville.

The stratigraphy of <sup>210</sup>Pb and <sup>137</sup>Cs content in the K4 short core was used to establish the sediment chronology in the Killarney Lake basin over a time-scale of the past 150 years. This analysis was conducted by Mr. P. Wilkinson at the Freshwater Institute, Winnipeg. Radiochemical analyses were carried out using a number of analytical techniques. Five to ten grams of sediment were sealed in 60 x 15 mm plastic petri dishes, aged for 30 days and counted on a gamma spectrometer (Ge (Li) semi-conductor detector) for the determination of <sup>137</sup>Cs and <sup>226</sup>Ra. In some cases, counting was done on a hyperpure germanium crystal and <sup>210</sup>Pb was determined directly along with <sup>137</sup>Cs and <sup>226</sup>Ra (Joshi, 1987). One to three gram samples were analysed for <sup>210</sup>Pb by leaching in 6N HCl in the presence of a <sup>209</sup>Po tracer, autoplating Po onto a silver disc (Flynn,

1968) and counting the disc on an alpha spectrometer to determine <sup>210</sup>Pb via its <sup>210</sup>Po daughter. <sup>226</sup>Ra was determined on selected slices by the radon de-emanation technique (Mathieu, 1977; Wilkinson, 1985). Excess <sup>210</sup>Pb was determined in each slice by subtracting the <sup>226</sup>Ra activity from the <sup>210</sup>Pb activity.

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The sediment slice mean ages were determined using three models. The linear fit model (Oldfield & Appleby, 1984) assumes a constant flux of<sup>210</sup>Pb to the sediments and a constant sedimentation rate. The constant flux model (Oldfield & Appleby, 1984) assumes a constant flux of<sup>210</sup>Pb to the sediment and changing sedimentation rates. The difference between these two models mathematically is that the linear fit is a best fit regression and the constant flux model is a regression point by point and then averaged. The third model used was the Rapid Steady State Mixing (RSSM) model (Robbins, 1978) which corrects for sediment mixing. It does a curve fit to the mixed profile and calculates the parameters based on no mixing having occurred.

# 5.0 Results

## 5.1 Sediment Chronology

The sediment of the three long cores (K1, K2, & K3) was unlaminated organic silt (Dr. W. Last, University of Manitoba; personal communication, 1993). Sediment colors were generally very dark greyish brown (2.5Y 3/2) to dark olive grey (5Y 3/2). The bottom 15 cm of the K2 core was a coarse sand and gravel. If this latter material is postglacial debris, <sup>14</sup>C dating of the organic stratum immediately above the sand indicated the Killarney Lake basin is at least 4,670 years old. The <sup>14</sup>C dates obtained from the K2 and K3 cores appear in Tables 4 and 5. Radiocarbon ages presented are  $\partial^{13}$ C corrected (correction = 16 ( $\partial^{13}$ C+ 25) years) and relative to 1950 AD; the  $\partial^{13}$ C values are ‰ relative to the PDB international standard. These <sup>14</sup>C dates provide the basis for the extrapolated ages used in the text, bearing in mind the probable false assumption of uniform deposition rates through the core.

The three <sup>14</sup>C dates obtained for the K2 core indicate that the sedimentation rate at this site averaged 0.59 mm year<sup>1</sup>. Comparison with data from the K3 core indicated that the sedimentation rate at this site was higher, averaging 0.75 mm year<sup>1</sup>.

The chronology of the K5 and K6 short cores is based on close-interval <sup>210</sup>Pb dating of the K4 core. The age-depth relationship, determined using the RSSM model results, is plotted in Figure 7. This model provides a reasonable explanation of the <sup>210</sup>Pb activity profile from the K4 core (Mr. P. Wilkinson, Freshwater Institute; personal communication, 1995). The 24 cm core represents 53 years, the base of the core was dated 1940AD. The average sedimentation rate was determined to be 49 mm year<sup>1</sup>.

The stratigraphy of <sup>137</sup>Cs provides independent evidence of the accuracy of the <sup>210</sup>Pb chronology (Figure 8). A maximum concentration of <sup>137</sup>Cs was found at 12 cm and a lower peak occurred at 17 cm. The dates of 1963 AD and 1959 AD are placed, respectively, on these levels based on the historical pattern of atmospheric fallout (Jaakkola *et al.*, 1983). These dates fall reasonably close

Depth below	Dated material	∂¹³C	<sup>14</sup> C age	AECV#
sediment surface (cm)		(‰)	years BP	
23-35	Bulk sediment	-26.1	490 ± 70	1661C
140-150	Bulk sediment	-26.2	2440 ± 70	1662C
264-270	Bulk sediment	-26.3	4670 ± 80	1663C

Table 4. Radiocarbon dates from the K2 core in Killarney Lake.

Table 5. Radiocarbon dates from the K3 core in Killarney Lake.

Depth below	Dated material	∂¹³C	<sup>14</sup> C age	AECV#
sediment surface (cm)		(‰)	years BP	
23-37	Bulk sediment	-26.9	570 ± 70	1727C
140-150	Bulk sediment	-26.8	$1710 \pm 90$	1728C
270-281.5	Bulk sediment	-27.0	$3250 \pm 90$	1729C



Figure 7. Age-depth relationship in the K4 core determined by <sup>210</sup>Pb.



Figure 8. <sup>137</sup>Cs activity in the K4 core.

to the <sup>210</sup>Pb age-depth curve (Figure 7). The low levels of <sup>137</sup>Cs below 20 cm may be due to downward mixing or diffusion.

# 5.2 Core K1

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### 5.2.1 Composition

The chemical parameters measured in the K1 core are profiled in Figure 9. Water and carbonate content did not vary much with depth. Water content gradually increased from ca. 60% at the base of the core to ca. 85% at the top of the core. The carbonate content was relatively constant over the length of the core fluctuating around the mean of 10% dw.

Organic matter content was high at the base of the K1 core (ca. 17% dw) then decreased to ca. 10% dw between 180 and 145 cm. Two maxima (ca. 20% dw) in organic matter content occurred between 145 and 75 cm and between 60 and 25 cm. Applying the <sup>14</sup>C dates obtained for the K2 core (also from this site), the former peak occurred between ca. 2,500 and 1,270 years BP and the latter between ca. 1,010 and 390 years BP. The phosphorus content also peaked during these two periods, although the earlier peak was less pronounced. Between 205 and 140 cm the phosphorus content averaged 200  $\mu$ g gdw<sup>-1</sup>. During the first peak (145 to 75 cm) phosphorus content increased to ca. 300  $\mu$ g gdw<sup>-1</sup> and in the second peak (60 to 25 cm) phosphorus reached 430  $\mu$ g gdw<sup>-1</sup>. Both organic matter and phosphorus were low in the surface sediments (ca. 15% dw and ca. 280  $\mu$ g gdw<sup>-1</sup>, respectively), but both showed an increasing trend in the top five centimeters. In the top 10 cm organic matter content increased from ca. 14 to 18% dw while phosphorus content increased from ca. 250 to 320  $\mu$ g gdw<sup>-1</sup>.

## 5.2.2 Plant pigments

Total chlorophyll was the only pigment parameter measured in the K1 core (Figure 9). Total chlorophyll was low (ca.  $5 \mu g \text{ gdw}^{-1}$ ) in the bottom sediments between 205 and 115 cm. As found with the organic matter and phosphorus content, total chlorophyll content also peaked twice. Between 115 and 75 cm (ca. 1,970 to 1,270 years BP) it reached ca. 14  $\mu g \text{ gdw}^{-1}$  and between 60 and 25 cm (ca. 1,010 to 390 years BP) the maximum total chlorophyll content (18  $\mu g \text{ gdw}^{-1}$ )



was reached. The percent native chlorophyll varied widely over the length of the K1 core. No native chlorophyll was found between 170 and 165 cm. Preservation conditions may have been very good between 145 and 140 cm, and at 25 cm as these samples contained 100% native chlorophyll.

# 5.3 Core K2

### 5.3.1 Composition

The chemical parameters measured in the K2 core are profiled in Figure 10. As in the K1 core, water and carbonate content remained relatively constant over the length of the K2 core. Water content was only 17% at 270 cm, at 265 cm it increased to 60% and increased gradually to 84% at the surface. Carbonates averaged 10% dw over the length of the K2 core except for a low value (6% dw) at 270 cm. Organic matter and total phosphorus content were also exceptionally low (1% dw and 42  $\mu$ g gdw<sup>-1</sup>, respectively) at 270 cm.

Organic matter content was ca. 17% dw between 265 to 240 cm (ca. 4,610 to 4,170 years BP). Two maxima of ca. 22% dw occurred between 200 and 110 cm (ca. 3,470 to 1,880 years BP) and between 80 and 20 cm (ca. 1,360 to 300 years BP). Total phosphorus was low (ca. 165  $\mu$ g gdw<sup>-1</sup>) between 265 and 175 cm (ca. 4,610 to 3,030 years BP). Between 175 and 110 cm (ca. 3,030 to 1,880 years BP) the phosphorus content of the sediments peaked at ca. 600  $\mu$ g gdw<sup>-1</sup>. There was a small decrease in phosphorus concentration until a second peak (ca. 700  $\mu$ g gdw<sup>-1</sup>) occurred between 80 and 20 cm (ca. 1,360 to 300 years BP).

# 5.3.2 Plant pigments

The pigment parameters measured in the K2 core are profiled in Figure 10. The percent native chlorophyll varied widely over the length of the K2 core. No native chlorophyll was measurable between 160 and 155 cm (ca. 2,760 to 2,670 years BP) and at 65 cm (ca. 1,090 years BP). One sample at 165 cm (ca. 2,850 years BP) contained 100% native chlorophyll.

Total chlorophyll and total carotenoids showed similar patterns of concentration in the K2 core. In the lowermost sediments (270 to 180 cm) total chlorophyll concentration was low (ca. 5



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Figure 10. Profile of the chemical parameters and s





the chemical parameters and sedimentary pigments in the K2 core.



 $\mu$ g gdw<sup>-1</sup>) compared to two maxima (ca. 20  $\mu$ g gdw<sup>-1</sup>) that occurred between 175 and 100 cm (ca. 3,030 to 1,710 years BP) and between 80 and 20 cm (ca. 1,360 to 300 years BP). Total carotenoids increased from ca. 2 to 7  $\mu$ g gdw<sup>-1</sup> during these two intervals but the peaks were less pronounced. In the uppermost sediments (top 20 cm) pigment concentrations were relatively low but showed an increasing trend.

The total chlorophyll to total carotenoid (CD:TC) ratio was very high (ca. 21) at the base (270 cm) of the K2 core. Values between 265 and 175 cm (ca. 4,610 to 3,030 years BP) were much lower (ca. two). The ratio was maximized at values of five to six between 170 to 145 cm (ca. 2,940 to 2,500 years BP). In the top 140 cm the ratio returned to lower values in the range of two to four.

Both oscillaxanthin and myxoxanthophyll fluctuated irregularly throughout the K2 core. The concentration of myxoxanthophyll showed a slight increasing trend if peak values are compared as follows. The first small peak in myxoxanthophyll concentration, ca. 15  $\mu$ g gdw<sup>-1</sup>, occurred at 245 cm (ca. 4,260 years BP), the concentration increased to ca. 28  $\mu$ g gdw<sup>-1</sup> at 195 cm (ca. 3,380 years BP), increased to ca. 31  $\mu$ g gdw<sup>-1</sup> at 155 cm (ca. 2,670 years BP), increased to ca. 35  $\mu$ g gdw<sup>-1</sup> at 50 cm (ca. 830 years BP), and reached a maximum concentration of ca. 40  $\mu$ g gdw<sup>-1</sup> at 30 cm (ca. 480 years BP). Major peaks in oscillaxanthin concentration (ca. 28  $\mu$ g gdw<sup>-1</sup>) also occurred at depths of 195 cm (ca. 3,380 years BP), 155 cm (ca. 2,670 years BP), and 30 cm (ca. 480 years BP). Values greater than one in the oscillaxanthin to myxoxanthophyll (OSC:MYX) ratio occurred most often in the lower half of the core between 270 and 75 cm (ca. 4,700 to 1,270 years BP). The OSC:MYX ratio averaged ca. 0.5 in the top 70 cm.

# 5.3.3 Diatoms

Diatom frustules were found at all levels of the K2 core (Figure 11). Total diatom concentration was low, ranging from ca. 16 to  $450 \times 10^6$  valves gdw<sup>-1</sup>, between 270 and 190 cm (ca. 4,700 to 3,290 years BP). Diatom concentration reached maximum values of ca. 9,000 to 12,000 x  $10^6$  valves gdw<sup>-1</sup> between 190 and 75 cm (ca. 3,290 to 1,270 years BP), with the exception of one



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Figure 11. Profile of the diatom concentration, community spectra, and diatom diversity in the K2 core.

low value (460 x  $10^6$  gdw<sup>-1</sup> valves) at a depth of 130 cm (ca. 2,240 years BP). Diatoms decreased to an average concentration of ca. 3,440 x  $10^6$  valves gdw<sup>-1</sup> between 75 and 10 cm (ca. 1,270 to 130 years BP), then increased in the top 10 cm (ca. 130 years BP to present) of the K2 core to near maximum values of 8,900 x  $10^6$  valves gdw<sup>-1</sup> at the surface.

Planktonic diatom taxa were always more abundant than benthic forms. However, benthic taxa did increase relative to planktonic taxa at depths of 255 cm (ca. 4,430 years BP), 120 cm (ca. 2,060 years BP) and 65 cm (ca. 1,090 years BP) (Figure 11). Planktonic taxa composed nearly all of the sample at 135 cm (ca. 2,320 years BP) and between 120 and 75 cm (ca. 2,060 to 1,270 years BP). This is evident in the planktonic:benthic ratio.

Diatom diversity (as estimated using the Shannon-Wiener (1963) formula) ranged from a low of 0.8 at depths of 180 cm (ca. 3,110 years BP) and at 240 cm (ca. 4,170 years BP), to a maximum value of 3.9 at 255 cm (ca. 4,430 years BP).

The major genera are profiled in Figure 12. The benthic taxa showed two peaks of greatest abundance between the depths of 225 and 125 cm (ca. 3,900 to 2,150 years BP) and between 100 and 25 cm (ca. 1,710 to 390 years BP). This is illustrated best by the species totals for the genera *Cymbella*, *Epithemia*, *Gomphonema*, and *Navicula* (Figure 12). In contrast, the planktonic genera were most abundant in the recent sediments (ca. 39 years BP to present) and between 125 and 75 cm (ca. 2,150 to 1,270 years BP).

A total of 108 diatom taxa have been identified from the K2 core; a complete listing is found in Appendix A. The most common taxa (determined as all taxa that were present in a minimum of two samples and had a relative abundance of  $\geq$ 1% in at least one sample) are listed in Table 6 and their stratigraphic distributions are illustrated in Figure 13. Light microscope photographs of the most common taxa are found in Appendix B.

Aulacoseira granulata, along with A. ambigua and A. subarctica were important euplanktonic components of assemblages throughout the K2 core. A. ambigua and A. subarctica have been summed together due to the difficulty in separating these two species at the light microscope level. These three species have similar distribution trends in the K2 core, although the





Table 0. List of the most common diatom taxa (with authorities	) in the K2 core.
Amphora ovalis Kütz.	Benthic
Amphora pediculus Kütz.	Benthic
Asterionella formosa Hass.	Planktonic
Aulacoseira ambigua (Grun.) Simons.	Planktonic
Aulacoseira granulata (Ehr.) Simons.	Planktonic
Aulacoseira subarctica (O. Müll.) Haworth	Planktonic
Cocconeis placentula Ehr.	Benthic
Cyclotella bodanica Eul.	Planktonic
Cymbella cymbiformis (Ag. Kütz.) V. Heurck	Benthic
Cymbella hustedtii Krasske	Benthic
Cymbella muelleri Hust.	Benthic
Epithemia smithii Carruthers	Benthic
Fragilaria brevistriata Grun.	Benthic
Fragilaria construens (Ehr.) Grun.	Benthic
Fragilaria crotonensis Kitt.	Planktonic
Fragilaria pinnata Ehr.	Benthic
Gomphonema subclavatum (Grun.) Grun.	Benthic
Navicula cuspidata Kütz.	Benthic
Navicula oblonga Kütz.	Benthic
Nitzschia sigmoidea (Ehr.) W. Sm.	Benthic
Small centric spp. (see text)	Planktonic
Stephanodiscus niagarae Ehr.	Planktonic
Synedra ulna (Nitz.) Ehr.	Planktonic

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Concentration (valves x 10<sup>4</sup>/g

Figure 13. The most common diatom taxa in the K





common diatom taxa in the K2 core presented as concentration data.



concentrations of *A. ambigua* and *A. subarctica* were less than concentrations of *A. granulata*. The *Aulacoseira* spp. all had the same peak in abundance between 130 and 75 cm (ca. 2,240 to 1,270 years BP).

Stephanodiscus niagarae, like the Aulacoseira spp., occurred in high concentrations throughout the K2 core. Several small centric taxa were also abundant throughout the K2 core. It was found that the Cyclotella and small Stephanodiscus taxa, with the exception of C. bodanica, could not be separated at the light microscope level. The group named 'Small centric spp.', therefore represents a mixture of C. caspia, C. meneghiniana, S. agassizensis, S. hantzschii and S. minutulus. These species were identified using SEM. These taxa were most abundant at 150 cm (ca. 2,590 years BP) and in the top 10 cm (ca. 130 years BP to present). C. bodanica was absent from the top 70 cm of the K2 core, and was most abundant at a depth of 85 cm (ca. 1,440 years BP).

Several Fragilaria taxa were major components of the flora. F. brevistriata was common in most portions of the K2 core. It reached high abundances at two depths, 70 cm (ca. 1,180 years BP) and 120 cm (ca. 2,060 years BP). F. construens was also abundant at these two depths, but was most abundant lower in the K2 core at 185 cm (ca. 3,200 years BP). Although it was present in much reduced quantities, F. pinnata had a similar stratigraphy to F. construens. These two taxa were rare in the bottom 40 cm (ca. 4,700 to 3,990 years BP) and top 25 cm (ca. 390 years BP to present) of the K2 core.

Several taxa were only abundant in the lower portion of the K2 core. These include *Cymbella cymbiformis* and *C. hustedtii* which were only found in the K2 core below 140 cm (ca. 2,410 years BP). *Amphora pediculus, Cymbella muelleri, Epithemia smithii, Navicula cuspidata,* and *N. oblonga* were abundant between 225 and 130 cm (ca. 3,900 to 2,240 years BP) and between 100 and 25 cm (ca. 1,710 to 390 years BP). These taxa were absent from the top 25 cm (ca. 390 years BP to present) of the K2 core. The stratigraphy of *Amphora ovalis, Cocconeis placentula, Gomphonema subclavatum* and *Synedra ulna* in the K2 core were quite similar. These species had their maximum abundance between 160 and 150 cm (ca. 2,760 to 2,590 years

BP).

Asterionella formosa, Fragilaria crotonensis, and Nitzschia sigmoidea were most abundant in the surface sediments. The former two were absent from the sediments at depths below 30 cm (ca. 480 years BP).

Cluster analysis was used to summarize changes in diatom assemblages over the length of the K2 core. Results identified five major clusters (Figure 14). Region A contains samples 15 to 0 cm (210 years BP to present). These samples contain higher concentrations of planktonic taxa that respond to nutrient influxes (e.g. *Asterionella formosa* and *Fragilaria crotonensis*). Samples 270 to 220 cm (ca. 4,700 to 3,820 years BP) and 25 to 20 cm (ca. 390 to 300 years BP) cluster in region B. This region contains high concentrations of epipelic taxa (e.g. *Amphora ovalis* and *Fragilaria brevistriata*). Region C includes samples from 105 to 80 cm (ca. 1,800 to 1,360 years BP). This association is dominated by planktonic diatom taxa (e.g. *Aulacoseira* spp.). Samples 160 to 135 cm (ca. 2,760 to 2,320 years BP) and 35 to 30 cm (ca. 570 to 480 years BP) cluster in region D. Both benthic and planktonic taxa are abundant in this region. Associations dominated by benthic taxa cluster in region E. These include samples 215 to 165 cm (ca. 3,730 to 2,850 years BP), 130 to 110 cm (ca. 2,240 to 1,880 years BP), and 75 to 40 cm (ca. 1,270 to 650 years BP).

### 5.4 Core K3

### 5.4.1 Composition

The chemical parameters measured in the K3 core are profiled in Figure 15. As in the previous two cores, water content and carbonates varied little over the length of the K3 core. Water content increased gradually from 74% at 280 cm to 86% at the surface of the K3 core. Carbonates averaged ca. 11% dw over the length of the K3 core. Organic matter content was high (ca. 22% dw) up until the interval 150 to 125 cm (ca. 1,830to 1,560 years BP) where organic matter content dropped to a low of 9% dw. It then returned to high levels peaking at 27% dw between



Figure 14. Sum of squares Euclidean distance cluster analysis of the log transformed concentration data of the major diatom taxa in the K2 core. Five groups (A to E) are recognized, separated by the shaded boxes.



Figure 15. Profile of the chemical parameters and sedimentary





chemical parameters and sedimentary pigments in the K3 core.


125 and 20 cm (ca. 1,560 to 400 years BP). In the top 20 cm of the K3 core organic matter content declined to 13% dw. Phosphorus concentration followed this same pattern, peaking at ca. 800  $\mu$ g gdw<sup>-1</sup> between 250 and 150 cm (ca. 2,940 to 1,830 years BP) and 125 and 20 cm (ca. 1,560 to 400 years BP). Phosphorus was at a minimum (ca. 300  $\mu$ g gdw<sup>-1</sup>) during the interval 150 to 125 cm (ca. 1,830 to 1,560 years BP) and was reduced to ca. 450  $\mu$ g gdw<sup>-1</sup> in the top 20 cm.

### 5.4.2 Plant pigments

The pigment parameters measured in the K3 core are profiled in Figure 15. The percent native chlorophyll fluctuated irregularly over the length of the K3 core. Values remained above zero until 165 cm (ca. 2,000 years BP), after which values of zero were frequently encountered with the exception of one sample value of 100% native chlorophyll at 80 cm (ca. 1,060 years BP).

Similar to the stratigraphy of organic matter content and phosphorus, total chlorophyll reached its maximum (ca.  $32 \ \mu g \ gdw^{-1}$ ) between 250 and 150 cm (ca. 2,940 to 1,830 years BP) and 125 and 20 cm (ca. 1,560 to 400 years BP). Low values of ca. 8  $\mu g \ gdw^{-1}$  occurred between 150 and 125 cm (ca. 1,830 to 1,560 years BP) and in the top 20 cm of the K3 core. Total carotenoids also showed this pattern but the peaks measuring ca. 13  $\mu g \ gdw^{-1}$  were not as pronounced. The CD:TC ratio fluctuated between values of two to four up until 50 cm (ca. 730 years BP). The ratio was slightly lower than two until 20 cm (ca. 400 years BP), then reached a maximum of 4.6 in the top 15 cm.

Oscillaxanthin concentration was maximized in sediment samples at 200 cm (ca. 2,380 years BP), 160 cm (ca. 1,940 years BP), and 50 cm (ca. 730 years BP), peaking at 26, 35, and 24  $\mu$ g gdw<sup>-1</sup>, respectively. The stratigraphy of oscillaxanthin and myxoxanthophyll was very similar but myxoxanthophyll concentration was slightly higher peaking at ca. 40  $\mu$ g gdw<sup>-1</sup>. The myxoxanthophyll stratigraphy also showed one dramatic increase to 101  $\mu$ g gdw<sup>-1</sup> at 165 cm (ca. 2,000 years BP). This caused the OSC:MYX ratio to be at its lowest (zero) at this point. The opposite occurred at 245 cm (ca. 2,880 years BP) where the low concentration of myxoxanthophyll caused the OSC:MYX ratio to be very high (48). Values remained low between 125 and 20 cm (ca. 1,560 to

400 years BP) and then increased again at 10 cm (ca. 290 years BP).

## 5.5 Core K5

## 5.5.1 Composition

The chemical parameters measured in the K5 core are profiled in Figure 16. The water content in this short core increased gradually from 78% at the base to 91% at the surface of the core. Likewise, the organic matter content and carbonates fluctuated minimally over the 40 years represented by this core. Organic matter content averaged ca. 16% dw and carbonates averaged ca. 9% dw over the length of the K5 core. Phosphorus increased gradually from 276 to 360  $\mu$ g gdw<sup>-1</sup> during the interval from 25 to 2 cm (ca. 1940 to 1990AD). The phosphorus concentration nearly doubled to 590  $\mu$ g gdw<sup>-1</sup> in the top 2 cm corresponding to ca. 1992 to 1993 AD.

#### 5.5.2 Plant pigments

The pigment parameters measured in the K5 core are profiled in Figure 16. The percent native chlorophyll was uniformly low (ca. 10%) from 25 to 20 cm (ca. 1940 to 1951 AD). The percent native chlorophyll increased to ca. 15% between 20 and 6 cm (ca. 1951 to 1983 AD) and reached a maximum of 22% between 6 and 1 cm (ca. 1983 to 1992 AD). Total chlorophyll increased gradually from 25 to 49  $\mu$ g gdw<sup>-1</sup> between 25 and 2 cm (ca. 1940 to 1990 AD) and then increased more dramatically to 70  $\mu$ g gdw<sup>-1</sup> in the top 2 cm. The total carotenoids averaged ca. 2.5  $\mu$ g gdw<sup>-1</sup> from 25 to 15 cm (ca. 1940 to 1964 AD). After 15 cm, the average value increased to ca. 3.4  $\mu$ g gdw<sup>-1</sup> and two maximum values of 4  $\mu$ g gdw<sup>-1</sup> occurred at 14 cm (ca. 1966 AD) and 3 cm (ca. 1988 AD). The CD:TC ratio stratigraphy is almost a mirror image of the total carotenoids stratigraphy. The ratio averaged ca. 12 between 25 to 3 cm (ca. 1940 to 1988 AD) and increased to 24 at the surface (ca. 1993 AD).

Oscillaxanthin concentration averaged ca.  $2 \mu g \, g dw^1$  from the base of the core to 5 cm (ca. 1985AD). The maximum value of  $3 \mu g \, g dw^1$  occurred at  $4 \, cm$  (ca. 1987AD) and the concentration of oscillaxanthin showed an increasing trend in the top 2 cm. Myxoxanthophyll concentration



Figure 16. Profile of chemical parameters and





pfile of chemical parameters and sedimentary pigments in the K5 core.



varied more over the length of the K5 core. Maximum values of  $3 \mu g \, g dw^{-1}$  were reached between 7 and 2 cm (ca. 1981 to 1990AD). In contrast to the oscillaxanthin stratigraphy in the top 2 cm, myxoxanthophyll showed a decreasing trend. The concentration of oscillaxanthin was almost always greater than the concentration of myxoxanthophyll which is reflected in the OSC:MYX ratio being greater than one.

### 5.5.3 Heavy Metals

The concentrations of copper, lead and mercury in the recent sediments of Killarney Lake are compared to values obtained for nearby Pelican Lake (Dr. L.G Goldsborough, University of Manitoba; unpublished data) (see Figure 1 for location) in Figure 17. The most obvious stratigraphic change in Killarney Lake metals was the dramatic increase in the copper concentration in the sediments from 80  $\mu$ g g<sup>-1</sup> at a depth of 23 cm (ca. 1943 AD) to 900  $\mu$ g g<sup>-1</sup> at the surface of the K5 core (ca. 1993 AD). The lead content at the base of the K5 core (24 cm) was 15  $\mu$ g g<sup>-1</sup> and gradually increased to a maximum of 34  $\mu$ g g<sup>-1</sup> at 13 cm (ca. 1968 AD). It declined gradually to ca. 20  $\mu$ g g<sup>-1</sup> in the top 3 cm. The mercury concentration in the K5 core averaged ca. 0.09  $\mu$ g g<sup>-1</sup> from the base of the core to 11 cm (ca. 1973 AD), at which point the concentration increased more sharply averaging ca. 0.12  $\mu$ g g<sup>-1</sup> between 10 to 1 cm (ca. 1975 to 1992 AD).

#### 5.6 Core K6

#### 5.6.1 Composition

The chemical parameters measured in the K6 core are profiled in Figure 18. As in the K5 core, the water content varied little, it ranged from 80% at the base of the K6 core and increased gradually to 96% at the surface. Organic matter content and carbonates both remained relatively constant from 19 to 3 cm (ca. 1953 to 1988AD). Organic matter content ranged from 15% dw to 16% dw and carbonates averaged ca. 9% dw during this interval. Both parameters increased in the top 3 cm. Organic matter increased to a maximum of 17% dw at the surface while carbonates reached a maximum of 24% dw at 2 cm and then decreased to 17% dw at the surface. Phosphorus



Figure 17. Profile of the concentration of three heavy metals (copper, lead and mercury) in the K5 core from Killarney Lake compared to nearby Pelican Lake (Dr. L.G. Goldsborough, University of Manitoba; unpublished data) (see Figure 1 for location).



Mar Contraction

Figure 18. Profile of chemical parameters and sedimenta

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c of chemical parameters and sedimentary pigments in the K6 core.

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content averaged ca. 240% dw from 19 to 9 cm (ca. 1953 to 1977 AD), after which it increased more sharply to reach a maximum of ca. 640% dw at the surface.

## 5.6.2 Plant pigments

The pigment parameters measured in the K6 core are profiled in Figure 18. The percent native chlorophyll averaged ca. 17% during the interval 19 to 14 cm (ca. 1953 to 1966AD), decreased to ca. 15% from 14 to 7 cm (ca. 1966 to 1981AD) and then increased to a maximum of 27% at 2 cm (ca. 1990AD), after which it decreased to 16% at the surface. The total chlorophyll and total carotenoids profiles showed the same trends as the organic matter and carbonates. Total chlorophyll increased from 22 to 40  $\mu$ g gdw<sup>-1</sup> from the base of the K6 core to 3 cm (ca. 1953 to 1988AD). A maximum chlorophyll concentration of 150  $\mu$ g gdw<sup>-1</sup> was reached at the surface (ca. 1993AD). During the interval 19 to 3 cm the total carotenoids increased gradually from 2 to 4  $\mu$ g gdw<sup>-1</sup> and then sharply reached a maximum concentration of 7  $\mu$ g gdw<sup>-1</sup> at the surface. The CD:TC ratio ranged from 10 to 15 and reached a maximum value of 21 at the surface (ca. 1993AD).

Oscillaxanthin concentration averaged 2  $\mu$ g gdw<sup>-1</sup> between 19 and 3 cm (ca. 1953 to 1988 AD) except for a peak that measured 5  $\mu$ g gdw<sup>-1</sup> at 7 cm (ca. 1981 AD). After 3 cm (ca. 1988 AD) the oscillaxanthin concentration increased to a maximum of 8  $\mu$ g gdw<sup>-1</sup> at the surface (ca. 1993 AD). Myxoxanthophyll concentration was initially higher than oscillaxanthin, averaging ca. 4  $\mu$ g gdw<sup>-1</sup> during the interval 19 to 12 cm (ca. 1953 to 1970 AD), but levels decreased to ca. 1  $\mu$ g gdw<sup>-1</sup> at a depth of 11 cm (ca. 1973 AD) and remained low until 9 cm (ca. 1977 AD). Like oscillaxanthin, myxoxanthophyll concentrations increased in the top 5 cm (ca. 1985 to 1993 AD) and reached a maximum of 9  $\mu$ g gdw<sup>-1</sup> at 2 cm (ca. 1990 AD). The ratio of OSC:MYX remained just below one except for a dramatic increase between 11 and 7 cm (ca. 1973 to 1981 AD) where the ratio approached four.

# 6.0 Discussion

#### 6.1 Sediment Chronology

The stratigraphy of <sup>210</sup>Pb and <sup>137</sup>Cs content in the K4 short core was used to establish the recent sediment chronology in the Killarney Lake basin. Since the area was first settled about 114 years ago, it should be possible to obtain a pre-settlement (prior to 1879) stratigraphy within the dating capacity of<sup>210</sup>Pb. Based on the age-depth relationship determined ( $r^2$ =.99), it was possible to reliably date back 150 years to 1843, corresponding to a depth of 69 cm. Unfortunately, the K5 and K6 cores were only 25 cm and 19 cm, respectively, in length, so they don't represent the entire settlement period. The Glew modified K-B coring apparatus did not penetrate deeply enough into the sediments to obtain a pre-settlement stratigraphy. Anderson (1993) found this to be the case for many eutrophic European lakes whose long histories of cultural disturbance and high variable sediment accumulation rates (30 cm sediment can represent only 30 years) resulted in short cores that rarely pre-date cultural perturbation. In Killarney Lake the sedimentation rate was comparably moderate to the aforementioned 10 mm year<sup>1</sup>, where 25 cm represents approximately 50 years. The sedimentation rate (4.6 mm year<sup>-1</sup>) agrees well with other values obtained for prairie lakes. Dr. D. Delorme (National Water Research Institute; personal communication, 1992) has found sedimentation rates for lakes in Manitoba based on <sup>210</sup>Pb profiles ranging from 1.6 mm year<sup>1</sup> to as high as 14.6 mm year<sup>1</sup>. The latter sedimentation rate was for William Lake, near Max Lake in the Turtle Mountains southwest of Killarney Lake.

Results from the <sup>14</sup>C analysis of the basal strata in the long sediment cores indicate that the Killarney Lake basin is at least 4,700 years old. It is likely that the lake is older than this since geologists believe the glaciers retreated from this area close to 11,000 years ago (Fenton et al., 1983). AMS (accelerated mass spectrometry) dates on seeds, mainly *Scirpus*, from a Killarney Lake core collected with a vibra-corer at Site 1 (Figure 2) during March of 1993 by Dr. D. Lemmen and Dr. R.E. Vance of the Geological Survey of Canada (GSC), yielded a date of 9,180

years BP for the depth interval 345 to 350 cm in a 420 cm long core (Dr. R.E. Vance, GSC; personal communication, 1993). Therefore, the bottom 15 cm of the K2 core that consisted of a coarse sand and gravel is likely not of glacial origin. Vance *et al.* (1992) state that coring can be difficult in lakes of the North American Great Plains as the mineral-rich sediments commonly contain desiccated and cemented horizons. The Reasoner coring apparatus I used for sediment core collection was likely unable to penetrate the sediment beyond this type of sediment horizon to obtain the complete postglacial record of Killarney Lake.

The K2 core <sup>14</sup>C date of 4,670 years BP obtained for the organic stratum immediately above this horizon, along with the observed transition from silt to coarser-grained sand suggests that this Killarney Lake record began during the warm and dry middle Holocene. The coarse material found in the horizon at the base of the K2 core may represent a zone similar to the zones found by Teller and Last (1982) in the postglacial sediment of Lake Manitoba. They postulated that the zones were formed by pedogenesis during dry or extremely low water conditions. The zones in Lake Manitoba were formed between 9,500 and 4,500 years BP during what is believed to be the warmest and driest postglacial period in the region (Teller and Last, 1982). Ritchie (1976) also found that changes in lake sediment type from organic silts to silty clays or sands at sites at Crestwynd, Saskatchewan and Russell, Manitoba suggested lowered lake level in the early postglacial probably in response to a drier climate. He postulated changes in lake sediment type at these and other sites in the aspen parkland and transitional zones resulted from past fluctuations in water level, particularly a lowering of the water table below its present level as a result of climatic change.

## **6.2 Historical Primary Production**

The history of primary production in Killarney Lake over the last 4,700 years is based on trends in sedimentary stratigraphies of organic matter, total carbonates, phosphorus, plant pigments and diatoms. As for all studies that attempt to reconstruct past environments from the fossil record, the interpretations depend on information from a variety of stratigraphic analyses. Despite slight

differences in core length, reflecting site-specific variation in sedimentation rate and perhaps core compaction, results from the three cores were in general agreement. The similar trends observed for the measured parameters between cores contributes to a more accurate reconstruction of primary production in Killarney Lake.

# 6.2.1 Sediment Composition

I observed that the percentage of residual bulk dry composition of organic matter remained relatively constant at all levels of the cores. This indicates that the contribution to organic matter from allochthonous sources has probably been relatively consistent over time. The peaks in organic matter content coincide with peaks in total chlorophyll, total carotenoids, and myxoxanthophyll, all of which are mostly autochthonous in origin, indicating that these peaks were due to increased *in situ* primary production.

The total carbonate content of the sediments remains constant throughout all the cores. There was no evidence in the sediments of higher carbonate levels which could result from increased carbonate precipitation associated with raised photosynthetic activity.

The phosphorus content of lake sediments can be used as a proxy for paleoproduction because of the close relationship between phosphorus concentration and primary production, and because lake sediments are an effective sink for phosphorus (Engstrom & Wright, 1984). The peaks in phosphorus correspond to peaks in organic matter, chlorophyll, and carotenoids, providing further evidence that these were periods of high primary production.

## **6.2.2 Sedimentary Plant Pigments**

It has been demonstrated that total chlorophyll derivatives and carotenoids preserved with little diagenesis in the sedimentary organic matter reflect changing *in situ* primary production (Sanger & Crowl, 1979). A greater production rate (at a given time) provides a higher concentration of pigments in the organic matter of the sediment profile (Gorham *et al.*, 1974). Pigment concentrations are superior to pigment accumulation estimates since algal abundance in water is not necessarily correlated to accumulation rate in the sediments (Leavitt, 1993). Pigment accumulation estimates may be biased by pigment degradation during sinking and incorporation into surface sediments (Leavitt, 1993). In addition, in this study measured accumulation rates may be only rough approximations of true fossil pigment flux, with errors arising from interpolations between widely spaced <sup>14</sup>C dates.

I have expressed the pigment concentration relative to the sediment dry weight. This is sometimes less satisfactory than expressing pigments relative to the organic matrix, due to variable dilution by pigment-free material (Swain, 1985). In Killarney Lake the percentage of residual bulk dry composition remains relatively constant at all levels of the cores, such that the trends observed in pigment concentrations were the same whether they were expressed relative to the sediment dry weight or its organic content.

The interpretation of sedimentary pigments, like that of the redox-sensitive elements, can be complicated by spatial and temporal variation in factors controlling preservation within the sediments (Engstrom & Swain, 1986). Factors believed to enhance pigment preservation include low oxygen concentration, low temperature, low light penetration, low sediment resuspension, high sedimentation rates, absence of benthic organisms in sediments, and increased levels of eutrophy (Sanger, 1988). In Killarney Lake's present shallow water condition, it may be difficult to meet many of these criteria. However, I did determine that there was a high sedimentation rate in Killarney Lake based on the <sup>210</sup>Pb stratigraphy in the short cores. The high sedimentation rate would have promoted rapid burial such that an increase in pigment concentration probably does reflect increased primary production.

A further independent measure of pigment preservation is the proportion of sedimentary chlorophyll not degraded to pheopigments, the percent native chlorophyll (Swain, 1985). In the Killarney Lake cores the total chlorophyll profiles did not decrease at points of poor pigment preservation indicated by lower percent native chlorophyll values. Similarly, peaks in percent native chlorophyll did not correspond to peaks in total chlorophyll profiles. This was also observed for the other pigment profiles. For example in Figure 10, the concentration of myxoxanthophyll and

oscillaxanthin pigments at 165 cm, the point of best preservation suggested by the high percent native chlorophyll, were low compared to the maximum values of these pigments at 30 cm where the percent native chlorophyll was less, suggesting preservation was lower. Therefore, because pigments did not increase during the hypothesized episodes of enhanced preservation, their rise must have resulted largely from increased production.

Given that total chlorophyll and total carotenoids are proportional to primary production in Killarney Lake, two major episodes of increased production were evidenced in the sedimentary pigments. The pigment stratigraphy in the long cores indicates that recent primary production was low in comparison with two maxima between ca. 2,980 and 1,780 years BP, and between 1,460 and 350 years BP (based on average peak ages for cores K2 and K3). However, caution must be used when interpreting the sediment stratigraphy from the top 25 cm of the long cores. The observed decrease in pigment concentrations in the top 25 cm of the long cores may reflect disturbance of the surface sediments due to the sampling apparatus as opposed to an actual reduction in pigment concentration. The high sediment water content at the top of the core likely promotes mixing of the sediments during transport, such that if there was a significant increase in pigment concentration in the most recent sediments, it may not be evidenced in the pigment stratigraphy due to dilution through mixing. Recent (last 50 years) primary production inferred from total chlorophyll levels in the short cores suggests that primary production in the recent sediments was high, and comparable with the two maxima observed in the long cores. The lack of disturbance of the sediments using the short coring method was evidenced in the field during core collection where I observed the presence of intact chironomid tubes on the sediment surface.

The maximum total chlorophyll and total carotenoid concentrations were observed in the top 0 to 3 cm of the short cores. This increase may not represent increased primary production in the water column in the past five years but may be due, in part, to an over-estimation of pigment concentration by inclusion of a living algae component in the sediment surface. In the field I observed a brown/green fuzzy layer at the sediment/water interface. Motile algae with intact chloroplasts were also apparent in the sediment when sediment samples from the top 0 to 3 cm were observed

under the microscope. Leavitt and Findlay (1994) found that the interpretation of recent historical events (<3 to 5 years old) was difficult using fossil pigments because of pigment decomposition in surface sediments before permanent burial. Elevated abundance of several pigments during 1988 to 1989 in Lake 227 in the Experimental LakesArea was consistent with high chlorophyll standing crops, but could not be reliably distinguished from incomplete *in situ* degradation (Leavitt & Findlay, 1994). Pigment degradation is normally most intense during sinking through the water column (Hurley & Armstrong, 1991). However, losses in water and sediments are partially compensatory, and residual pigments can continue to decompose in surface deposits (Hurley & Armstrong, 1991). Once below the zone of active loss, pigment preservation can be excellent for hundreds of years (Leavitt & Findlay, 1994).

The ratio of total chlorophyll to total carotenoids (CD:TC) is useful in stratigraphic studies where shifts may indicate a qualitative change in the algal flora. The CD:TC ratio in Killarney Lake was always high ( $\geq$ 2), indicating a predominance of chlorophyll derivatives over carotenoids. Swain (1985) found that carotenoid concentrations tended to be disproportionately higher in eutrophic lake sediments because cyanobacteria tend to dominate in eutrophic lakes and produce more carotenoids than do green algae. Oligotrophic lakes yielded higher CD:TC values (2.0  $\oplus$ 0.5) than more eutrophic lakes (0.6  $\oplus$  0.2) (Swain, 1985).

In Killarney Lake the high CD:TC values may reflect the input of terrestrial material that was rich in chlorophyll derivatives. Sanger (1988) states that high but variable CD:TC ratios could occur if well-preserved parenchymatous plant fragments brought in undecomposed chlorophyll molecules. Sanger and Gorham (1972) also interpreted high CD:TC values in a core from Kirchner Marsh as indicating periods of greater inputs of allochthonous organics and possibly a greater degree of aerobic decomposition of the autochthonous organics because of lake shallowing. In the K2 core (Figure 10) evidence for this is suggested by the increase in the CD:TC ratio between 150 and 165 cm which parallels an increase in epiphytic diatom taxa, which may be responding to an increase in aquatic macrophytes due to lake shallowing. At the base of the K2 core pigment concentrations were much reduced relative to other levels of the core and the CD:TC ratio reaches

a maximum value of 21. This suggests a period of drought. If drying of the sediment occurred, the result would be intense pigment destruction, especially of carotenoids (Sanger, 1988).

Blooms of cyanobacteria have occurred irregularly in Killarney Lake throughout the period represented by the long cores. Myxoxanthophyll, an indicator of cyanobacteria in general, reaches peak concentrations during the first peak in primary production between ca. 1,460 and 350 years BP (based on average peak ages for K2 and K3). Swain (1985) found that the similarity of the ratio of oscillaxanthin to myxoxanthophyll (OSC:MYX) values between lakes, coupled with the constancy of the ratio regardless of degradation, suggests that the OSC:MYX values in cores are a measure of relative production where higher values (usually  $\geq$ 1) indicate *Oscillatoria* dominance of the cyanobacteria flora (Swain, 1985). OSC:MYX values from the long cores were almost always below 1; for example, the average value from the K2 core was 0.66 (SD  $\Rightarrow$ 0.21). In contrast, the values from the short cores were most often above 1; for example, the average value for the K5 core was 1.11 (SD  $\pm$  0.54). *Oscillatoria* has, therefore, been more important in the cyanobacteria flora since settlement.

The short cores from Killarney Lake did not record any dramatic increases in the concentration of oscillaxanthin or myxoxanthophyll suggesting that in the last 50 years their production has been less than historically found in the lake. The oscillaxanthin and myxoxanthophyll concentrations in the short cores were very reduced, ranging from 1 to 3  $\mu$ g gdw<sup>-1</sup>, compared to concentrations reaching  $\geq$ 20  $\mu$ g gdw<sup>-1</sup> in the long cores. The reduced concentration of these pigments in the short cores may be a result of the copper sulfate additions to the lake effectively reducing cyanobacteria from historically high levels.

While this method may successfully reduce excessive algal growth, it can have deleterious effects due to the persistence of copper and its ability to form stable complexes with organic matter and mineral salts; total copper concentrations in sediments tend to be cumulative (S.E.P.S., 1989). Copper concentrations in the top 0 to 5 cm depth segment of Killarney Lake range from 800 to 950  $\mu$ g g<sup>-1</sup>. Hansen and Stefan (1984) suggest that total sediment copper concentrations approaching or exceeding 1,000  $\mu$ g g<sup>-1</sup> are excessive and can have serious deleterious effects on

bottom dwelling organisms. Four sediment samples analyzed for copper from the K2 core indicate that natural levels of copper range from 15 to 21  $\mu$ g g<sup>-1</sup>.

For comparison, the copper concentration in three other Manitoba lakes and three water bodies in Saskatchewan with a history of copper sulphate use are presented in Table 7. An investigation of four Saskatchewan surface waters (S.E.P.S., 1987) determined that total copper concentration in the sediments of municipal raw water supply reservoirs reached 620  $\mu$ g g<sup>-1</sup>. Accumulations of sediment copper as high as 5,600  $\mu$ g g<sup>-1</sup> after 58 years of successive use for algae control have been documented in the Fairmont Lakes, Minnesota (Hansen & Stefan, 1984).

# 6.2.3 The Diatom Record

Diatom results are most commonly reported as proportional data. While this form of data representation is advantageous because it is easily calculated, it is misleading in that it does not allow comparisons of changing species numbers with depth. When using proportional data, shifts in species numbers are only comparable at a given depth. To avoid this problem of depth comparison of proportional data, I have used diatom concentrations in this study. The use of diatom concentrations in lake sediments as an estimate of past diatom production has been criticized for providing misleading estimates of past standing crop since the amount of sediment accumulating at one point in the lake's basin can vary with time. For example, if watershed erosion rates are high during a certain period in a lake's history, the fossil concentration, as a result of sediment dilution, will underrepresent standing crop (Smol, 1979). If the depth-time profile of a sediment core is determined it is possible to correct diatom concentrations to accumulation rates which would account for changes in sedimentation rates. However, in this study even if the three <sup>14</sup>C dates obtained for the K2 core are treated as a conformable sequence of dates, the sediment age between dated levels and hence accumulation rates must be interpolated. Ultimately the rates would be averaged over long intervals of time. Therefore, in the case of Killarney Lake, diatom accumulation rates would not provide any more information than can be garnered from diatom concentrations.

The most abundant taxa present throughout the K2 core were characteristic of alkaline, eutrophic

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Table 7. A comparison of total copper (Cu) concentration in sediment cores from Killarney Lake, Max Lake<sup>1</sup>, Pelican Lake<sup>1</sup>, Rock Lake<sup>1</sup>, and Lake Winnipeg<sup>2</sup> in Manitoba, and Oyama Lake<sup>3</sup>, Creelman Dugout<sup>3</sup>, and Conquest Reservoir<sup>3</sup> in Saskatchewan. Values presented are for the 0 to 10 cm depth segment, except for Lake Winnipeg where the value presented is an average for the 0 to 5 cm depth segment from 31 sample sites.

Sample Location	Cu Concentration ( $\mu g g^{-1}$ )	
Killarney Lake	800	
Max Lake	22	
Pelican Lake	18	
Rock Lake	26	
Lake Winnipeg	36	
Oyama Lake	48	
Creelman Dugout	97	
Conquest Reservoir	25	

<sup>1</sup>Dr. L.G. Goldsborough (University of Manitoba) & Provincial Water Quality Branch, unpublished data. <sup>2</sup>Lockhart, 1996. <sup>3</sup>S.E.P.S., 1989. or mesotrophic waters. *Aulacoseira ambigua*, *A. granulata*, *A. subarctica* and *Stephanodiscus niagarae* were the most abundant diatom taxa in the Killarney Lake sediments. It is generally known that in highly productive lakes, diatom phytoplankton associations are dominated by *Aulacoseira* spp. and *Stephanodiscus* spp. The diatom flora indicates that Killarney Lake has had water with high nutrient concentrations throughout the 4,700 year record represented by the K2 core.

Cluster analysis identified five diatom regions (A to E, Figure 14). On the basis of these regions which identify stratigraphic patterns of diatom concentration and notable increases, decreases, appearance, and disappearances of taxa, I separated the core into nine diatom zones (A, B<sub>1</sub>, B<sub>2</sub>, C, D<sub>1</sub>, D<sub>2</sub>, E<sub>1</sub>, E<sub>2</sub>, & E<sub>3</sub>) (Figure 13).

<u>Diatom Zones B, & B, :</u> 270 to 220 cm (ca. 4,700 to 3,820 years BP) & 25 to 20 cm (ca. 390 to 300 years BP)

The diatom flora at the base of the core was diverse and low in total diatoms. While taxa belonging to the centric groups *Aulacoseira*, *Cyclotella*, and *Stephanodiscus* were most abundant throughout the core, they occurred in reduced concentration during this interval (B<sub>1</sub>). The initial diatom assemblage comprised primarily pioneering benthic taxa. Small species of diatoms such as *Amphora ovalis* and *Fragilaria brevistriata* were important at this time. These taxa are primarily epipelic, living upon the submerged sediments. These taxa are widely adapted forms common to shallow lakes and ponds. In several Alberta lakes, they comprise the dominant pioneers in the early Holocene as well as the mid-Holocene in response to reduced water levels (Hickman *et al.*, 1984; Hickman & Schweger, 1996). Their initial dominance suggests that Killarney Lake was shallow, recovering from a period of being dry or nearly so. The more recent occurrence of these species in zone B<sub>2</sub> may indicate lower water levels perhaps resulting from an arid climate during the Little IceAge, ca. 500 to 100 years BP.

<u>Diatom Zones  $E_{1x} E_{2x} & E_{3x}$ </u>: 215 to 165 cm (ca. 3,730 to 2,850 years BP), 130 to 110 cm (ca. 2,240 to 1,880 years BP), & 75 to 40 cm (ca. 1,270 to 650 years BP)

Despite the dominance of euplanktonic taxa mainly belonging to Aulacoseira and Stephanodiscus, the benthic taxa of zone  $B_1$  increased in abundance during zone  $E_1$ . Present in

large concentrations were epipelic species such as Amphora ovalis, Fragilaria brevistriata, and F. construens together with epiphytic species such as Cocconeis placentula, Cymbella spp., and Epithemia spp. The increase in epiphytic taxa likely reflects an increase in aquatic macrophytes, which provide substratum for many benthic diatoms. Fragilaria brevistriata is known to prefer shallow eutrophic, littoral waters (Hickman *et al.*, 1984). Navicula oblonga, usually found in the littoral zone, occurred largely in zones  $E_1$  and  $E_2$ . Patrick and Reimer (1966) describe this taxon as showing a preference for alkaline or slightly brackish water of high mineral content. Total diatom concentration increased from zone  $B_1$  to  $E_1$  along with pigment concentrations. The species present suggests a shallow more nutrient rich lake existed during these three intervals. Diatom Zones  $D_1 \& D_2$ : 160 to 135 cm (ca. 2,760 to 2,320 years BP) & 35 to 30 cm (ca.

570 to 480 years BP)

These two zones appear to represent transitional zones, containing high numbers of both benthic and planktonic taxa. Benthic taxa including *Amphora ovalis*, *Cocconeis placentula*, and *Cymbella cymbiformis* reached maximum concentrations in zone D<sub>1</sub>.

Diatom Zone C: 105 to 80 cm (ca. 1,800 to 1,360 years BP)

Total diatom concentrations reached maximum values during this zone due to the predominance of the planktonic diatoms *Aulacoseira ambigua*, *A. granulata*, and *A. subarctica*. Benthic, particularly epipelic species such as *Fragilaria brevistriata*, disappeared during this interval. According to Hickman (1978), this situation would only occur if water levels increased and large phytoplankton populations developed. Higher water levels often result in increased erosion of a lake's margin soils and hence increase nutrient inflow. Elevated diatom concentrations may reflect increased total algal production caused by a change in nutrient concentrations and/or in the seasonality of nutrient inputs that favored diatoms over other algae, such as greens (Fritz *et al.*, 1993).

The major increase in these planktonic diatoms may also have been due to a reduction in cyanobacteria. Decreases in diatom concentrations that accompany increases in oscillaxanthin levels have been reported in cores from other lakes (Engstrom *et al.*, 1985; Fritz, 1989), and have been variously attributed to dominant *Oscillatoria* populations inhibiting diatom growth through allelopathy (Keating, 1978), through the exclusion of diatom species through nutrient competition

(Fritz, 1989), or summer cyanobacteria blooms may decrease light penetration limiting the growth of diatoms (Liukkonen*et al.*, 1993). The concentration of the cyanobacterial pigments oscillaxanthin and myxoxanthophyll were low in the Killarney Lake sediments during this period of increased phytoplankton production. This suggests that the *Aulacoseira* spp. may have been more successful during zone C because cyanobacterial populations were reduced.

Diatom Zone A: 15 to 0 cm (210 years BP to present)

Total diatom concentration was high in zone A and was composed largely of planktonic species. Increases in total diatom concentration during this zone may imply greater siliceous algal production as nutrient inputs increased due to the influence of settlement in the Killarney area.

Asterionella formosa and Fragilaria crotonensis occurred in high concentrations and were unique to this zone. They are often not found in the sediments because their long needle-like frustules are easily broken into unrecognizable fragments. In Killarney Lake it could be argued that that is why I only encountered these two species in the surface sediments (zone A). However, other thin elongate species, for example *Synedra* spp. and *Nitzschia* spp., were found at the base of the core.

Asterionella formosa and Fragilaria crotonensis are considered to be taxa that respond to nutrient influxes (Wolin, 1996). They also may indicate less turbulent conditions and little resuspension of sediments, and perhaps as well, deeper water (Hickman *et al.*, 1984). They are capable of maintaining themselves high in the water column, giving them an advantage if the photic zone was reduced by shading from other phytoplankton or cyanobacteria. The increase in these and other planktonic diatoms suggest higher water levels in Killarney Lake accompanied by a change in nutrient levels.

### 6.3 Summary of Sediment Stratigraphies

The purpose of my study was to infer, based on stratigraphic profiles of sedimentary plant pigments, fossil diatoms and selected chemical parameters, trends in Killarney Lake's primary production during the postglacial period. Interpretation of several cores has allowed me to reconstruct with greater certainty the general trends in historical primary production for the last 4,700 years of Killamey Lake's existence.

#### 6.3.1 Killarney Lake's Postglacial History

A summary of the postglacial history of primary production is provided by a composite diagram of key stratigraphic variables in Figure 19. Radiocarbon years presented here in the text are based on average peak ages for K2 and K3. My analyses suggest that primary production was low in Killarney Lake during the period 4,670 to 2,980 years BP. Presumably because of dry conditions, the planktonic diatoms were much reduced in number and the diatom flora was characterized by pioneering epipelic diatoms such as *Fragilaria brevistriata*.

The presence of myxoxanthophyll and oscillaxanthin with depth indicates that cyanobacterial blooms were not a recent phenomenon, but have occurred irregularly throughout the period represented by the long cores. Recent (last 50 years) primary production appears to be low in comparison with two maxima between 2,980 to 1,780 years BP, and between 1,460 to 350 years BP. Benthic diatoms, including *Amphora ovalis, A. pediculus, Fragilaria brevistriata*, and *F. construens*, were more abundant during these two intervals. Shallow water conditions likely resulted in a highly productive littoral zone, contributing to overall high primary production.

Primary production was reduced between 1,780 to 1,460 years BP. The diatom record indicated, based on an increase in the ratio of planktonic to benthic taxa, a decrease in the proportion of littoral habitat during this period. Higher water levels may have reduced benthic growth and the size of the littoral zone, resulting in reduced primary production.

The diatom flora was found to not have changed significantly over the last 4,700 years in Killarney Lake. Indicative of water with high nutrient concentrations, *Aulacoseira granulata*, *A. ambigua*, *A. subarctica*, and *Stephanodiscus niagarae*, along with several small centric taxa were important euplanktonic components of diatom assemblages throughout the core. Notable increases and decreases of diatom taxa appeared to be more related to fluctuating lake water



Figure 19. Summary diagram of the stratigraphic trends and interpretation for Killarney Lake. Note: only the K2 core radiocarbon dates are shown. levels than to changing nutrient status.

# 6.3.2 Killarney Lake's Recent History

The most recent phase in the history of Killarney Lake, which began about 1940 AD, was indicative of stable conditions, relative to earlier periods, during which time only minor fluctuations were observed in sediment chemistry and pigments. The Town of Killarney's long history of copper sulphate use has resulted in very high sediment copper levels compared to other lakes in the region. Copper levels in the top 2 cm (ca. 1990 to 1993 AD) approached biologically toxic levels. This approach to controlling the levels of cyanobacterial blooms appears to have been effective given the low concentrations of myxoxanthophyll and oscillaxanthin in the short cores.

# 7.0 General Conclusions

Paleolimnological records in the southern Canadian prairies are an underutilized archive of detailed information on past hydrologic and climate change in this important and climatically-sensitive region (Vance & Last, 1994). Effective management of aquatic resources almost always requires long-term environmental data. However, long-term observations are rarely available to assess water quality changes resulting from human activities. Paleolimnology can often provide these missing historical data sets. While it is generally believed that the water quality in a large number of North American lakes has deteriorated as a result of anthropogenic activity, certain lakes, like Killarney Lake, appear to have been naturally productive prior to anthropogenic impact. Without paleolimnological data, these sites could be wrongly classified as disturbed in monitoring programs and could be subjected to costly, and in fact potentially damaging, remedial actions (Dixit & Smol, 1994).

The interpreted lake levels and primary production during the past 4,700 year history of Killarney Lake can be correlated with changes in records from other sites and with changes in past climate inferred for the region. Vance and Last (1994) report that sediment core data from lakes in southern Alberta, Saskatchewan, and Manitoba indicate that significant water level and chemical variations have occurred during the Holocene over this broad geographic area (Figure 1). Because historic hydrologic fluctuations in prairie watersheds are closely related to the balance between evaporation and precipitation, climate is considered the driving force behind Holocene lake level dynamics (Vance & Last, 1994).

The stratigraphic profiles of sedimentary plant pigments, fossil diatoms and selected chemical parameters from Killarney Lake indicate that a shallow lake with low primary production existed about 4,700 years BP. Several studies of prairie lakes indicate a distinctly warmer and drier climate during the mid-Holocene. In Manitoba, Teller and Last (1981) found lithological, mineralogical, and chemical analyses in Lake Manitoba indicated a period of fluctuating wet and dry conditions from 9,200 to 4,500 years BP. Last and Schweyen (1985) found changes in physical, mineralogical,

and paleobiological parameters in sediment cores from Waldsea Lake in south-central Saskatchewan indicated that a shallow hypersaline lake with extensive mudflats existed about 4,000 years BP. Sauchyn & Sauchyn (1991) interpreted the vegetation record from Harris Lake, Saskatchewan and found that the maximum warmth and aridity in the Cypress Hills occurred approximately 7,700 to 5,000 years BP. Also in Saskatchewan, the Ceylon Lake record indicated high-salinity conditions with episodes of desiccation from ca. 8,000 to 6,000 years BP and continued low lake levels until 4,000 years BP (Last, 1990; Teller & Last, 1990). Chappice Lake in southeastern Alberta, oscillated between relatively high stands and desiccation from 7,300 to 6,000 years BP (Vance *et al.*, 1993). From 6,000 to 4,400 years BP, lake levels were consistently low and production was high. At Moon Lake, North Dakota a mid-Holocene period of high salinity from 7,300 to 4,700 years BP, indicated low effective moisture (precipitation minus evapotranspiration) (Laird *et al.*, 1996). These data suggest a pattern of a drier mid-Holocene with regionally recurring drought on the prairies during the period from ca. 8,000 to 4,000 years BP.

Water levels and primary production began to rise in Killarney Lake likely in response to a cooler and wetter climate about 3,900 years BP. By about 2,100 years BP a deep lake with low primary production existed. Many sites on the prairies indicate a climatic change from a more arid mid-Holocene to one of increasing moisture about 4,000 years BP, which continues until about 2,000 years BP. Waldsea and Ceylon lake paleorecords show increasing lake levels about 4,000 years BP, culminating in deep-lake stands by about 3,000 and 2,000 years BP, respectively (Last & Schweyen, 1985; Teller & Last, 1990). Between 4,400 and 2,600 years BP, lake level was more stable but gradually rising and production was high at Chappice Lake (Vance *et al.*, 1993). A large relatively fresh lake existed from 2,600 to 1,000 years BP.

A change in the climate about 1,200 years BP again caused low water levels and increased primary production in Killarney Lake. Low lake level at about 1,000 years BP is evident at several other sites, including Chappice Lake (ca. 1,000 to 600 years BP) (Vance *et al.*, 1993) and Waldsea Lake (ca. 1,000 to 700 years BP) (Last & Slezak, 1986). These low lake stands roughly correspond to the Medieval Warm Period, about 950 to 750 years BP (Laird *et al.*, 1996).

Water levels in Killarney Lake increased again about 500 years BP but did not reach the level of the previous deep water stand (2,100 years BP). Primary production was low at this time but showed a trend toward increasing production during the last 100 years. Evidence of a high lake stand at Chappice Lake from ca. 600 to 100 years BP (Vance *et al.*, 1993) suggests wetter conditions may have existed during the Little IceAge (about 500 to 100 years BP).

This project resulted from the expressed concerns of the residents of the Town of Killarney regarding the frequent occurrence of cyanobacterial blooms in the lake and numerous undesirable effects this has on water quality. It was believed by the residents that the water quality in Killarney Lake had deteriorated as a result of anthropogenic activity. In the context of the historical changes in primary production that I have documented, it appears that anthropogenic influences in the past 100 years or so have had only a minor impact on the trophic history of Killarney Lake. It appears from these analyses that the lake has been naturally productive for at least 4,700 years. It may be that the effects of modern events have not had the profound influence on the lake's trophic status that previous climatic and geological events have had.

Paleolimnology reveals cause and effect best when a number of parameters are examined together. For this reason several other independent lines of evidence are currently being investigated including pollen analysis by Dr. R.E. Vance (GSC), mineralogy by Dr. B. Last (University of Manitoba), invertebrate remains by Dr. B. Hann (University of Manitoba), ostracods by Dr. D. Naldrett (Environmental Earth Science Associates Inc.), and cyanobacteria by Ms. H. Kling (Freshwater Institute). As each of these stratigraphic parameters is added, the number of hypotheses that can account for the data will be further reduced providing an even clearer reconstruction of the history of Killarney Lake. This record of lake responses may provide land use planners and policy makers with a realistic view of the range of extremes experienced in the past, their frequency of occurrence, and ultimately clues regarding the nature of changes that may occur in future.

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#### Appendices

Appendix A. K2 Diatom Species List

Amphora ovalis Kütz. Amphora pediculus Kütz. Amphora sp. 1 Anomoeoneis sphaerophora (Ehr.) Pfitz. Asterionella formosa Hass. Aulacoseira ambigua (Grun.) Simons. Aulacoseira granulata (Ehr.) Simons. Aulacoseira subarctica (O. Müll.) Haworth Caloneis bacillum (Grun.) Cl. Caloneis leptosoma Krammer Caloneis ventricosa (Ehr.) Meist. Cocconeis placentula Ehr. Cyclotella bodanica Eul. Cyclotella caspia Grun. Cyclotella meneghiniana Kütz. Cymatopleura elliptica (Bréb.) W. Sm. Cymatopleura solea (Bréb.) W. Sm. Cymbella cistula (Hemp.) Grun. Cymbella cymbiformis (Ag. Kütz.) V. Heurck Cymbella cymbiformis var. nonpunctata Font. Cymbella ehrenbergii Kütz. Cymbella hustedtii Krasske Cymbella lanceolata (Ehr.) V. Heurck Cymbella muelleri Hust. Cymbella minuta var. silesiaca (Bleisch) Reim. Cymbella parva (W. Sm.) Cl. Cymbella proxima Reimer Cymbella tumida (Bréb.) V. Heurck Epithemia adnata (Kütz.) Bréb. Epithemia argus Kütz. Epithemia smithii Carruthers Epithemia sorex Kütz. Epithemia turgida (Ehr.) Kütz. Epithemia turgida var. granulata (Ehr.) Brun Epithemia turgida var. westermanii (Ehr.) Grun. Eunotia sp. 1 Fragilaria brevistriata Grun. Fragilaria capucina Desm. Fragilaria construens (Ehr.) Grun. Fragilaria crotonensis Kitt.

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Fragilaria pinnata Ehr. Gomphonema acuminatum Ehr. Gomphonema angustatum (Kütz.) Rabh. Gomphonema gracile Ehr. Gomphonema intracatum Kütz. Gomphonema parvulum (Kütz.) Grun. Gomphonema sphaerophorum var. augur (Ehr.) Grun. Gomphonema subclavatum (Grun.) Grun. Gomphonema truncatum Ehr. Gyrosigma acuminatum (Kütz.) Rabh. Hantzschia amphioxys (Ehr.) Grun. Mastogloia elliptica var. danseii (Thw.) Cl. Mastogloia muradii Voigt Mastogloia recta Hustedt. Mastogloia smithii Thw. Mastogloia smithii var. amphicephala Grun. Navicula clementis Grun. Navicula cuspidata Kütz. Navicula decussis Østr. Navicula elginensis (Gregory) Ralfs. Navicula graciloïdes A. Mayer Navicula laevissma Kütz. Navicula libonensis Schoeman Navicula mutica Kütz. Navicula oblonga Kütz. Navicula pupula Kütz. Navicula pupula var. rectangularis (Greg.) Grun. Navicula radiosa Kütz. Navicula reinhardtii Grun. Navicula salinarum var. intermedia (Grun.) Cl. Navicula sclesvicensis Grun. Navicula tripunctata (O.F. Müll.) Bory Navicula tuscula (Ehr.) Grun. Nedium bisulcatum (Lagerst.) Cl. Nitzschia amphibia Grun. Nitzschia angustata (W. Sm.) Grun. Nitzschia commutata Grun. Nitzschia dissipata (Kütz.) Grun. Nitzschia hantzschiana Rabh. Nitzschia palea (Kütz.) W. Sm. Nitzschia romana Grun. Nitzschia sigmoidea (Ehr.) W. Sm.

Nitzschia tryblionella Hantzsche

Pinnularia borealis Ehr. Pinnularia borealis var. rectangularis Carlson Pinnularia brebissonii (Kütz.) Rabh. Pinnularia brevicostata Cl. Pinnularia burkii Patr. Pinnularia lata (Bréb.) W. Sm. Pinnularia maior (Kütz.) Cl. Pinnularia viridis (Nitz.) Ehr. Pinnularia viridis var. minor Cl. Rhoicosphenia marina (W. Sm.) M. Schmidt. Rhopolodia gibba (Ehr.) O. Müll. Stauroneis phoenicenteron Ehr. Stephanodiscus agassizensis nov. sp. Stephanodiscus hantzschii Grun. Stephanodiscus minutulus (Kütz.) Cl. & Möll. Stephanodiscus niagarae Ehr. Stephanodiscus sp. 2 Surirella biserata Bréb. Surirella ovata Kütz. Synedra acus Kütz. Synedra capitata Ehr. Synedra pulchella Kütz. Synedra ulna (Nitz.) Ehr. Synedra ulna var. oxyrhynchus (Kütz.) V. Heurck Synedra vaucheriae Kütz.





- A Amphora ovalis Kutz.
- B Aulacoseira spp.
- C Cocconeis placentula Ehr.
- D Asterionella formosa Hass.



- *Cyclotella bodanica* Eul. *Cymbella muelleri* Hust. A
- B
- Epithemia smithii Carruthers С
- Fragilaria construens (Ehr.) Grun. D



- A Cymbella cymbiformis (Ag. Kütz.) V. Heurck E Fragilaria brevistriata Grun.
- B Fragilaria crotonensis Kitt.
- C Amphora pendiculus Kütz.
- D Gomphonema subclavatum (Grun.) Grun.
- F Fragilaria pinnata Ehr.
- G Cymbella hustedtii Krasske



- A Small centric sp.
- B Synedra ulna (Nitz.) Ehr.
- C Small centric sp.
- D Navicula oblonga Kütz.



- A Nitzschia sigmoidea (Ehr.) W. Sm.
  B Stephanodiscus niagarae Ehr.
  C Navicula cuspidata Kütz.