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FACTORS INFLUENCING FLUX, MINERALIZATION AND AVAILABILITY OF PHOSPHORUS IN CLEAR AND ORGANIC LAKES IN THE ATLANTIC REGION.

by

Stephen Beauchamp

Submitted in partial fulfilment of the requirements
for the degree of Doctor of Philosophy

at

Dalhousie University
Halifax, Nova Scotia
October 1990

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DEDICATION

This work is dedicated to my friend GERALD MELNYK who died tragically long before he should have. He taught me how to get the most out of life and I shall never forget him for that or the years of adventure and companionship that we shared together. Never a day goes by that I do not think of him and feel the loss and sadness that is shared by his friends and family. I'm sorry that I cannot share this accomplishment with him as I have shared so many others.

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Abstract

Water chemistry, sediment geochemistry, and acid phosphatase activity were examined in selected lakes in Atlantic Canada to assess the impact of lake water acidification on phosphorus availability. Sediment phosphorus flux rates in 25 lakes ranged from -0.007 to 0.361 $mgP\cdot m^{-2}\cdot d^{-1}$. Sediment phosphorus flux was not significantly correlated with lake water acidity, but was correlated ($p < 0.01$) to lake trophic status and dissolved organic carbon (DOC) concentration. Comparisons with lake phosphorus budgets, suggest that sediment phosphorus loading was negligible.

Lower Ca concentrations in surface sediments was evident in some lakes. Greater Al flux from sediments was measured with increasing lake acidity. Lower pH in experimentally acidified cores indicated that aluminum, iron, manganese and calcium were mobilized from sediments, while soluble reactive phosphorus (SRP) was removed from the water column.

Greater phosphatase activity in lake water was generally associated with low pH and high DOC, aluminum and iron concentrations. Phosphatase activity was found to be highly pH dependant. Enzyme pH optima closely approximated that of ambient lake water in 4 lakes ranging in pH from 4.5-6.3. Little Springfield Lake (pH 3.8) showed a pH optima closer to its preacidification pH suggesting that enzyme modification to acidification may be slow. Inorganic Al added to water samples was found to inhibit enzymatic hydrolysis of organic phosphorus substrates to varying degrees depending on DOC content. The lack of substantial interference in the presence of large Al concentrations mobilized from sediments in acidified cores suggested that the Al mobilized from sediments was unreactive. Phosphatase activity in core water and surface sediments decreased with increased acidity down to pH 4.0, largely due to reductions in enzyme efficiency due to pH. Enzyme activity normalized for changes in efficiency due to pH, indicated greatest increases enzyme production at pH < 4.0. Increased acid phosphatase activity under increasingly acidic conditions may be related to removal of soluble reactive phosphorus (SRP) by direct phosphorus-metal interactions or enzyme inhibition but may also be a response reduced enzyme activity at lower pH.

Greater acidity was found to reduce DOC concentrations which may reduce enzyme substrate availability and reduce metal-organic complexation which could increase metal toxicity or reduce phosphorus availability through direct phosphorus-metal interactions.

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1. INTRODUCTION

The availability of phosphorus is especially important because of its role as the primary limiting nutrient controlling the epilimnetic productivity of many lakes (Vollenweider and Kerekes 1980; Tarapchak _et_ _al_. 1986 a,b).

1.1. Oligotrophication - The Hypothesis.

Grahn _et_ _al_. (1974) were the first to suggest that the continuous input of acidifying substances into aquatic ecosystems might lead to reductions in lake productivity, and coined the phrase "oligotrophication". Their conclusions were based, in part, on the loss of more alkiphilic plant species (i.e. _Lobelia_ _sp_. and _Isoetes_ _sp_.) from the benthic plant community and the subsequent expansion of _Sphagnum_ _sp_. The expansion of _Sphagnum_ _sp_ was determined to have two important consequences. First, due to the strong ion exchange capacity of _Sphagnum_, several ions important to biological productivity were thought to bind to the tissues of this moss and would no longer be available to other species and, second, the change in habitat structure towards a moss dominated community (in addition to two filiform alga and dense growths of fungal hyphae) would cause a deterioration in the invertebrate benthic community. They further hypothesized that the increased dominance of _Sphagnum_ _sp_. would accelerate the exchange and loss of base cations leading to further acidification and that the feedback established would cause acidification to be a self-accelerating process.

Oligotrophication of lakes was thought to occur primarily through the increased accumulation of coarse detritus (leaves) and increased coverage of sediments by leaves, moss, algae and fungi. In addition to reduced decomposition rates of the litter, coverage of the benthos prevents the exchange of nutrients and base cations between sediments and the overlying water. Although fungi also decompose organic material, they do so more slowly than bacteria meaning that the recycling of nutrients from litter would be impeded. This concept has been supported by recent increases of accumulation rates of organic bottom sediments in acidified Scandinavian lakes (Grahn and Hultberg 1974).

Studies of acidified waterbodies elsewhere have also shown an increase in the accumulation rate of organic material in bottom sediment which has been linked to reductions in microbial activity and subsequent organic decomposition rates (e.g. Leivestad et al. 1976; Kelly et al. 1984). Bick and Drews (1973) studied the effects of acidity on bacterial communities taken from natural and artificially acidified waters. With decreasing pH, decreased total bacterial cell counts were accompanied by reduced decomposition rates and reduced nitrification. A shift in the decomposer community from bacteria to fungi was also noted. Traaen (1974, 1976) examined the effect of reduced pH on decomposition rates by incubating homogenized wilted birch leaf litter for one year in flow through tanks using naturally acidic water (pH 4.5-5.2) and water adjusted to pH 6 and 4. There was a significantly greater leaf decomposition rate at pH 6 than at lower pH and decomposition rates (based on weight loss) were lowest at pH 4. However, it was cautioned that there could be other factors besides acidity affecting leaf processing.

Several studies have reported changes in bacterial communities or bacterial activity in relation to pH changes. Boylen _et_ _al_. (1983) measured bacterial activity in 1200 sediment samples collected from 9 Adirondack lakes. There were no significant differences in bacterial numbers isolated at different pH levels. However, only 10% of bacteria grew at pH < 5.0 regardless of the original isolation Ph. For bacteria isolated from circumneutral lakes (Ph 7.0), only 98% grew at pH 6.0 and 44% at pH 5.0. Hoeniger (1985) measured bacterial abundance and cellulose breakdown rates in the water column and sediments of lakes sensitive to acid deposition in Ontario. However, no significant differences in decomposition rates were found in sediments or the epilimnion over the pH range of 5.5 to 6.9. Kelly _et_ _al_. (1984) also found that, based on methane and inorganic carbon release, _in_ _situ_ decomposition rates in sediments were unaffected over a lake water pH range of 5.1-6.7. It was suspected that alkalinity generation by sulphate and nitrate bacteria in sediments maintained a higher pH microcosm at the sediment/water interface (Carignan 1985). When freshly sedimented material was mixed and maintained at a controlled pH, decomposition rates decreased at pH < 5.25. These studies indicate that the effects of acidification may not be severe until below pH 5.0.

Decomposition rates are a function of several processes including leaching, microbial, fungal, protozoan and macroinvertebrate activity (Francis et al. 1987). Anderson (1985) studied the processing of allochthonous material in acid and none acid lakes using alder leaves. Samples were incubated in 4 lakes ranging in pH 4.8 - 6.4. Weight loss in leaves exposed in situ in the lakes showed reduced decomposition rates at lower pH but results were inconsistent. Experiments on leaf litter decomposition were conducted with and without invertebrate shredders (Acellus) to test the relative importance of microbial activity versus invertebrate abundance. These experiments showed that leaves were quickly skeletonized and weight loss was much greater in the presence of Acellus sp., compared to samples where shredders were excluded, regardless of pH. The reductions in decomposition rates of alder leaves were found to be more closely correlated to invertebrate activity (which was also lower in more acidic lakes) than with pH. The positive effect of invertebrates on litter decomposition has been documented elsewhere (Webster and Simons 1978; Danell and Sjoberg 1979; Burton et al. 1985) although the extent of their role can be variable between lakes.

A study involving experimental acidification of benthic microbial communities collected from three Nova Scotia lakes, indicated that active bacterial populations were two orders of magnitude smaller in acid stressed samples (Rao 1982). Decomposition of organic material was also found to be adversely affected by acid stress. A similar study of five Ontario lakes showed that bacterial populations were an order of magnitude smaller or completely absent in acidic lakes compared to non-acid lakes which were similar in other features. In addition, surface sediments of acid lakes contained up to four times more organic matter than did an adjacent non-acidic lake (Rao 1983).

Studies have indicated that the effects of acidification may be reversible. Anderson et al. (1975) and Scheider et al. (1975a,b) measured increased microbial activity and organic decomposition rates in lakes treated with lime to raise the ambient pH. These studies have generally involved artificial manipulation of pH which could bias results by causing acid shock effects. However, similar results have been obtained by comparison of streams under natural conditions. Friberg et al. (1980) found significantly lower leaf breakdown in the more acidic of two streams similar in other environmental parameters (pH 4.3-5.9 versus 6.5-7.3). Measurements of sediment oxygen uptake and glucose turnover rates in seven lakes ranging in pH from 4.5 to 6.8 were also found to be lower in more acidic lakes indicating reductions in decomposition rates with increased acidity (Granstrom et al.

1980). Conclusions regarding the effects of acidification on decomposition and mineralization of organic material are not unanimous. Studies on the effects of artificial acidification of Lake 223 in Ontario did not show significant changes in decomposition rates of organic material in the water column or sediment (Schindler 1980).

Most of the research on the effects of acidification on decomposition rates of organic material has focused on the benthos. Unfortunately, studies concerning the effcts of acidification on mineralization processes in the water column are lacking.

1.2. Acidity and Primary Productivity.

The studies described above provide indirect evidence that there may be reductions in nutrient cycling in acidified lakes but do not provide any indication that the potential changes in phosphorus availability are actually manifested in lakes. A number of laboratory studies have shown relationships between either presence-absence or growth rates of different algae and pH. Moss (1973) studied growth rates of different algal species at different pH and found that optimum pH varies between species although a lower limit of growth for most species tested was found to be above 4.5 to 5.1. However, 3 of 33 species grew well at pH levels below 4.0. Brock (1978) studied biota in extremely acidic waters in Yellowstone National Park and found that some species flourished at pH levels as low as 0.5 (eg. *Cynanidium caldarium*). Havas and Hutchinson (1982) found the eugleniod (*Euglena mutablis*) present at pH 1.8 in ponds exposed to sulphur fumigations from burning bituminous shales. Apparently, many aquatic algal species are able to tolerate high levels of metal contamination (see reviews by Stokes 1983; Dillon *et al*. 1983). Most of these studies appear to relate more closely to algal physiology and metabolism rather than nutrient cycling and there is not as much direct evidence concerning decreases in primary or secondary production in acid lakes.

Evidence from the field has generally shown no clear correlations between acidification and phytoplankton biomass or primary productivity in lakes although numerous surveys and studies have shown changes in phytoplankton community structure and species composition (Yan and Stokes 1978; EPA 1983, Stokes 1986). In a study of primary production and plankton biomass in six lakes in the Sudbury region of Ontario, Kwaitkowski and Roff (1976) found no significant relationship between acidity and lake productivity. Primary productivity measured in the most acidic lake was $3\ \mathrm{mgC\cdot m^{-3}\cdot hr^{-1}}$ which was well within the range of values observed in non-acid lakes in the region (NRC 1981). However, surveys of this nature tend to be short term measurements of planktonic primary productivity which are of limited usefulness in interpreting anything except large changes. They do not account for physiological or metabolic changes in algae related to pH. Surveys and infrequent or short term measurements of plankton biomass or productivity are insensitive to plankton community relationships intrinsic in determining lake productivity. They do not adequately account for changes in zooplankton or planktivore grazing pressure on algae or other, more complex, predator-prey relationships (i.e. fish -> zooplankton -> algae) as well as annual variations in lake hydrodynamics. Changes in fish and zooplankton populations as lakes acidify have been widely documented and reductions in grazing pressure may give the false impression in increased biomass or productivity in acid lakes where the detrimental effects of acidification are masked. Short-term changes in hydrology can also produce substantial changes in lake productivity without significant changes in pH. Beauchamp and Kerekes (1989) have shown that planktonic primary productivity can vary by as much as 40% between consecutive years due to between year differences in hydrology and DOC export from lake catchments. Dissolved organic matter (DOM) in lakes affects light extinction coefficients and reductions in DOM concentrations accompanying lake acidification can increase euphotic depth and lake productivity (Schindler et al. 1980; Schindler and Turner 1982). Long-term studies are required in order to provide more representative data. Clearly, observational data such as this are inadequate in determining processes involved in the effects of acidification on phosphorus dynamics and a more mechanistic approach is needed.

Schindler (1980) disputes the oligotrophication hypothesis since no changes in total phosphorus concentrations, plankton biomass or productivity were noted in Lake 223 as a result initial study of acidification of the whole lake from pH 6.6 to 5.6. However, it was pointed out that a pH of 5.6 may not be low enough to show measurable changes or, since only the lake itself was acidified, metals responsible for reduced inorganic phosphorus in the water, would not have been mobilized from the lake catchments. After 8 years of study and a pH reduction from 6.8 to 5.0 in Lake 223, Schindler et al. (1985) still found no decrease in lake phosphorus concentrations or planktonic primary productivity. Decomposition rates at the sediment surface were also unaffected by acidification because microflora at the sediment water interface maintained a microenvironment with a higher pH.

Hendry (1976) added sulphuric acid to stream water and compared chlorophyll to carbon ratios and specific activity (carbon uptake per unit chlorophyll) in the acidified water (pH 4) and the natural stream water (pH 4.3-5.5). The ratio of chlorophyll to carbon was found to be low which was interpreted as an indication that much of the chlorophyll was inactive. Specific activity was also reduced at pH 4.0 which supports this conclusion.

1.3. Phosphorus Dynamics in Undisturbed Organic Lakes.

Phosphorus dynamics and productivity in undisturbed, organic lakes are not well understood. Much of the research on primary productivity in organic lakes has focused on the effects of dissolved organic matter (DOM) on light attenuation (e.g. Effler et al. 1985; Davis-Colley and Vant 1987). It has been found that increased DOM concentrations causes greater attenuation rates and decreased euphotic depth. Lower production, phosphorus uptake and increased respiration below the compensation level in the water column may allow an accumulation of mineralized phosphorus which can be brought up to the euphotic zone by normal turbulent mixing. This may explain the greater productivity maxima observed at optimum light levels in coloured lakes (Beauchamp and Kerekes 1989) although whole column productivity remains comparatively low when compared to similar clear water lakes. This suggests that DOM may have, to some extent, the physical effect of lowering competitive phosphorus uptake in subsurface layers of the water column.

Several studies have demonstrated that DOM may reduce phosphorus availability through abiotic interactions, primarily phosphorus-DHM complexation in the presence of iron (e.g. Franko and Heath 1982, 1983; Franko 1986; De Haan and De Boer 1986). Steinberg and Baltes (1984) studied orthophosphate-DHM interactions in an acid bog (pH 3.9) and found significant reductions in inorganic phosphorus availability associated with increased DHM concentrations. Low molecular weight DHM was found to bind more inorganic phosphorus than high molecular weight compounds but the role of the different compounds (determined by gel chromatography) was questionable since the pH of sample was raised from the ambient pH of 3.9 to 7.0 and samples were concentrated from 1000 ml to 3 ml by evaporation prior to analysis. Such highly manipulative techniques are likely to alter the structure of DHM. Brassard and Auclair (1984) examined orthophosphate uptake rate constants in the presence of different DHM molecular weight fractions and found that DHM could moderate orthophosphate uptake rates. Jones et al. (1988) studied the interaction between humic material and inorganic phosphorus in a small Finnish Lake (pH 4.5) under conditions as similar as possible to those found in situ and found that inorganic phosphorus labelled with a phosphorus radioisotope was bound rapidly to two size fractions of DHM, one high molecular weight (>100,000) and one low (10,000-20,000). A chemical equilibrium existed between free phosphorus and the bound fractions, however, the exchangeability (movement) of phosphorus was different between fractions and even within fractions over time. These results were very similar to those of Levine et al. (1986) who examined phosphorus dynamics in a clear water Ontario lake. Thus, the overall effect and interactive potential of DHM with inorganic phosphorus could be expected to vary in relation to the relative concentrations of individual chemical components of the DOM pool.

Additions of ferric iron to lake water samples have been found to enhance the movement of phosphorus from the inorganic to the organically bound forms (Jones et al. 1988). The involvement of iron in the formation of phosphorus-humic complexes appears to be very important. Young and Comstock (1984) found that DHM alone had little capacity to bind inorganic phosphorus in the absence of ferric iron. De Haan and De Boer (1986) suggest that bound phosphorus exists as both inorganic colloids and colloidal Fe-fulvic acid chelate to which the phosphorus is connected. Jackson and Hecky (1980) also found that much of the phosphorus in 3 reservoirs and a natural lake was in the form of humic-iron-phosphate complexes. However, based on the results of their study, they concluded that primary productivity was depressed by DHM by making iron and other trace metals unavailable to phytoplankton and not through light attenuation, lowering pH or sequestering inorganic phosphorus.

Other metals, such as aluminum, have also been implicated in reduced phosphorus availability. Jackson and Schindler (1975) found that humic complexes associated with phosphorus and iron also had high concentrations of aluminum.

Greater concentrations of dissolved aluminum, iron, and other metals occur in surface waters in many regions subjected to increased acidification (Cronan and Schofield 1979; Johnson et al. 1981; LaZerte 1984; Havas 1986). Inorganic aluminum and iron are known to sequester orthophosphate in soil and water (Jackson and Schindler 1975; Jackson and Hecky 1980; Nalewajko and O'Mahoney 1988), thereby rendering phosphorus unavailable for uptake by algae. In acidic Lake Gardsjön, a long-term decline in total phosphorus concentration was attributed to the fixation of phosphorus by aluminum complexation in lake water and the soils of the surrounding watershed (Jansson et al. 1986). Adsorption or precipitation of substantial amounts of inorganic phosphorus by aqueous aluminum oxyhydroxides could potentially have serious detrimental effects on planktonic primary productivity in aquatic ecosystems. The effects of aluminum and iron on inorganic phosphorus and the mineralization of phosphorus from dissolved organic phosphorus compounds may be an important mechanism in the oligotrophication of acidic lakes.

Specific information concerning the chemistry of aluminum-phosphorus interactions is lacking. Huang (1975) found that orthophosphates were readily adsorbed by Al_2O_3. Dickson (1978) found that orthophosphate added to acidic lake water with elevated concentrations of aluminum was quickly removed from solution. Dickson (1980) noted that mineral dissolution with increased acidity should lead to higher phosphorus concentrations in lakes. However, phosphorus concentrations in acidified lakes in Sweden are lower than similar non acidic lakes. Experimental additions of 50 and 100 ugP l^{-1} to clear lake water and 100 ugP$\cdot l^{-1}$ to coloured lake water showed that phosphorus was lost from solution at pH between 3 and 8 with maximum losses in the pH 5.6 to 6 range in clear water. The presence of high concentrations of humic matter prevented phosphorus-aluminum interaction since the former tends to be bound to organic ligands. Evidence from the clear lakes suggests that elevated aluminum concentrations decreased the concentration of biologically available phosphorus. However, no attempt was made in this study to separate the effects of aluminum from other mechanisms which may cause reductions in phosphorus concentrations, such as the activity of biota. Since maximum adsorption closely followed the Al solubility profile (Stumm and Morgan 1981) it is likely that Al was important in phosphorus reductions.

The results of the studies discussed above imply a strong tendency for inorganic phosphorus to move into bound (unavailable) fractions. The possibility that DHM may be a source of phosphorus is a subject which has received considerable debate in the literature. Because primary production in lakes is limited by the availability of PO_4^{-3}, it has generally been assumed that DOP can only be present if it is in a refractory form which cannot be not utilized as a PO_4-P source by phytoplankton. However, this may be an excessively broad generalization which does not apply to all DOP compounds. Attention has recently focused the various pathways of epilimnetic phosphorus regeneration including studies of certain organic phosphorus-containing compounds which can be metabolized as sources of orthophosphate by some planktonic organisms (Kuenzler 1970; Johannes 1964; Harris 1957). This heterotrophic phosphorus utilization mechanism has been the subject of substantial controversy.

Phosphorus loading models developed by Vollenweider (1975) to predict lake response to phosphorus enrichments, recognized the fact that the models were inappropriate for use on dystrophic lakes. Phytoplankton production and biomass in dystrophic lakes were found to be consistently low when total phosphorus concentrations was used as a predictor. This was strong evidence that much of the total phosphorus in organic lakes was not available for planktonic uptake. Evidence also supporting the refractory nature of DOP in lakes are provided by Rigler (1968) and Berman (1970) who found that a substantial fraction of the DOP in their study lakes did not release orthophosphate. Franko and Heath (1979) measured changes in soluble unreactive phosphorus (SUP) in the water samples from a variety of lake types and demonstrated that conditions suitable for orthophosphate release from DOP were not always present. Lean and Nalewajko (1976) added colloidal ^{32}P to algal cultures but found that most of the isotope added was recoverable. In contrast, Franko (1984) found that most of the SUP in some lakes was comprised of low molecular weight compounds which commonly indicates the presence of suitable enzyme substrates from which orthophosphate can be released.

Ultra-violet (UV) radiation may also play a role in phosphorus dynamics in organic lakes (Jones et al. 1988). Ultra-violet radiation is known to break down organic material including high molecular weight compounds, including refractory humic substances which are abundant in dystrophic lakes (Franko and Heath 1979, 1982, 1983). Simpler compounds resulting from the breakdown of high molecular weight organic molecules by UV radiation can provide substrates suitable for further degradation by enzymes. This suggests that the ability of plankton to utilize organic or other complex phosphorus compounds is closely related to the chemical nature of the compounds in question and their availability in lakes. It seems reasonable to view organic phosphorus compounds found in lakes as consisting of a broad spectrum of compounds with different breakdown rates. Highly labile species breakdown most quickly and tend not accumulate in the water column while highly refractory compounds breakdown slowly and persist for long periods. Simple measurements of static DOP, DHM or DOM concentrations are inadequate in assessing the role of organic phosphorus in phosphorus dynamics in dystrophic lakes.

1.4. Phosphatase Enzymes.

The production of phosphatase enzymes has been suggested as a mechanism by which the competitive ability of algae may be enhanced by permitting the use of complex phosphorus substrates as a source of phosphorus under phosphorus limiting conditions (Rifkin and Swift 1980; Konopka 1982). The extent to which the DOP pool is utilized by phytoplankton, and whether the production of phosphatase enzymes allows phytoplankton to at least partially circumvent phosphorus limitation by hydrolysis of organically bound phosphorus, is uncertain.

Phosphatases are present on and within cell membranes (Brandes and Elston 1956; Moller et al. 1975) suggesting that they function in the hydrolysis of exogenous phosphorus containing substances. Jansson (1976) identified two classes of phosphatase enzymes in lake water, phosphatase A and phosphatase B based on molecular weight. Phosphatase A either had a very high molecular weight (> 500,000), or was associated with colloidal material or cell fragments, while phosphatase B had a molecular weight of about 80,000. Sephadex fractionation of phosphatases showed that free phosphatases and seston-associated phosphatases were structurally similar, indicating that free phosphatase may be released from seston into solution. In a later study using similar methods, Jansson et al. (1981) found at least four different phosphatase fractions in lake water, all of which were associated with particulates. Two fractions (phosphatase I and II) were also found in solution, while two seston-associated fractions (phosphatase III and IV) were not. Phosphatase I was very large (>200,000) while phosphatase II had a lower molecular weight (150,000). Both of the seston phosphatases were smaller, with phosphatase III having a molecular weight of 100,000 and 30,000 for phosphatase IV.

Enzymes extracted from lake water lose activity fairly rapidly. Reichardt et al. (1967) measured a 50% loss in activity after 3.2 days at 18°C. Free phosphatases are especially short-lived compared to other phases (Pettersson 1980). Reichardt et al. (1967, 1971) reported that free phosphatase activity had a half-life ranging from 7 to 72 hours, while Berman (1970) reported a 20% decrease in activity within 10 days. Phosphatase activity measured in chloroform and formalin treated samples was also found to decline rapidly with most of the activity being lost within 5 days, however 10% remained after 69 days indicating some degree of persistence (Jansson et al. 1981). In the field, phosphatases do not appear to be long lived since they do not accumulate in the epilimnion of lakes, nor do they persist after the decline of algal blooms (Pettersson 1980). Declines in in situ phosphatase activity are due to the loss of dead cells by settling, and the rapid degradation of free enzymes released by cell lysis.

The release of orthophosphate from substrates as a result of the activity of alkaline and acid phosphatases was first suggested by Steiner (1938). Since then phosphatases have been found to work on a range of substrates including organic and inorganic condensed polyphosphates (Fernley and Walker, 1967), certain colloidal phosphorus compounds (Paerl and Downes, 1978), and phosphomonoesters (Fitzgerald and Nelson

1966). Clesceri and Lee (1965) also found that certain algae could hydrolyse pyrophosphate and tripolyphosphate in culture.

Phosphatases, known to act primarily on low-molecular weight organic compounds, especially phosphomonoesters, might also act upon any other compounds with weak oxygen-phosphorus bonds. Phosphomonoesters are considered to be preferred phosphatase substrates and have been found to comprise a substantial portion of the DOP pool in some lakes (Heath and Cooke 1975; Wetzel 1983). However, in most lakes, low-molecular weight organic compounds which are suitable phosphatase substrates and known to be excreted by phytoplankton, are generally found in low concentrations indicating rapid uptake by heterotrophs (Wright and Hobbie 1966). Rapid uptake does not allow them to accumulate in water making them difficult to measure directly. However, if substrates suitable for attack by phosphatase enzymes occur in lake water, their presence would be expected to reduce the size of the DOP pool and increase the concentration of orthophosphate. Because of the rapid uptake of orthophosphate by phytoplankton under nutrient-limited conditions, it is also difficult to measure organic phosphorus hydrolysis using increases in ambient orthophosphate. Instead, orthophosphate release by enzyme hydrolysis has been estimated by decreases in DOP concentrations while in the presence of phosphatase enzymes. Franko (1984a) incubated lake water samples with phosphatase and found a weak negative correlation ($r^2 = -0.16$)

between phosphatase activity and DOP concentration. The weak correlation was attributed to seasonal variations in SRP and phosphomonoester substrate concentrations. However, the measurable decrease in soluble unreactive phosphorus (SUP) indicated SUP was hydrolysed to orthophosphate. The addition of glucose-6-phosphate and glucose- 1-phosphate as an artificial organic phosphatase substrates to algal cultures was also found to stimulate (in this case double) phosphatase production by Ochromonas danica (Aaronson and Patni 1976). Increased growth rates by O. danica while cultures were orthophosphate-limited indicated that they could supply needed orthophosphate from suitable organic substrates.

Phosphatases are synthesized by a wide variety of freshwater organisms, including fungi, yeasts, protozoans and metazoans (Karl and Craven 1980), bacteria and algae (Jones 1972; Currie and Kalff 1984a,b) and zooplankton (Jansson 1976). However, phosphatase production has been most intensively studied in algal and bacterial populations (Jones 1972).

Currie et al. (1986) found that the proportion of phosphatase activity associated with various planktonic particle size classes varied among 13 lakes sampled. Much of the phosphatase activity (an average of 44%) was associated with algal cells although a substantial portion (an average of 40%) was extracellular in solution. Other studies have also indicated that phosphatase is predominantly associated with algal-sized particles (Berman 1970; Pettersson 1980; Heath and Cooke 1975). Berman (1970) found that approximately 80% of the total phosphatase activity was associated with phytoplankton while an average of 16% was in solution, but this varied seasonally where, on an annual scale, between 0-57% of the total phosphatase could be found in the dissolved form.

Pettersson (1980) measured bacterial abundance in one lake and considered low numbers and biomass indicative of negligible bacterial contributions to the total lake phosphatase activity. In contrast, Wetzel (1981) and Stewart and Wetzel (1982) found that much of the phosphatase in the lakes they sampled was either free in solution or associated with bacteria. In four lakes, Stewart and Wetzel (1982) found that the maximum possible algal contribution to total lake phosphatase activity was consistently < 34% , and in some cases as low as 5-6% . It appears that there is substantial variability in planktonic community structure and species composition which complicates interpretation of the relative contributions of various organisms between lakes and probably within lakes on spatial and temporal scales.

There is also evidence that some of the "non-algal" phosphatase described as free in solution could actually be associated with nannobacteria that are capable of passing through the commonly used 0.45 um filters (Stewart and Wetzel 1982). Therefore, bacterial-derived phosphatase may comprise an under-estimated, but important component of the phosphatase pool. Franko and Heath (1979) found that 0.45 um filters retained 18-100% of the phosphatase activity in lake water but < 6% could pass through a 0.22 um filter, indicating that an important but variable bacterial component was probably present. Phosphatase activity associated with smaller, non-algal particulates accounted for as much as 73% of the total phosphatase activity. Jansson et al. (1981) found that 50% of the total phosphatase in their study lake was dissolved while 40% was associated with particles < 5 um in size, 8% with particles between 5-30 um and 2% with particles 30-100 um. No phosphatase was found in association with particles larger than 100 um.

Jansson et al. (1981) also found that different phosphatases and different proportions of phosphatase appeared to be associated with different size classes. Phosphatase I was present in all size classes as well as free in solution while phosphatase II was only found in solution. Only seston < 5 um produced phosphatase III and IV. However, phosphatase I and II accounted for almost 90% of the total phosphatase activity in the lake.

Attempts to correlate phosphatase activity with the abundance of algae and bacteria have not generally been successful (Goldman et al. 1968; Jones 1971). This has been particularly true of bacterial populations where size fractions have been measured using filtration techniques. In some habitats, the majority of respiring bacteria can be found attached to particles (Harvey and Young, 1980), including algae (Jones 1972). Using alternate techniques to examine bacterial abundance, Stewart and Wetzel (1982) concluded that non-algal particulate phosphatase activity can be a major contributor to the particulate phosphatase component previously described as algal. The ecological importance of various taxa to phosphatase activity is difficult to assess until the relative contribution by autotrophs and heterotrophs can be determined.

The distribution of phosphatase activity within lakes is also strongly influenced by season and lake hydrodynamics. Phosphatase activity tends to be low during periods of overturn when hypolimnetic orthophosphate is more readily available. Increased phosphatase activity usually occurs immediately after spring circulation, coincident with the beginning of orthophosphate limitation to phytoplankton productivity (Jansson _et al._ 1981). Peaks in phosphatase activity sometimes occur about the same time as peaks in algal biomass (Berman 1970) although this is not always the case. Phosphatase activity tends to persist for a short time after algal blooms decline, coinciding with increases in bacterial abundance. Consistent post-bloom increases in bacterial activity do not always occur. They may appear during, after algal blooms, or not at all (Jones 1972).

In most lakes phosphatase activity is greater in the epilimnion than in the metalimnion, but depth profiles in lakes sometimes indicate a strong presence of free phosphatase at depths corresponding to high rates of cellular decomposition and lysis, such as at the thermocline (Reichardt et al. 1967).

Diurnal changes in phosphatase activity have also been measured in lakes. Berman (1970) found that phosphatase activity was highest in the late afternoon and evening, suspected to be caused by local exhaustion of orthophosphate following intense daily uptake during periods of high insolation. Diurnal changes in phosphatase activity may also be related to variations in substrate availability. Experiments have shown that the rate of extracellular release and chemical composition of organic compounds change rapidly during the day as different metabolic pathways within cells alternate (Nalewajko and Schindler 1976). The rate of release of extracellular substrates is also affected by light intensity, photosynthetic rate and, nutrient availability (feedback). Low molecular weight compounds (1500- 5000) dominate release during initial daily photosynthesis, while larger molecules predominate later in the day (Nalewajko and Lean 1972; Nalewajko et al. 1976; Dunstall and Nalewajko 1976).

Studies have shown that the relative proportions of dissolved and particulate phosphatases also vary seasonally, possibly in relation to the pattern of orthophosphate availability. For example, Berman (1970) found that most of the phosphatase activity was associated with the soluble fraction when orthophosphate limitation was not severe, compared to conditions of severe orthophosphate limitation when there was a marked shift in phosphatase activity to the particulate fraction.

Some studies suggest that phosphatase may be opportunistically produced by some phytoplankton species, providing a competitive advantage by utilizing organic phosphorus to supplement the demand for orthophosphate not otherwise available (e.g. Fitzgerald and Nelson, 1966; Berman, 1970; Heath and Cooke, 1975; Jones, 1972; Jansson, 1976; Pettersson, 1980). Heath and Cooke (1975) found that phosphatase was produced during the latter part of algal blooms, when the concentration and external loading of orthophosphate were low and phosphorus became limited. They hypothesized that increased phosphatase production under these conditions was induced to take advantage of the coincident increases in phosphomonoesters, suggesting that increases in phosphatase activity and release of orthophosphate from phosphomonoesters may be an important phosphorus cycling process (see also Wetzel 1981; Franko 1984a).

The potential importance of phosphatase to lake productivity has been demonstrated (Berman, 1970; Jansson, 1977). For example, Heath and Cooke (1975) found that in their study lake, a bluegreen algae (Aphanizomenon flos-aquae) bloomed in two stages. The first bloom was of moderate intensity, occurring shortly after the spring overturn when orthophosphate was relatively abundant in the water column and phosphatase activity was low. A second, more intense bloom, occurred in late summer and was accompanied by a 20-fold increase in phosphatase activity and attained the highest algal standing crop measured over a 2 year period. The onset of high phosphatase activity coincided with relatively high concentrations of phosphomonoesters, and the inverse relationship between the two suggests phosphomonoesters served as a primary substrate for orthophosphate regeneration. It was estimated that enough orthophosphate could have been released from the phosphomonoesters present to account for the orthophosphate demand of the bloom. Elsewhere, Berman (1970) found that orthophosphate was released at an average rate of 4.0 ugP l^{-1} d^{-1} and that an average of 53% of the total phosphorus was hydrolysed to orthophosphate within 9-10 days. The amount of orthophosphate released through enzyme hydrolysis exceeded the initial amount of orthophosphate present. Bierman et al. (1980) found that orthophosphate excretion combined with that released by the decomposition of phytoplankton accounted for 70% of the orthophosphorus available for uptake during the middle of the growing season. They also reported that microbial conversion of unavailable to available phosphorus contributed 10%-25% of the annual net phosphorus uptake. These examples illustrate that enzyme mediated release of orthophosphate can be important in the phosphorus and plankton dynamics in some lakes, contingent upon the availability of suitable phosphorus-containing substrates. In some lakes, potential phosphatase substrates dominate the DOP pool, while in other lakes they may not be present at all.

However, other studies contradict the view that phosphatase activity mineralizes DOP into available phosphorus regardless of chemical form. Herbes et al. (1974) added a commercially prepared phosphatase to lake water samples containing naturally occurring organically bound phosphorus compounds and found that no orthophosphate was released indicating that the DOP pool may not always be an important source of orthophosphate in lakes. Heath (1986) used phosphorus uptake kinetics, enzyme kinetics and changes in the size of the DOP and SRP pool to determine whether the rate of release of orthophosphate from ambient DOP could satisfy planktonic orthophosphate demand in a variety of freshwater systems including eutrophic and dystrophic lakes. In the set 5 lakes studied, the release of orthophosphate from DOP was sufficient to satisfy less than 1% of planktonic demand. Among the lakes sampled in this study, phosphomonoester concentrations ranged from 0-100% of the soluble unreactive phosphorus pool and phosphatase activity ranged from zero to moderate levels. In spite of substantial evidence to the contrary, Heath (1986) concluded that phosphatases provided no nutritional benefit to plankton even though phosphatase hydrolysable compounds formed a major fraction of the DOP pool. He further suggested that phosphatase enzymes may be important to phytoplankton, but in non-nutritive ways such as providing informational messages involved in regulating plankton metabolism.

The direct link between phosphorus availability and phosphatase activity has been well documented. The enrichment of phosphorus-limited lake water with orthophosphate has been shown to lead to a reduction in phosphatase activity (Franko 1984) and phosphatase activity has been measurably inhibited by increases in orthophosphate concentrations as small as 0.1 $ugP \cdot l^{-1}$ (Reichardt et al. 1967). The level below which phosphatases are produced appears to be in the range of 0.2-0.3 $ugP \cdot l^{-1}$ (Jones 1972). Jansson (1976) tested the effect of orthophosphate additions on two phosphatase fractions (A and B) and showed that increased orthophosphate concentration inhibited the activity of phosphatase A (produced by phytoplankton) but had no effect on phosphatase B (thought to be a digestive enzyme produced and excreted exclusively by zooplankton). Since these experiments were carried out on filtered-sterilized samples it is apparent that the reduction of enzyme activity was due to direct inhibition of phosphatase enzymes, and not due to the repression of enzyme synthesis. Similar results were obtained by measuring phosphatase activity in lake water samples treated with formalin and chloroform (Jansson et al. 1981).

In many species of phytoplankton acute orthophosphate limitation depletes the internal reserves of orthophosphate inducing the production of plasmalemma-bound phosphatase (Franko 1983). Pettersson (1980) measured alkaline phosphatase activity and algal surplus phosphorus as phosphorus-deficiency indicators in an eutrophic lake. Specific alkaline phosphatase activity (enzyme activity normalized to chlorophyll-a concentration) increased up to ten-fold during periods of phosphorus limitation. Alkaline phosphatase activity increased rapidly below surplus phosphorus concentrations of < 0.2 ugP/100 ugC which corresponded to inlake orthophosphorus concentrations < 1 ugP l^{-1}.

Although linked to external orthophosphate concentration, enzyme synthesis is more likely to be regulated by cellular available phosphorus concentration. In addition, most algae have the ability to store surplus orthophosphate (although probably not as orthophosphate), and to subsequently undergo several cell divisions (Rhee 1973). This implies that the presence or absence of surplus intracellular phosphorus is important in understanding the relationship between phosphatase production, phosphate uptake, and algal growth. High alkaline phosphatase activity per unit biomass has also been shown to correspond with other physiological indicators of nutrient deficiency, such as ratios of cellular

ATP to biomass (Cavari 1976); phosphorus: carbon (Pettersson 1980); nitrogen: phosphorus Pettersson 1980); protein: carbohydrate; chlorophyll-a: carbon (Healey 1973a,b) and ATP: carbon (Holm-Hansen 1970). Although the latter three ratios are general indicators of nutrient deficiency the others have been closely linked to phosphorus deficiency (Healey and Hendzel 1979, 1980).

Experiments with algal monocultures have shown that different planktonic species may have different abilities to produce phosphatase in response to phosphorus limitation. Healey and Hendzel (1979a,b) measured phosphatase activity of various algal species at different orthophosphate concentrations to examine species-specific differences in response to orthophosphate limitation. The rate of increase and peak phosphatase activity differed between species. Anabaena flos-aquae was shown to have exceptionally high phosphatase activity, probably because of its relatively high phosphorus demand (Bone 1971). A. flos-aquae already has the advantage of being able to fix inorganic dinitrogen, which when coupled with the production of large amounts of phosphatase, could account for the wide distribution and dominance of this species in marginal phosphorus-nitrogen limited lakes.

Species-specific differences in phosphatase response to orthophosphate limitation measured in the laboratory may not be ecologically important. Reviews by Healey (1973b; 1975) indicate that although organisms from diverse taxonomic and ecological groups respond to nutrient deficiencies in different ways, when examined in mixed culture their response is sufficiently similar to compare phosphatase activity in cultures to that of naturally occurring mixed populations. Smith and Kalff (1981) also found that species composition did not appear to affect or alter phosphatase response to orthophosphate limitation by the community as a whole. Instead, it was determined that phosphatase response in natural communities was more closely linked to the relationship between nutrient supply and community growth. In Lake Memphramagog community growth rates showed significant inverse correlations with phosphatase activity, indicative of a response to nutrient deficiency. The highest phosphatase activity was found in the most oligotrophic parts of the lake and corresponded to a growth rate of 0.06 d^{-1}. Areas of low phosphatase activity had higher growth rates of up to 0.93 d^{-1}. Smith and Kalff (1981) also showed that while algal abundance varied with total phosphorus concentration, community growth rate was relatively consistent over a four-fold range of total phosphorus. The consistently high growth rates in the most nutrient deficient areas of the lake were attributed to changes in phosphatase activity, which apparently compensated for changes in orthophosphate availability. It was suggested that under orthophosphate limited conditions phosphatase activity may be a useful physiological indicator of average community growth rate. Compared to the direct measurement of growth rates of natural phytoplankton communities, phosphatase bioassays are relatively easy to perform and are subject to fewer sources of error.

Information about phosphatase activity has also helped elucidate the effects of nutrient limitation on phytoplankton production. Attempts to quantify the relationship between growth and limiting nutrients based on the measurement of nutrient concentrations in lake water, have provided useful indices, but have also proven to be imperfect in several ways. The metabolism of nutrients in lake water is complex, involving an array of mechanisms including transfers between chemical forms, uptake, storage, release, oxidation, reduction, sorption, precipitation, and more (Hooper 1972; Lean and Rigler 1974; Jackson and Schindler, 1975; Koenings 1976; Nur and Bates 1979; Richardson and Marshall, 1986). There is a need for more precise, relevant, and easily obtainable specific indicators of the degree of cellular phosphorus deficiency, and of the immediate phosphorus requirements of phytoplankton in order to more accurately assess the relative effects of varying degrees of nutrient limitation on algal growth and biomass. Smith and Kalff (1981) and Pettersson (1980) have found specific phosphatase activity (the ratio of total phosphatase activity to a biomass indicator, usually chlorophyll- a) to be a good index. Phosphatase activity may also be a useful indicator of temporal changes in the nutritional status of plankton communities. For example, compared to other years when turnover occurred, phosphatase activity in Lawrence L. was an order of magnitude higher during a two year period when the lake did not turn over in the spring, so that nutrient rich hypolimnetic water did not mix into the epilimnion (Stewart and Wetzel 1982).

Phosphatase activity may also a useful index of small-scale spatial differences in planktonic orthophosphate stress. Most microorganisms live in microenvironments that are defined on scales of micrometers or millimetres. The chemical composition and nutritional status of such a microenvironment may be distinct from that of the bulk macroenvironment. Karl and Craven (1980) suggested that phosphatase activity could be useful as a sensitive bioassay or metabolic indicator of microscale orthophosphate limitation in plankton assemblages.

Phosphatase activity may also be useful in distinguishing between systems which are nitrogen or phosphorus-limited, particularly in lakes with marginal N:P ratios, where nitrogen and phosphorus limitation may alternate temporally or spatially (Elser et al. 1988). Phosphatase activity may also help in determining whether changes in phytoplankton biomass are due to non nutrient factors, such as light-limitation.

Phosphatase activity has only recently received attention as a potentially useful index of environmental perturbations which may affect phosphorus cycling. An example concerns the effects of acidification on phosphorus availability and the sequestering of orthophosphate by aluminum (Jansson _et_ _al_. 1981; Broberg 1984). In some acidic lakes (pH <5.0) phosphatase activity bears an indirect relationship to metal concentrations, especially aluminum and iron. High phosphatase activity in an acidic lake was found to be about 10x greater than in non acidic lakes of similar trophic status, suggesting that the acidic environment may create a situation where the phosphorus supply to planktonic organisms is reduced (Jansson _et_ _al_. 1986).

Phosphatase production may not necessarily be induced by phosphate limitation alone and that other molecular species may be involved (Kuo and Blumenthal, 1961; Wilkins, 1972). Research on non-aquatic (animal) bacterial systems suggests that a variety of agents including nucleotides and nucleotide derivatives are capable of binding with phosphatases (Franko 1984), thereby altering phosphatase activity. Several of these nucleotides and their derivatives are known to occur in freshwater (Franko, 1983; Franko and Wetzel, 1982) but their interactions with phosphatases are not understood. Franko and Wetzel (1982) found that the concentration of cyclic adenosine 3',5'-monophosphate (CAMP) was linearly correlated to the rate of primary production. This suggest that CAMP and possibly other nucleotide derivatives are involved in regulating cell metabolic processes, including phosphorus metabolism. Franko

(1984) found that phosphatase activity could be stimulated (by as much as 525%) or repressed by very small changes in cAMP concentration. Additions of other compounds structurally similar to cAMP also affected phosphatase activity, suggesting a certain degree of non-specificity of phosphatase response to nucleotide compounds. Bacterial and algal phosphatases were affected differently, indicating differences in their phosphatase regulation mechanisms. This evidence suggests that other compounds may play a role in the regulation of *in situ* planktonic phosphatase activity.

1.5. Sediment Phosphorus.

Phosphorus exchange across the sediment-water interface has been recognized as an important nutrient cycling pathway in some lakes (Mortimer 1941, 1942). Traditional views have suggested that, under aerobic conditions, the movement of phosphorus is largely unidirectional into sediments (Wetzel 1975) and that sediments are a net phosphorus sink (Evans and Rigler 1980; Doremus and Clesceri 1982). However, recent studies have described a substantial release of inorganic phosphorus from oxic lake sediments (e.g. Lee *et al*. 1977; Neame 1977; Starkel 1985; Quigley and Robbins 1986; Shaw and Prepas 1989). Lakes throughout the Atlantic region tend to be shallow and have sediments exposed year-around to oxygenated lake water but little is known about the rate of exchange of inorganic phosphorus across the sediment-water interface in these lakes. Lakes in the region also vary in trophic status, dissolved organic carbon (DOC) concentration and acidity, providing a wide range of conditions in which sediment phosphorus release can be studied.

Under anerobic conditions, phosphorus release has usually been measured as the rate of accumulation of inorganic phosphorus in the hypolimnion where it is trapped. Phosphorus release from shallow sediments cannot be measured by this method due to the larger volume of water in the trophogenic zone (dilution) and the rapid uptake of inorganic phosphorus by plankton in phosphorus limited lakes. Phosphorus release from aerobic sediments has usually been estimated from phosphorus budgets or core incubations. Phosphorus release calculated as the surplus of lake phosphorous budgets have been criticized because they include errors compounded from the measurement of other components of the phosphorus budget (Shaw and Prepas 1989). Phosphorus release rates from core incubations fail to account for important factor such as bioturbation, mixing and ground water flow (Holdren and Armstrong 1980). Although in situ measurements of sediment phosphorus release rates based on pore water gradients are considered preferable to the above methods, this method may slightly underestimate release since gradients are usually based on the upper 10 cm but gradients are often steeper in the upper 3-4 cm (Shaw and Prepas 1989). Although these authors (op cit.) suggest that pore water gradients do not reflect bioturbation and mixing, Starkel (1985) has used pore water gradients to estimate bioturbation since the pore water gradient is a composite of different processes including diffusion and bioturbation. By estimating the flux based on diffusion alone the effects of bioturbation can also be assessed.

The potentially most serious shortcoming of pore water gradients occurs as a result of changes in pore water chemistry occurring at the oxidized boundary layer in sediments. It is generally assumed that the decline in the sediment pore water phosphorus profile reflects a diffusion gradient. Carignan and Flett (1981) have shown that a similar profile can, at least in part, be produced by co-precipitation of iron with phosphorus and the formation of Fe-PO_4 complexes. Chemical gradients produced by PO_4 loss through complexing are indistinguishable from diffusion gradients and can easily be mistaken for the latter. Measurements of total sediment and pore water phosphorus and iron concentration profiles are necessary to make the required distinction between gradient types.

Most sediment phosphorus flux rates have been based on single sampling or multiple sampling over short time periods and do not account for seasonal variability in diffusive flux. Very few studies have also addressed spatial variability in relation to release rates which would be required to calculate accurate sediment release budgets. The effects of acidification may affect phosphorus mineralization in both the water column and sediments. In order to assess the net effect of acidification on phosphorus supply, it is necessary to quantify flux from both sources and monitor changes in relation to acidity.

1.6. Sediment Geochronology.

Acid deposition and its ecological effects are a major environmental concern in the Atlantic region due to the sensitivity of large areas which include many lakes. However, the paucity of reliable historical data makes the interpretation of the effects of disturbances, such as the increase in acid deposition, difficult. Lake sediments accumulate and integrate material providing records related to changes in lake conditions, watershed activities and atmospheric inputs which have been used to reconstruct past environmental conditions (Kemp and Thomas 1976; Nriagu _et_ _al_. 1982; Ogden _et_ _al_. 1988). Paleolimnology has received considerable attention with respect to acidification in an effort to infer historical changes in lakes through detailed examination of the chemical and biological characteristics of lake sediments (Smol _et_ _al_. 1984a,b; Charles _et_ _al_. 1987).

Sediments in oligotrophic lakes are laid down and accumulate slowly over a period of years. The sediment deposited consists of allocthonous material as well as autochthonous debris settling from the water column. Most the sediment sampling takes place at the deepest point in a lake. Sediments at this location also consist of material resuspended from shallower zones subjected to turbulence. Sediment focusing, a physical process by which sediments always tends to move downslope to deeper areas, also tends to cause greater accumulation rates at the deep station. Resuspension, sediment focusing and the activity of macrobenthos are all processes which tend to homogenise sediments and obscure short term changes (seasonal or annual) and smooth chemical profiles. In undisturbed, oligotrophic lakes with sediment accumulation rates comparable to those in the Atlantic region, the sediment record usually reflects an integration of the last 10 years of deposition. In lakes which are very deep or strongly stratified, very little mixing occurs and sediments can exhibit detailed deposition patterns easily observed by the presence of sharp, thin laminations on sections obtained by freeze cores (Smol pers. comm). In shallow lakes, sediment vertical profiles may not provide much useful information, particularly over short time scales (years to decades) because of continual and deep mixing from wind driven turbulence. It is clearly evident that familiarity with lake morphometry and climatology is a crucial aspect of core analysis.

Upon deposition, sedimented material can undergo a variety of changes from various physical and chemical processes. These changes are collectively referred to as post-deposition sediment diagenesis (Berner 1980). The breakdown and mineralization of organic material by bacteria or larger invertebrates generally occurs at or near the sediment surface. Movements of large invertebrates, especially burrowing species, homogenize the upper few centimetres of sediment and enhance the diffusion of oxygen into deeper layers. Oxygen does not usually penetrate more than 1 or 2 cm because diffusion is slow and O_2 rapidly consumed by chemical and microbial oxidation processes. Below the oxidized layer anerobic bacteria dominate and a strong reducing environment exists (Berner 1980). Within the layer between 2 and 10 cm, much of the diagenesis is governed by chemical processes.

Many chemical species are present in their reduced forms. Electrochemical imbalances and diffusion cause some species to migrate within this layer while others show little movement (ie. titanium). Thus, paleolimnological interpretations are not suited to chemical species which show a highly mobile or reactive and may precipitate at different layers (such as iron). Below about 10 cm, sediments tend to remain in a relatively steady state since physical processes are at a minimum and chemical equilibria have been attained (Norton 1984b). A great deal of care must be taken in interpreting vertical profiles of chemicals in sediments.

1.7. Acid Deposition in the Atlantic region.

The long range transport of air pollutants (LRTAP) program of the Canadian Wildlife Service (CWS) has demonstrated that surface water acidification has occurred in sensitive areas of the Atlantic region at current acid deposition levels of wet excess sulphate of 15-20 $kg \cdot ha^{-1} \cdot yr^{-1}$ (Kerekes et al. 1986 a,b). Acidification of surface waters in Nova Scotia has also been indicated by comparisons of current levels of surface water acidity historical measurements in several lakes. Watt et al. (1979) attempted to assess changes in the pH and water chemistry of 23 lakes located near Halifax which were previously measured 21 years earlier by Gorham (1957). Using techniques similar to those used by Gorham (1957), Watt et al. (1979) found that pH in 16 lakes had declined significantly ($p < 0.001$; ANOVA) and that this decline was due to acid deposition and not other causes although they did note that local acid emissions could have been the source of the pollutants. However, comparisons with data from other, more rural lakes in the Atlantic region measured previously by Hayes and Anthony (1958), tend to support the concept of lake acidification by the long range transport of air pollutants (LRTAP). Thompson et al. (1980) compared current trends in the pH of 3 Nova Scotia rivers with data collected by Thomas (1960) collected in 1955. Results indicated that pH declined in all 3 rivers (5.2 to 4.4 in the Tusket; 5.7 to 4.9 in the Medway and 6.2 to 5.5 in the St. Mary's Rivers). None of these rivers is close to large anthropogenic sources of sulphate of nitrate emissions. Howell et al. (1988) reviewed data from twenty-eight rivers in Atlantic Canada which were sampled monthly since as far back as 1965 providing records up to 21 year. Statistical analyses, consisting two way ANOVA of annual median pH values weighed according to the number of observations, indicated that rivers in areas of Nova Scotia and Newfoundland which were geologically sensitive to acidification had pH values which were significantly lower in the late 1960's and early 1970's. Annual hydrogen ions exports were also greater during this period which corresponded with a peak period in sulphur dioxide emissions in North America. Clair and Whitfield (1983) also found similar trend in the acidity of rivers in the Atlantic region accompanied by changes in decreased calcium and increased sulphate. Unfortunately, water chemistry records generally do not go back to pre-industrial periods and pH depressions due to anthropogenic activity are difficult to estimate. However, surface water acidification and increased sulphate concentrations have been found to reflect anthropogenic emissions. Underwood et al. (1987) compared sulphate deposition gradients and lake water chemistry in Nova Scotia. Water chemistry of lakes, particularly excess sulphate in the province was closely correlated with deposition gradients in both urban and rural areas.

The effects of acidification in the Atlantic region were first brought to the attention of the public through declines in Atlantic salmon (Salmo salar) populations. Although much of the decline in salmon catch and abundance has been brought about by land use activities (logging and log running), hydro developments and overharvesting, there have been recruitment failures correlated with acidification and problems associated with ion regulation (LaCroix 1988). Reproductive problems in Atlantic salmon have also been found in acidic Nova Scotia streams. Abnormally low sex hormone metabolism, lower weight gain, lower fecundity and higher egg mortality have been measured for salmon in an acidic stream (pH 4.7-5.3) compared to a less acidic stream (5.4-6.2; Freeman and Sangalang 1986). Metal toxicity appears to be less of a problem in this region due to the coloured nature of most waters although structural alterations in fish gills including epithelial edema, exfoliation and increased gill debris have been found in lakes with low pH (4.6-5.2; Garside and Daye 1983). Kerekes (1982) sampled 29 lakes in Kejimkujik National Park for fish species composition and found that below pH 5.5, species richness declined to only two species compared to 5-12 species found in higher pH lakes.

1.8. Objectives.

The effects of acidification on phosphorus cycling in sediments and the water column of acidic lakes is not well understood. However, any reduction in the decomposition rate in sediment could potentially impede the rate of mineralization of organically bound phosphorus, inorganic phosphorus flux and the availability of PO_4 to primary producers. These indirect effects of acidification have been suggested as a potential cause of long-term declines of total phosphorus concentration in lake water and the oligotrophication of lakes subjected to high levels of acidic deposition (Grahn et al. 1974). Given the importance of inorganic phosphorus in regulating primary productivity, any perturbation which impedes phosphorus mineralization or availability could reduce productivity of all trophic levels in lakes. Several studies have clearly demonstrated that lakes can maintain a high level of productivity under extremely acidic conditions if nutrient supply is maintained Scheider et al. 1975a,b; Dillon et al. 1977, 1979, 1980; Kerekes et al. 1984; Davison et al. 1989).

This study examines a variety of physical and chemical characteristics of lake waters and sediments of clearwater and coloured lakes to test the null hypothesis that:

" Acidity does not affect phosphorus
mineralization or availability in lakes".

The null hypothesis was examined by finding answers to three basic questions:

(1) does the sediment chemical record provide any evidence of increased lake acidity or decreased phosphorus availability?

(2) is inorganic phosphorus flux from lake sediments important in shallow oligotrophic lake sand is acidity a dominant factor in determining sediment phosphorus flux?

(3) does acidity affect dissolved organic phosphorus (DOP) mineralization or inorganic phosphorus availability and do organisms have any ability to compensate for any detrimental effects?

Many studies concerning the biological effects of acid deposition and increasing lake water acidity have focused on cause-effect relationships or dose response. Few studies have attempted to examine compensation capacity or the ability of biota to responde by altering activities or behaviour to reduce the impact of changes related to increased lake water acidification. This study also examines a potential method by which planktonic (algae and bacteria) may be able to compensate for modest reductions in phosphorus supply.

2. MATERIALS AND METHODS

2.1. The Study Areas

Of 25 lakes sampled, 10 were located in New Brunswick and 15 in Nova Scotia (Table 1, Figure 1). Lakes located in Kejimkujik National Park, N.S., have been described in detail by Kerekes and Schwinghamer (1973), Cape Breton Island lakes by Kerekes et al. (1978), Halifax County lakes (Drain and Little Springfield) by Kerekes et al. (1984) and Laytons Lake by Howell and Kerekes (1982). Lakes located in Fundy National Park, New Brunswick (Bennett and Wolfe Lakes and McLaren Pond), are described by Kerekes et al. (1975). The other lakes have not been studied previously. Most of the waterbodies sampled are small headwater lakes, but a few are of a higher order.

Additional information describing selected physical and chemical characteristics of the 25 study lakes taken from the above reports is presented in Tables 2 and 3. A complete set of physical data is not available for many of the lakes. Chemical measurements presented in Table 3 are summaries of variable data sets consisting, in some cases results of only two samples (i.e. Charlotte County N.B. lakes) or several years of regular (monthly) sampling as in the case of the Beaverskin, Kejimkujik and Pebbleloggitch Lakes. Readers are advised to consult the original sources for further information concerning the nature of the data sets used to calculate the averages presented in Table 3.

Figure 1: Locations of study lakes (Lake numbers and corresponding names are given in Table 1).

FIGURE 1

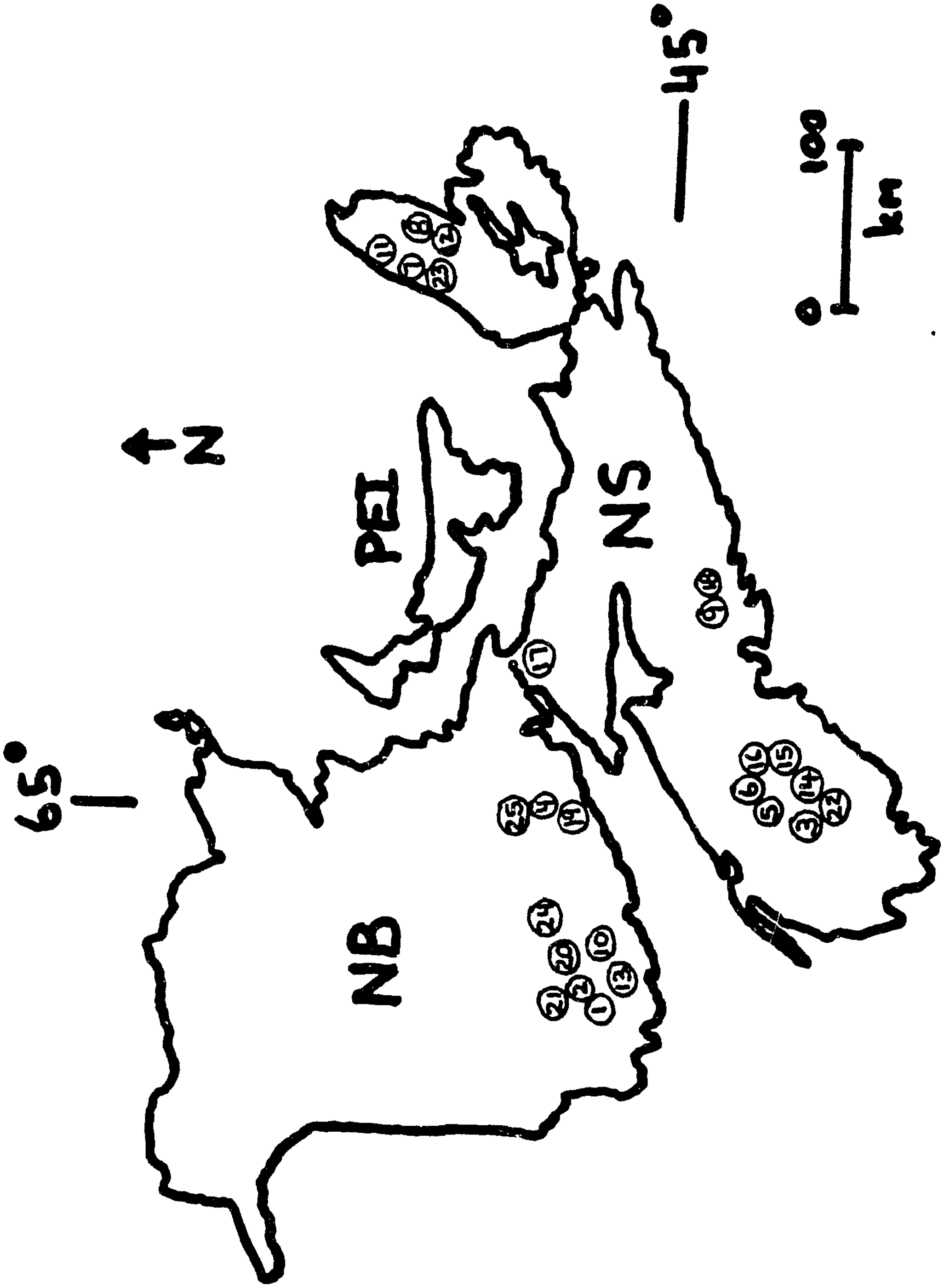
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Table 1. Location and coordinates of 25 study lakes (Lake numbers are shown in Figure 1).

No.	Site	Latitude			Longitude			County
		o	'	"	o	'	"	
1	Adelaide Lake	45	19	00	66	38	50	Charlotte N.B.
2	Anthony Lake	45	16	10	66	43	60	Charlotte N.B.
3	Beaverskin Lake	44	18	30	65	20	00	Queens N.S.
4	Bennet Lake	45	38	12	65	05	51	Albert N.B.
5	Big Dam East	44	27	00	65	16	00	Digby N.S.
6	Big Dam West	44	28	00	65	17	30	Digby N.S.
7	Bog Exhibit	46	44	22	60	49	48	Inverness N.S.
8	Canns Lake	46	40	20	60	26	00	Victoria N.S.
9	Drain Lake	44	47	50	65	45	20	Halifax N.S.
10	East Twin Lake	45	18	40	66	36	50	Charlotte N.B.
11	French Lake	46	43	41	60	51	56	Inverness N.S.
12	Freshwater Lake	46	38	40	60	23	47	Victoria N.S.
13	Jake Lee Pond	45	14	60	66	38	80	Charlotte N.B.
14	Jordan Lake 1[a]	44	71	22	65	13	23	Queens N.S.
15	Jordan Lake 2	44	73	20	65	14	21	Queens N.S.
16	Kejimkujik Lake	44	22	30	65	14	00	Queens N.S.
17	Laytons Lake	45	47	40	64	15	20	Cumberland N.S.
18	L. Springfield	44	48	00	63	44	50	Halifax N.S.
19	McLaren Pond	45	36	45	64	57	57	Albert N.B.
20	Mud Lake	45	21	00	66	36	50	Charlotte N.B.
21	Newton Lake	45	16	10	66	43	00	Charlotte N.B.
22	Pebbleloggitch L	44	18	00	65	21	00	Digby N.S.
23	Presquile Lake	46	41	25	60	57	25	Inverness N.S.
24	West Twin Lake	45	18	30	66	37	00	Charlotte N.B.
25	Wolfe Lake	45	39	45	65	08	57	Albert N.B.

[a] Jordan 1 is artificially fertilized (see TP in Table 3). Jordan 2 is untreated as a control to Jordan 1.

Table 2. Selected physical characteristics of the 25 study lakes.

Lake	Drainage Area (km^2)	Surface Area (ha)	Flushing Rate (yr^{-1})	Mean Depth (m)	Maximum Depth (m)
Adelaide	-	70	-	-	-
Anthony	-	29	-	-	-
Beaverskin	1	40	1.0	2.2	6.3
Bennet	12	31	22	2.3	11.1
Big Dam East	2	46	1.6	2.3	4.2
Big Dam West	40	105	13.1	2.5	9.5
Bog Exhibit	0.1	2	-	-	-
Canns	0.8	10	6.3	2.0	9.2
Drain	16.	1	-	-	3.0
East Twin	-	-	-	-	-
French	-	-	-	-	-
Freshwater	3.4	42	2.0	6.5	16.
Jake Lee	-	-	-	-	-
Jordan 1	-	5	-	-	-
Jordan 2	-	5	-	-	-
Kejimkujik	682	2435	5.5	4.4	19.
Layton's	0.6	11	3.9	1.8	8.0
L. Springfield	13.	4	-	-	7.2
Mclaren Pond	0.2	1	6.9	5.5	12.5
Mud	-	12	-	-	-
Newton	-	10	-	-	-
Pebbleloggitch	1.6	33	2.9	1.4	2.5
Presquile	0.0	4	14.7	2.1	3.0
West Twin	-	-	-	-	-
Wolfe	1.3	22	1.9	3.8	9.1

Table 3. Selected chemical characteristics of the study lakes in order of increasing pH.

Lake	pH	Colour H.u	Conductance $umho \cdot cm^{-1}$	TP $ugP \cdot l^{-1}$
L. Spring	3.6	5	370	9.0
Drain	4.0	10	260	27.0
Bog Exhibit	4.4	160	29	9.2
Pebbleloggitch	4.5	80	41	10.5
Kejimkujik	4.8	55	34	9.1
East Twin	4.9	45	17	-
Jake Lee	5.1	50	21	-
Mud	5.2	10	20	5.0
Beaverskin	5.3	5	32	5.0
Big Dam West	5.4	80	29	10.9
West Twin	5.4	50	20	-
Jordan L. 1	5.5	45	30	170.
French	5.8	30	38	11.9
Newton	5.9	20	28	5.0
Adelaide	6.0	5	20	3.1
Anthony	6.0	5	24	3.6
Big Dam East	6.1	10	27	5.0
Cann's	6.1	5	34	6.8
Wolfe	6.5	3	25	12.5
Bennet	6.6	15	34	6.4
Jordan L. 2	6.6	60	45	9.
Mclaren Pond	7.0	25	140	21.5
Freshwater	7.2	0	350	6.4
Layton's	7.3	15	534	44.
Presquile	7.3	5	271	17.6

A summary of the sampling program carried out in each of the study lakes is presented in Table 4.

2.2. Water Chemistry

Water samples were collected from just below the lake surface at a site located directly over the deepest point in the lake. Samples for analysis of pH, conductance and water colour were collected in clean Nalgene (PVC) bottles. Bottles were scrubbed with a nylon brush after use and rinsed three times in distilled, deionized water. These bottles were not acid washed to avoid carry over and interference with pH measurements. Bottles were kept tightly capped until use. Just prior to sample collection, bottles were opened, rinsed three time with lake water, filled such that air was excluded, capped and stored without treatment at 4.0 °C until analysis (usually within 3 days).

Specific conductance was measured in an aliquot of this sample at NTP using a Radiometer^{TM} Model CDM2c conductivity meter. Laboratory pH was measured in a fresh aliquot using a Radiometer ^{TM} PM29 pH meter equipped with a combination glass electrode. Lakewater and peeper porewater pH were measured in situ using a Fisher^{TM} Model 156 pH meter and 5 probe switch box equipped with 5 combination electrodes (150 mm long x 3mm wide).

Water colour was measured using another aliquot of the sample collected for pH and specific conductance, by visual

Table 4. Summary of analyses carried out at the following 25 study sites.

Lake	Sediment[a] Geochem.	Sediment[b] Porewater	Sediment Phosphorus Flux	Phosphatase[c] Bioassay
Adelaide		X	X	
Anthony		X	X	
Beaverskin	X	X	X	X
Bennet		X	X	
Big Dam East	X	X	X	X
Big Dam West	X	X	X	X
Bog Exhibit		X	X	
Canns		X	X	
Drain		X	X	
East Twin		X	X	
French		X	X	
Freshwater		X	X	
Jake Lee		X	X	
Jordan 1		X	X	
Jordan 2		X	X	
Kejimkujik		X	X	
Layton's		X	X	
L. Springfield	X	X	X	X
Mclaren Pond		X	X	
Mud		X	X	
Newton		X	X	X
Pebbleloggitch	X	X	X	X
Presquile		X	X	X
West Twin		X	X	
Wolfe		X	X	

[a] includes total elemental concentrations, porewater metals and Al flux calculations.
[b] includes porewater pH, conductivity, TDP and SRP concentrations.
[c] results of core experiments were not reported for Little Springfield Lake.

comparison with standards using a 100 mm Nessler tube and a Hellige^{TM} Aqua Tester. Measurement of water colour by visual comparison lacked precision (± 5 - 10 H.u.) since colour standards were only available in increments of 10 Hazen units (H.u.) between 0 and 80 H.u. and every 20 H.u. over the range of 80 to 100 H.u. Samples with water colour greater than 80 H.u. were diluted 50:50 until they could be read on the 0-80 H.u. scale. Water colour can be measured with greater precision by measuring the absorbtion of water samples spectrophotometrically at a standard 420 nm. The spectrophotometric method was not used because of concerns regarding its accuracy and comparability. Different organic compounds show peak absorbance at different wavelengths and the absorbtivity of samples vary according to the relative composition and absorbtion spectra of absorbing substances (primarily dissolved organic matter) in the samples. Measurement of absorbance at a single wavelength would vary considerably between samples with different dissolved organic matter (DOM) composition. The comparison of water colour against standard coloured disks provides an estimate of absorbance of white light (all wavelengths)removing the selective absorbtion bias of spectrophotometry although this method lacks precision. Colour was only used as an general descriptive approximation of DOC concentration. Where accurate and precise DOC measurements were required, it was measured directly. Another reason for using visually compared colour standards was data comparability. The colour disks are based on the platinum-cobalt (Pt-Co) scale which has been used extensively throughout the world for a long time. Measurements in Hazen units are synonymous with the Pt-Co scale and results expressed in these units are more easily compared to literature values.

Dissolved organic carbon (DOC) was measured from a sample collected as described above. Concentrations of DOC in water samples was measured using infrared analysis according to Environment Canada (1979). The sample was filtered through a 0.45 um filter and a small volume was injected into a combustion tube at 950 °C containing cobalt oxide on asbestos. The resulting CO_2 was measured by an irferred analyzer and compared to standard organic carbon solutions. The detection limit was 0.5 $mg \cdot l^{-1}$. Analysis of DOC was carried out by the Inland Waters Laboratory in Moncton, N.B.

Total (TP), total dissolved (TDP) and soluble reactive phosphorus (SRP) were collected as described above except in acid washed glass bottles. Samples were analyzed in duplicate using the molybdate blue method of Murphy and Riley (1962) modified according to Menzel and Corwin (1965). Samples for analysis of TDP and SRP concentrations were filtered through a 0.45 um glass fibre filter prior to analysis. Duplicate 25 ml sample volumes were placed in reacti^{TM} flasks with 0.1 g of potassium persulphate and digested at 550°C for 30 minutes to release organically bound phosphorus. Blanks and standards were prepared in-house were run with each batch of samples analyzed. Absorbance was measured at 885 nm on a LKB™ Ultraspec 4051 spectrophotometer. Detection limits for phosphorus analysis were 0.5 ugP$\cdot$l^{-1}. Analytical precision was monitored and tested by continuous comparisons to a library of blank and standard absorbances. Participation in inter-laboratory round-robin comparisons indicated a high level of accuracy and precision in the analytical techniques used.

Dissolved oxygen was measured in the laboratory using the Winkler method and azide modification (APHA 1975). Dissolved oxygen measurements were made in situ using a Winkler-calibrated dissolved oxygen meter (YSI™ Model 54).

Water samples for metal analysis (Al and Fe) were collected in acid washed 250 ml plastic bottles (Nalgene PVC). Bottles were rinsed with sample three times prior to collection and acidified with 2 drops of 2N nitric acid immediately after collection. Samples were collected at the same location and depth as those described above. Samples were refrigerated at 4°C until analysis. Analyses were carried out by the Inland Waters laboratory of the Water Quality Branch of Environment Canada in Moncton, N.B. Aluminum concentrations in lake water, experimental cores and sediment porewaters were measured spectrophotometrically following a solvent extraction (NAQUDAT 1983) and summarized as follows. Samples were acidified with dilute mineral acid, shaken and left for a minimum of 15 hours. An 8-hydroxyquinoline solution and a buffer (pH = 8) solution were added to the sample solution and the pH was adjusted to 7.5 - 8.5. The solution was extracted twice with $CHCl_3$. The extracts were combined and aspirated. The absorbance of the combined extracts were measured spectrophotometrically at 309 mu and compared to those of identically prepared standard Al solutions. A N_2O-C_2H_2 reducing flame was used. The detection limit was 0.05 $mg \cdot l^{-1}$ (Environment Canada 1979 . Results of aluminum analyses are always expressed as extractable aluminum unless otherwise noted.

Iron was also measured by atomic absorbtion using direct aspiration. Sample collection was described above. Prior to analysis this sample was also acidified with dilute mineral acid, shaken and left for a minimum of 15 hours. The sample was then aspirated. The absorbance was measured at 248.3 mu and compared to those of identically prepared standard Fe^{3+} ion solutions. An acetylene-air oxidizing flame was used. The detection limit was 0.05 $mg \cdot l^{-1}$. Results are expressed as extractable Fe unless otherwise noted.

Manganese samples were collected as described above. Samples were acidified with dilute mineral acid, shaken, left overnight then analyzed by direct aspiration. The absorbance was measured spectrophotometrically at 279.8 mu and compared to those of standard Mn^{+2} (manganous) ion solutions. An acetylene-air oxidizing flame was used. This method had a detection limit of 0.01 $mg \cdot l^{-1}$. Results are expressed as extractable manganese unless otherwise noted.

Dissolved calcium was measured by automated atomic absorbtion. Samples were collected in clean, non-acid washed 1l Nalgene (PVC) bottles rinsed with distilled, deionized water and lake water three times prior to sample collection. Samples were stored untreated at 4 °C until analysis. The sample was passed through a 0.45 um membrane filter. A $CaCO_3$ solution was added to a filtrate aliquot which was then aspirated. The absorbance of the aliquot was measured spectrophotometrically at 422.7 mu and compared with those of standard Ca solutions and reagent blanks. The detection limit was 0.01 $mg \cdot l^{-1}$. An autoanalysis unit consisting of an automated sampler, manifold and proportioning pump was used. A secondary sample line and a transmission delay line were incorporated so that the sample was diluted where necessary. Precision and accuracy of the latter 4 constituents were assessed on a regular basis by comparison with standards prepared in-house and periodic blind duplication of samples. Regular monthly inter-laboratory comparisons using a combination of prepared and National Bureau of Standards (NBS) standards indicated that this laboratory maintains a high level of precision and accuracy in its analyses. Accuracy of the analyses was also assessed by comparison of results to historical data for the individual study sites. Results greater than two standard deviations from the mean were questioned and rejected if cause could be traced to collection, handling or analytical problems.

2.3. Sediment Geochemistry

Sediment cores were collected by SCUBA divers at the deepest point in Beaverskin, Big Dam East, Big Dam West, Kejimkujik, Pebbleloggitch, and Little Springfield Lakes. Extreme care was taken to avoid disturbance of the sediment column. Compression of sediment within the cores was minimized by inserting the core tube slowly by hand only until the sediment surface within the core indicated a tendency to sink below the level outside the core. There was no visible evidence of disturbance of the fragile surface layer in any of the cores accepted for analysis. Sediment collected in the cores ranged from 16 to 26 cm in total length. Core sections were by extruded with a piston inserted from the bottom of the tube. Cores were sectioned at 1 cm intervals for the first 5 cm of the core and at 2-3 cm intervals for the remainder using plastic cutters and placed in a plastic Whirl-Pak™ bag. The outer edge (0.5 cm) of each section was carefully removed and discarded to minimize contamination from carryover caused by friction along the core tube walls. Sediment samples were frozen until analysis.

Duplicate or triplicate cores were taken adjacent to each other at the deep station in Beaverskin, Little Springfield and Pebbleloggitch Lakes to assess within site variability and analytical consistency.

2.3.1. Water, organic and mineral content. The water content in sediments was determined by drying 50 g wet sediment at 100°C for 24 hours to a stable weight. Organic concentration was determined by weight loss of the same dried sample after ignition at 500°C for 6 hours. Water concentration was expressed in percent of wet weight while organic and mineral concentration were expressed as a percent of the dry weight.

2.3.2. Oxidation-reduction potential. Redox potential was measured inside core tubes immediately following collection by inserting a platinum tipped microprobe into the centre of the sediment at 1 cm intervals through access holes drilled in the sides of the core tubes. Cores were maintained in a glove bag under a nitrogen atmosphere while electrode potentials were being measured. Redox is expressed as electrical potential in millivolts (mV).

2.3.3. Sediment Geochemistry. Total chemical concentrations in sediment were determined by OceanChem Ltd. from core sections collected according to methods described above. Thawed wet sediment sections were passed through a 120 mesh stainless steel screen to remove particles larger than 125 nm. Sediments were oven dried for 12 hr at 100 °C, lightly ground and blended in a mixer. Dry sediment samples (0.5 g) were weighed out then placed in PTFE™ (teflon) pressure decomposition vessels. Nitric, hydrofluoric and perchloric acids (3:3:1) were added to a total volume of 7 ml and the vessels were sealed. Sample digestion was carried out at

100°C in a boiling water bath for three hours. The cooled solutions were transferred to Teflon beakers and evaporated to dryness on a low temperature hot-plate. The residue was redissolved in 1N hydrochloric acid and diluted to 50 ml. Any remaining undissolved residue was removed etiher by settling overnight or by centrifugation.

Lead was determined using flame atomic absorption spectrophotometry at 283.3 nm with a detection limit of 1 mg kg^{-1} dwt. The remaining elements (Al, Ba, Be, Cd, Ca, Cr, Co, Cu, Fe, Mn, Ni, P, Sr, Sn, Ti, V, Zn) were analyzed by inductively coupled plasma emission spectroscopy (ICP) according to methods described by McLaren et al. (1981). Arsenic and molybdenum were also measured but are not presented due to inadequate sensitivity. Silicon and boron, also measured, are volatilized by the digestion procedure and are not presented. However, silicon was estimated by another procedure described below. Detection limits (ug g_{-1}) for individual constituents are as follows: Al (0.1), Ba (0.2), Be (0.05), Cd (0.2), Ca (0.2), Cr (0.5), Co (0.5), Cu (0.1), Fe (0.2), Mn (0.05), Ni (0.6), P (0.2), Sr (0.5), Sn (0.5), Ti (0.1), V (0.3), Zn (0.1). Results are expressed in $mg \cdot kg^{-1}$ dwt (ppm,. Samples were co-analyzed with National Research Council (NRC) standard reference materials consisting of Merimichi estuary (MESS1) and Baie du Chaleur (BCSS1) sediment samples with certified values for all constituents measured. Analytical precision and accuracy was also assessed using blanks and standards prepared in-house as well as submission of blind replicates.

Concentrations of major constituents (Al, Ti, Ba, Fe, Mn, Ca, Mg, and P) were also expressed in percent of ignited weight (pph) to examine the effect of differences in organic content. Selected metals (Cu, Pb, V, Zn, Ni) were expressed in ppm ignited weight for reasons concerning significant figures. SiO_2 concentration was calculated as the difference of the cumulative percent of all major constituents from 100% and expressed as percent of the ignited (ash) weight.

Sediment compaction due to coring was corrected for using the following relationship:

$$\% \text{ compaction} = 1 - \frac{(\% \text{ water at depth } z_i - z_{i+1})}{(\% \text{ water at depth } z_{(4-5)})} * 100$$

where z_i = depth in cm.

Sediment accumulation rates were approximated using the beginning of the increase in the slope on the Pb profile as a marker corresponding with the increased use of leaded automobile fuels around 1940 (Ouellet and Jones 1983). Depth of the overlying sediment (corrected for sediment compaction) divided by 50 years, was used to estimate the average annual sediment accumulation rates for each lake. Sediment accumulation rates are expressed in $cm \cdot yr^{-1}$.

2.4. Sediment Porewater.

2.4.1. Porewater samplers. Sediment porewater samples were obtained *in situ* by dialysis using porewater samplers (peepers) to determine compositional changes in porewater pH, specific conductance, total dissolved phosphorus (TDP), soluble reactive phosphorus (SRP), and dissolved Al, Fe, Mn and Ca with increasing sediment depth.

Peepers were constructed of clear plexiglass and consisted of two 17.5 x 80 cm sheets, one 0.3 cm thick and the other 1.3 cm thick (Hesselin 1976; Carignan 1984). The two pieces were held together by stainless steel machine screws. Seventy paired compartments 7 cm long, 0.6 cm wide and 1.0 cm deep were inscribed at 1 cm intervals over the length of the sampler. Each cell held approximately 4 ml. The sampler was prepared for use by immersing the compartmented section in a bath of distilled, deionized (Super-Q™) water previously deoxygenated by vigorous bubbling for at least two hours with ultrapure N_2. A sheet of polysulphone dialysis membrane (Gelman Tuffryn HT-450™, pore size = 0.45u) was placed over the compartments and held in place by the thin plexiglas sheet and machine screws. The peeper was held in the bath and continually bubbled with ultrapure N_2 until placement into the lake sediment. Peepers were placed vertically into the sediment by SCUBA divers, leaving a minimum of the upper 10 cm exposed above the sediment-water interface. Exposure times varied from 15 to 83 days (depending on sampling schedules, travel to retrieve peepers) which allowed diffusive equilibration between the chemical constituents in porewaters and the water contained in the peeper cells.

After use peepers were disassembled, scrubbed mechanically and placed in a dilute acid bath (4% HCl) for a minimum of 7 days. Before reuse peepers were scrubbed, rinsed a least three times in distilled water and allowed to air dry.

Peeper samples were analyzed according to the methods outlined in the above section on water chemistry.

2.4.2. Methodology Controls. Field trials were performed to verify the suitability of peeper exposure time for equilibration of pH, conductivity and phosphorus fractions between sediment porewater and peeper cells. Several replicates were measured in selected lakes to confirm the site-specific representativeness of single peeper samples.

The effect of exposure to aerobic conditions on pH after peeper retrieval was also tested. To do this pH was analyzed immediately upon retrieval, again after 15 min, 30 min and 2 days. Sediments heterogeneity was tested by the placement of duplicate pairs of peepers in three locations according to water depth (3.0, 5.0 and 7.0 m) in Beaverskin Lake. Peepers were placed and retrieved at all locations simultaneously and analyzed for pH, conductance and phosphorus fractions. Except for this test, within lake variability was not addressed in this study. All sampling, unless otherwise indicated, was confined to the deepest point of each lake.

Sample containers and peepers were tested periodically for contamination using peepers filled with double distilled, deionized water. Peepers were set up for normal use except that they remained in the laboratory for two weeks. Samples were then collected and analyzed for contaminants resulting from procedure.

2.5. Sediment Phosphorus Flux

Porewater samplers (peepers) were used to estimate phosphorus flux rates based on sediment porewater gradients. Phosphorus flux rates (J_s) were calculated according to Ficks first law of diffusive transport in the sedimentary environment and were based, in part, on SRP porewater gradients in the upper 10 cm of sediment as well as physical properties of the sediments according to Berner (1980) where:

$$J_s = - o \, \frac{D}{O^2} \cdot \frac{dC}{dx} \Big|_{x=0} \quad A$$

where o = sediment porosity.

D = diffusion coefficient of PO^4 in freshwater solution.

O = tortuosity term that depends on size, shape and packing of sediment particles (see Quigley and Robbins 1986).

dC/dx = SRP[a] gradient based on 5-6 points in the upper 10 cm of sediment.

A = proportionality constant used to convert flux units to mg PO_4-P$\cdot m^{-2} \cdot d^{-1}$.

[a] For the purposes of this study, inorganic phosphorus is operationally defined as soluble reactive phosphorus (SRP) using the molybdate blue method. Inorganic phosphorus, orthophosphate, PO_{4-} and SRP are used synonymously.

2.6. Phosphorus Loading

Annual total phosphorus load, L(P), was estimated from mean annual inflow phosphorus concentration based on water residence time, hydraulic load and lake water concentration according to formulae given by Kerekes (1983) where:

$$[P]_i = [P]_r \cdot (1 + \sqrt{T_w})$$

and

$$L(P) = [P]_i \cdot q_a$$

where: $[P]_i$ = average inflow total phosphorus concentration ($mgP \cdot m^{-3}$).
$[P]_r$ = average annual concentration of total phosphorus in the lake ($mgP \cdot m^{-3}$).
$T(_w)$ = water residence time in years.
q_a = hydraulic load ($m \cdot yr^{-1}$).
L(P) = loading of total phosphorus per unit lake surface area ($mgP \cdot m^{-2} \cdot yr^{-1}$).

The ratio of sediment phosphorus load to the total annual load provided an index of the relative contribution of sediment derived phosphorus to total annual lake phosphorus load in various lake types. This model assumes that lakes are well mixed during the ice free season. Three lakes violate this assumption (Bennett, Freshwater and McLaren Pond) and results from these lakes should viewed within this limitation.

2.7. Phosphatase Bioassay.

2.7.1. Phosphatase Bioassay. Water samples used for determination of phosphatase activity were collected from just below the water surface of each lake at the deep station. Extracts for the determination of sediment phosphatase activity were prepared by shaking 50 g fresh weight of surface sediment (sectioned from undisturbed cores) in 125 ml of 3 M urea for 30 min, followed by centrifugation to clear the extract (Freedman 1978).

Phosphatase activity was analyzed spectrophotometrically using *p*-nitrophenyl phosphate (pNPP) as a model substrate (Tabatabai and Bremner 1969). Phosphatase activity was determined by adding 1-2 ml of unfiltered lake water (or sediment extract) to 2.0 ml of 0.3 M potassium acetate in duplicate 6 ml test tubes. Duplicate test tubes were incubated at 25°C for 90 min in the presence of 0.5 ml of 54 mmolar pNPP. The activity was stopped and pNP colour was developed by adding 0.4 ml of 2 N NaOH, and reading the absorbance at 410 nm. Initial sample absorbance (mostly due to water colour) was subtracted from final absorbance. Reagent blanks were also subtracted from sample absorbance. The change in absorbance due to enzyme hydrolysis of pNPP to produce *p*-nitrophenol (pNP) was expressed in umoles pNP produced per litre per minute. The concentration of pNP was calculated from a regression equation derived from a standard curve (Appendix A).

In order to further calibrate the phosphatase method and verify that enzyme activity was being measured, tests were performed on water samples collected from Beaverskin Lake, a clear water lake and a coloured lake, Pebbleloggitch Lake (Appendix A). The effect of incubation time was tested by removing samples from the incubator at selected times from 0 to 150 min (Appendix A). Ninety minutes was found to be adequate to provide sufficient colour change at relatively low phosphatase activities. The effect of substrate concentration on phosphatase activity was tested by incubation of various amounts of sediment extract. Substrate concentration must saturate the enzyme to be a valid measure of maximum enzyme activity. The effect of the increased substrate availability (extract volume) on the rate of enzyme hydrolysis approached an asymptote at a substrate concentration of 0.5 $\text{mmole}\cdot\text{l}^{-1}$ in both lakes indicating enzyme saturation.

2.7.2. Enzyme Kinetics. Michaelis-Menten constants K_m and V_{max} were determined by the method of Woolf (see Christensen and Palmer 1974) where:

$$\frac{[S]}{v} = \frac{K_m}{V_{max}} + \frac{1}{V_{max}} \cdot [S]$$

where: K_m = the concentration of substrate corresponding to 1/2 of V_{max}.
V_{max} = the maximum substrate uptake velocity.

The regression of substrate concentration (S) divided by the initial rate of hydrolysis (v) versus substrate concentration generally had r^2 values > 0.98.

2.7.3. Enzyme-pH Relationships. Enzyme efficiency at selected pH levels was tested by incubating water samples from the five lakes at 0.5 pH unit increments between pH 3.0 and 7.0 using the methodology outlined above.

2.7.4. Enzyme Inhibition. The effects of Al and Fe on substrate hydrolysis were examined by raising the ambient Al or Fe concentrations in freshly collected lake water samples by 200 $ug \cdot l^{-1}$ using either $AlCl_3$ or $FeCl_3$. No effect occurred with Fe at this concentration so additional tests were prepared at concentrations ranging from 50 $ug \cdot l^{-1}$ to 2000 ug l^{-1} in increments of 50 $ug \cdot l^{-1}$.

2.7.5. Core Incubations. Twenty six cores consisting of 20 cm of surface sediment and 20 cm of overlying water were collected by SCUBA divers from the deepest point of Beaverskin, Big Dam East, Big Dam West, and Little Springfield Lakes. Phosphatase activity in the water and surface sediment of two cores was determined within 24 hrs. Three sets of six replicate cores had the pH of the overlying water adjusted daily to three of four pH values (6.0, 5.0, 4.0 or 3.0), depending on the ambient pH of the lake. The pH in the cores was initially adjusted by no more than 0.5 pH units in an attempt to minimize acid shock. A fourth set of 6 cores was left untreated as a control. Cores were checked daily and pH in the treated cores was adjusted by additions of either 0.1N NaOH or 0.1N H_2SO_4. Stagnation of the overlying water and sediment was prevented by constantly bubbling air into the surface water through a small-bore plastic tube. Oxygen concentration of the water was measured daily, and remained at or near saturation throughout the incubation period. Cores were maintained at room temperature under a diffuse natural light-dark regime for between 14 and 18 days, after which the phosphatase activity in water and surface sediment was determined.

Water samples from the core tubes were collected for the determination of water colour and determination of aluminum, iron, manganese, calcium, and soluble reactive phosphorus concentrations according to methods described above. The pH of surface sediment was measured when the cores were sectioned for phosphatase determination. Sediment pH was measured by direct insertion of the pH probe in a homogenized sub-sample of the uppermost 2 cm of sediment.

2.8. Data Analysis

Water chemistry data analysis (pH, Al, Fe, Mn, Ca and total phosphorus concentrations) was based on monthly means (May to November) for all years in which the lakes were sampled.

Nonparametric treatment of the core data was carried out because two important assumptions in analysis of variance (ANOVA) and multiple comparison testing were violated: i) small numbers of replicates per treatment (n=6) prevented testing for normality; and ii) Bartlett's test for homogeneity of variance indicated unequal group variances for some (although few) variables in some treatment groups. Since the data were ranked by acidity, the Kruskal-Wallis nonparametric ANOVA was more appropriate, as was the "Tukey-type" nonparametric multiple comparison test (Zar 1984). All testing was done *a posteriori*.

3. RESULTS

3.1. Water Chemistry

The 25 lakes sampled for sediment phosphorus flux covered a wide range in acidity (pH: 3.6-7.3), organic content (water colour: 0-160 H.u.), conductivity (specific conductance: 25-534 umho·cm^{-1}) and trophic status (total phosphorus: 5.4-44 ugP l^{-1}). A subset of 5 lakes (Beaverskin, Big Dam East, Big Dam West and Pebbleloggitch Lakes) selected for more detailed analyses also covered a relatively wide range in pH (3.6-6.1), water colour (5-80 H.u.) and conductivity (26-370 umho·cm^{-1}). These lakes were selected because of their contrasting differences in acidity, metal concentrations and organic influence. Analyses were restricted to oligotrophic lakes (TP = 5.4 - 10.9 ugP·l^{-1}) where phosphorus normally limits planktonic primary production. More detailed chemistry of the lakes may be found in the references cited in the section outlining the study areas.

For the sub-set of 5 lakes (Beaverskin, Big Dam East, Big Dam West, Little Springfield and Pebbleloggitch Lakes), monthly growing season (May-November) mean pH, DOC, Al, Fe, Mn, and Ca concentrations were compared against each other using Person correlation. The results are presented in a correlation matrix (Table 5). Mean monthly growing season pH was negatively correlated to all of the variables except DOC concentration. The relationship between pH and metals was found to be the strongest. The strong inverse relationship between pH and Al concentration is indicated by the regression line and 95% confidence limit boundaries for the regression line illustrated in Figur The Al concentrations for each lake generally formed disti non-overlapping groups for each lake. The only 2 lakes with comparable pH (Beaverskin and Big Dam West Lakes) show that there was substantially more Al in the latter, more coloured, lake. A similar comparison along the horizontal, indicated that over a 0.5 pH unit difference, the changes in Al concentrations were relatively small in the two coloured or two clear water lakes in Kejimkujik National Park. The most acidic lake (Little Springfield) had the greatest Al concentrations (~3 $mg \cdot l^{-1}$) which was 10 times the highest concentration measured in the other 4 lakes.

Iron concentrations among the 5 lakes showed a relationship with pH similar to that of Al (Figure 3). Comparison of Fe concentrations between Beaverskin and Big Dam East Lakes or Pebbleloggitch and Big Dam West Lakes show that Fe also did not have large changes in concentration with small changes in lake water pH. Aluminum and iron concentrations were strongly correlated with each other (Figure 4; Table 5).

Figure 2: Aluminum concentration (mg l^{-1}) versus pH in 5 lakes (each circle represents a monthly growing season mean (May - November), open circles indicate clear water lakes, dark circles represent coloured lakes; the regression line is presented as the straight line bounded by two lines showing the 95% confidence limits of the regression).

BL = Beaverskin Lake
BE = Big Dam East Lake
BW = Big Dam West Lake
LT = Little Springfield Lake
PL = Pebbleloggitch Lake

FIGURE 2

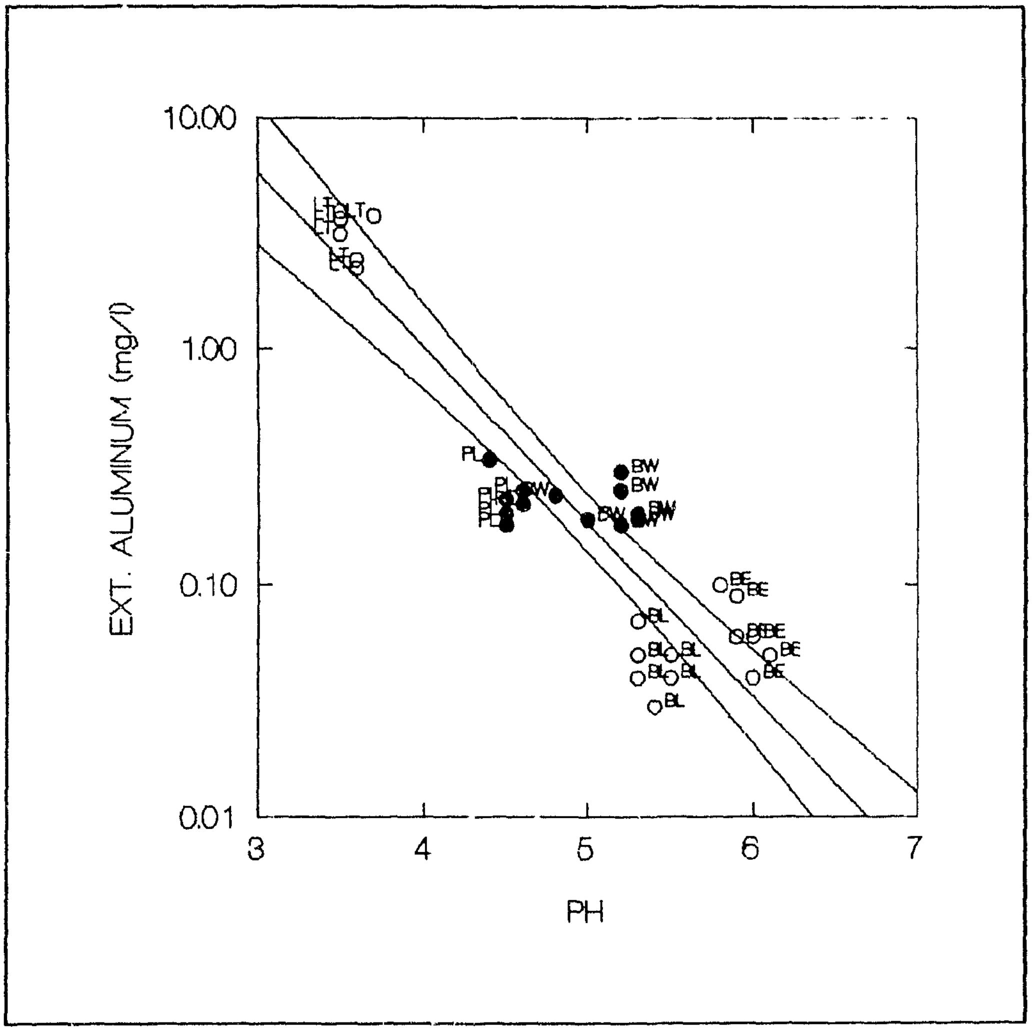


Figure 3: Iron concentration ($mg \cdot l^{-1}$) versus pH in 5 lakes (each circle represents a monthly growing season mean (May - November), open circles indicate clear water lakes, dark circles represent coloured lakes; the regression line is presented as the straight line bounded by two lines showing the 95% confidence limits of the regression).

BL = Beaverskin Lake
BE = Big Dam East Lake
BW = Big Dam West Lake
LT = Little Springfield Lake
PL = Pebbleloggitch Lake

FIGURE 3

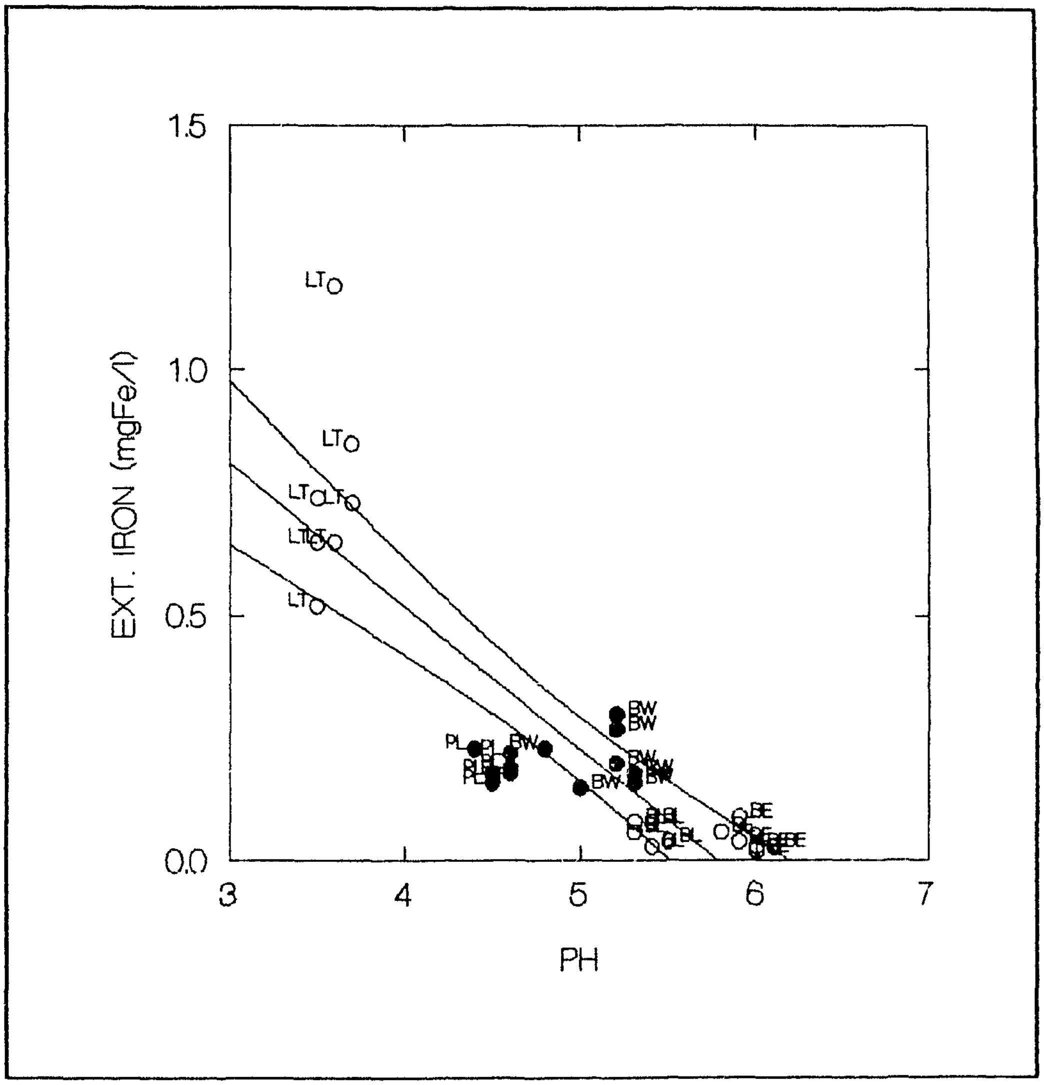


Figure 4: Aluminum versus iron concentration (mg·l^{-1}) in 5 lakes (each circle represents a monthly growing season mean (May - November), open circles indicate clear water lakes, dark circles represent coloured lakes; the regression line is presented as the straight line bounded by two lines showing the 95% confidence limits of the regression).

BL = Beaverskin Lake
BE = Big Dam East Lake
BW = Big Dam West Lake
LT = Little Springfield Lake
PL = Pebbleloggitch Lake

FIGURE 4

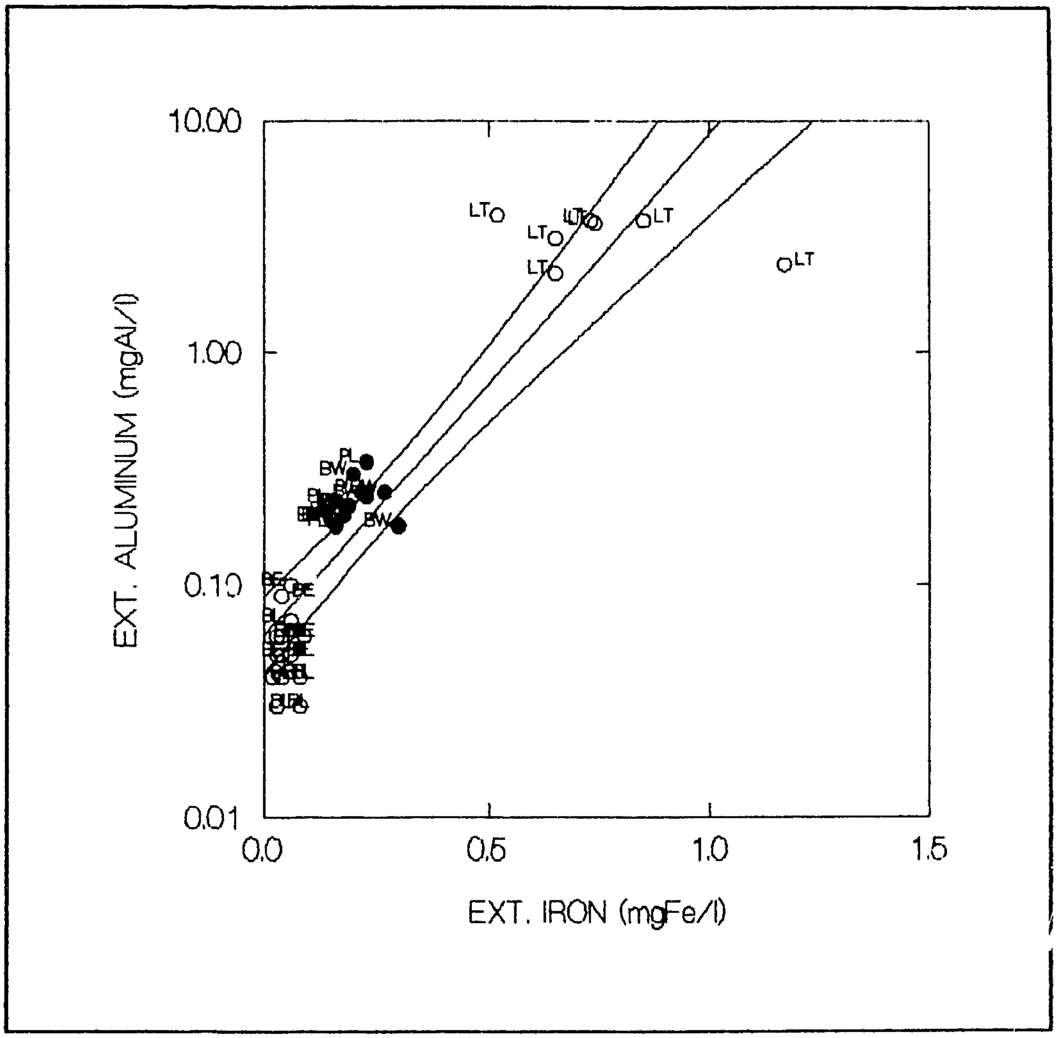

10.00
1.00
0.10
0.01
0.0
0.5
1.0
1.5
EXT. ALUMINUM (mgAl/l)
EXT. IRON (mgFe/l)
LT
BW
PL
BE

Table 5. Correlation matrix of season (month) and selected water chemistry variables in 5 lakes. Data are monthly growing season mean concentrations (May-November) for the various constituents in lake water (n=35; input data is presented in Appendix B).

	MONTH	PH	DOC	AL	FE
MONTH	1.000				
PH	-0.026	1.000			
DOC	0.164	0.051	1.000		
AL	0.013	-0.825**	-0.431*	1.000	
FE	-0.018	-0.852**	-0.242	0.875**	1.000
MN	0.004	-0.825**	-0.496*	0.978**	0.902**
CA	-0.008	-0.797**	-0.488*	0.973**	0.915**
TP	-0.049	-0.443*	0.442*	0.038	0.083

	MN	CA	TP
MN	1.000		
CA	0.993**	1.000	
TP	0.007	-0.035	1.000

* = $p < 0.05$
** = $p < 0.01$

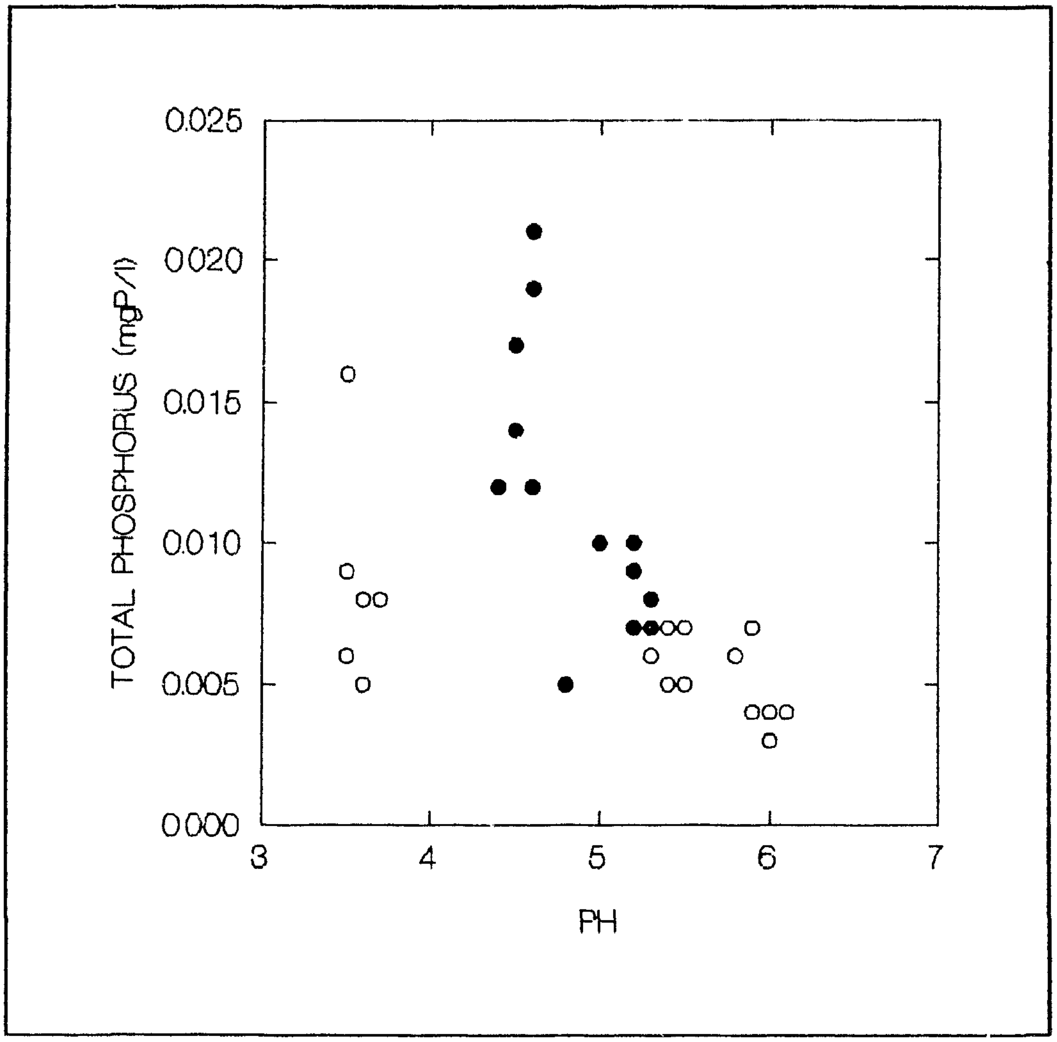
Total phosphorus concentration in lake water was also significantly but negatively correlated with pH. However, the relationship was weaker than was found for either Al and Fe versus pH (Table 5). The curvilinear nature of the TP versus pH relationship for the 4 Kejimkujik Lakes (Figure 5; Little Springfield Lake not included), reflected the effect of the association between TP and DOC (Figure 9). Increased TP with decreasing pH reflected organically bound phosphorus associated with the DOC. If only the 3 clear water lakes are considered (Beaverskin, Big Dam East and Little Springfield Lakes), the slope of a regression would still indicate an increase in TP concentration could be expected over a pH range of 6.1 to 3.8 in the absence of substantial differences in DOC concentration in the water. Increasing phosphorus concentrations with decreasing pH in the clear lakes suggests that some phosphorus may be mobilized by acidification. However, it is equally possible that this increase was not due to pH effects but related to differences in phosphorus loading between the lakes.

Dissolved organic carbon (DOC) concentration was significantly correlated with Al, Ca, Mn and TP ($p < 0.05$) but was not strongly correlated with pH or Fe (Table 5). Lake water DOC concentration and pH (Figure 6) showed a curvilinear relationship in the 4 Kejimkujik lakes where DOC concentration (organic acidity) increased with decreasing pH.

Figure 5: Total phosphorus concentration (ugP$\cdot$l^{-1}) versus pH in 5 lakes (each circle represents a monthly growing season mean (May - November), open circles indicate clear water lakes, dark circles represent coloured lakes.

BL = Beaverskin Lake
BE = Big Dam East Lake
BW = Big Dam West Lake
LT = Little Springfield Lake
PL = Pebbleloggitch Lake

FIGURE 5


0.025
0.020
0.015
0.010
0.005
0.000
TOTAL PHOSPHORUS (mgP/l)
3
4
5
6
7
PH

The range of acidity was also greater in the absence of large differences in DOC concentration as indicated by differences in pH between Beaverskin, Big Dam East and Little Springfield Lakes. The differences between the 5 lakes illustrated the influence of both mineral and organic acids.

Dissolved organic carbon (DOC) concentrations exhibited a distinct curvilinear relationship with Al and Fe in the Kejimkujik Lakes (Figures 7 and 8) but both metals had the greatest concentrations in the most acidic lake (Little Springfield Lake) which had consistently low DOC concentrations ($< 2.0 \text{ mg} \cdot \text{l}^{-1}$). DOC concentration was also significantly and positively correlated with total phosphorus concentration (Figure 9; Table 5).

Data structures and associations within the water chemistry data set for the 5 lakes were investigated using principal components analysis (PCA). Table 6 shows 3 principal factors with most of the variance (59 %) explained by the first component which described the inverse relationship between pH and metals. The second component suggests that total phosphorus was more closely associated with DOC than with the metal-acidity component. The first 2 principal axes together explained 79 % of the variance in the data while last component (which described seasonality) explained 13 % for a collective total of 92 % of the variance in the data being explained by the 3 components collectively.

Figure 6: Dissolved organic carbon ($mgC \cdot l^{-1}$) versus pH in 5 lakes (each circle represents a monthly growing season mean (May - November), open circles indicate clear water lakes, dark circles represent coloured lakes.

BL = Beaverskin Lake
BE = Big Dam East Lake
BW = Big Dam West Lake
LT = Little Springfield Lake
PL = Pebbleloggitch Lake

FIGURE 6

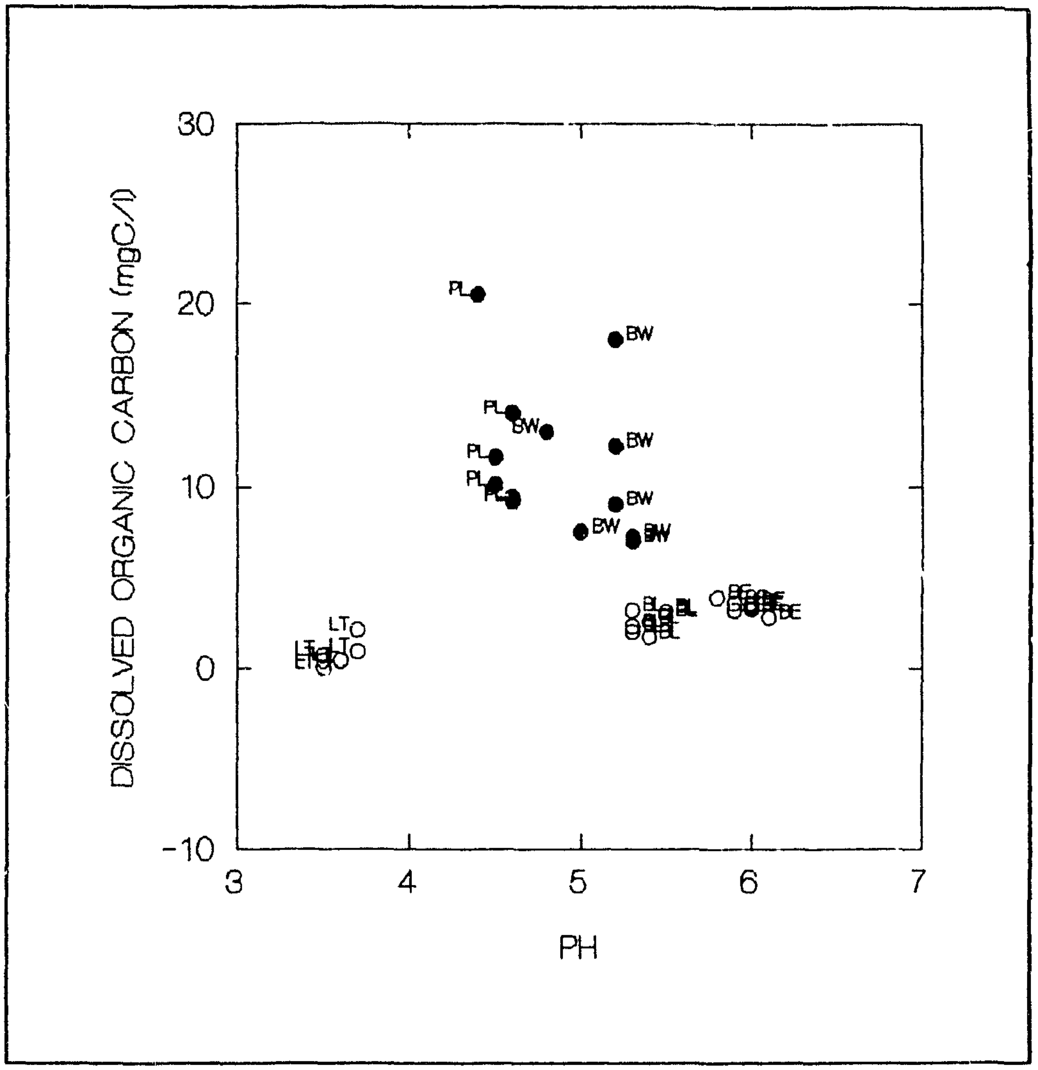

DISSOLVED ORGANIC CARBON (mgC/l)
30
20
10
0
-10
3
4
5
6
7
PH
PL
BW
LT
BL
BE

Figure 7: Aluminum versus DOC concentration (mg·l^{-1}) in 5 lakes (each circle represents a monthly growing season mean (May - November), open circles indicate clear water lakes, dark circles represent coloured lakes.

BL = Beaverskin Lake
BE = Big Dam East Lake
BW = Big Dam West Lake
LT = Little Springfield Lake
PL = Pebbleloggitch Lake

FIGURE 7

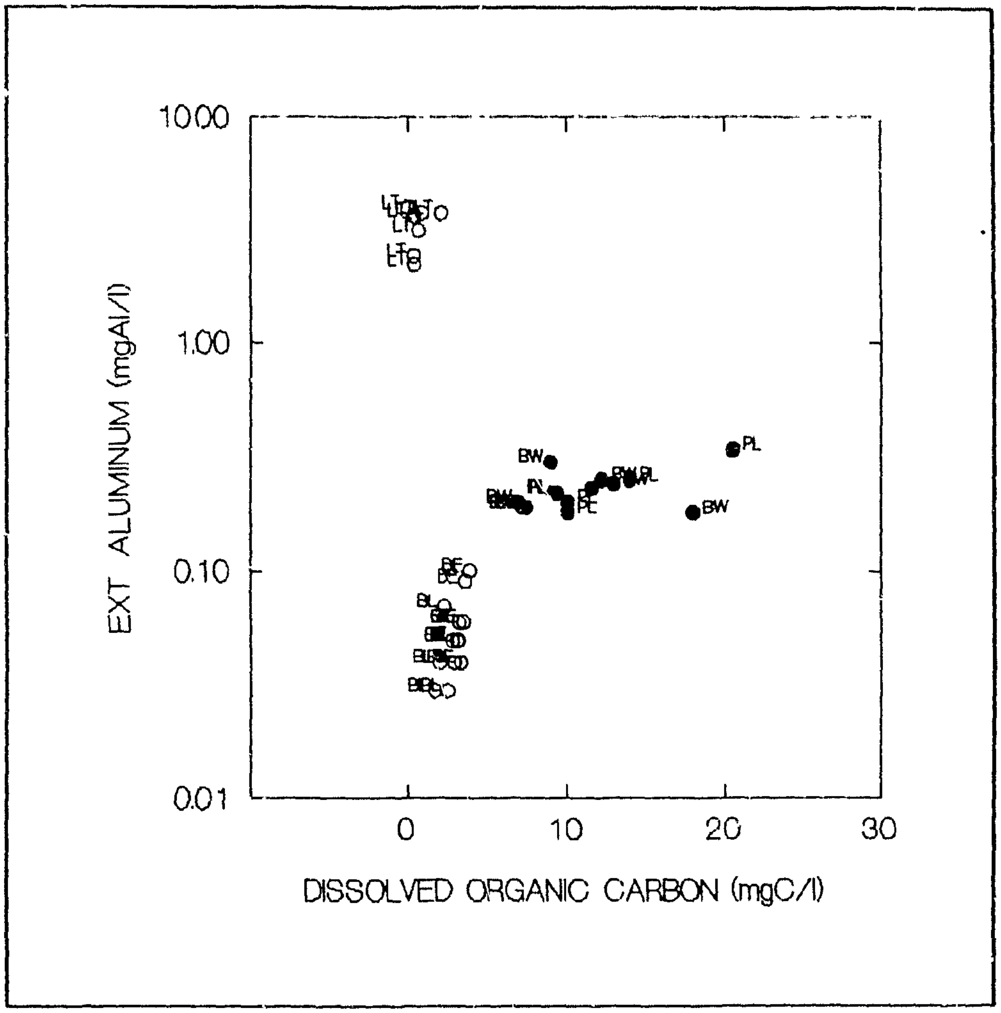

10.00
1.00
0.10
0.01
EXT ALUMINUM (mgAl/l)
0
10
20
30
DISSOLVED ORGANIC CARBON (mgC/l)
LT
BE
BL
BW
PL
PE

Figure 8: Iron versus DOC concentration (mg·l^{-1}) in 5 lakes (each circle represents a monthly growing season mean (May - November), open circles indicate clear water lakes, dark circles represent coloured lakes.

BL = Beaverskin Lake
BE = Big Dam East Lake
BW = Big Dam West Lake
LT = Little Springfield Lake
PL = Pebbleloggitch Lake

FIGURE 8

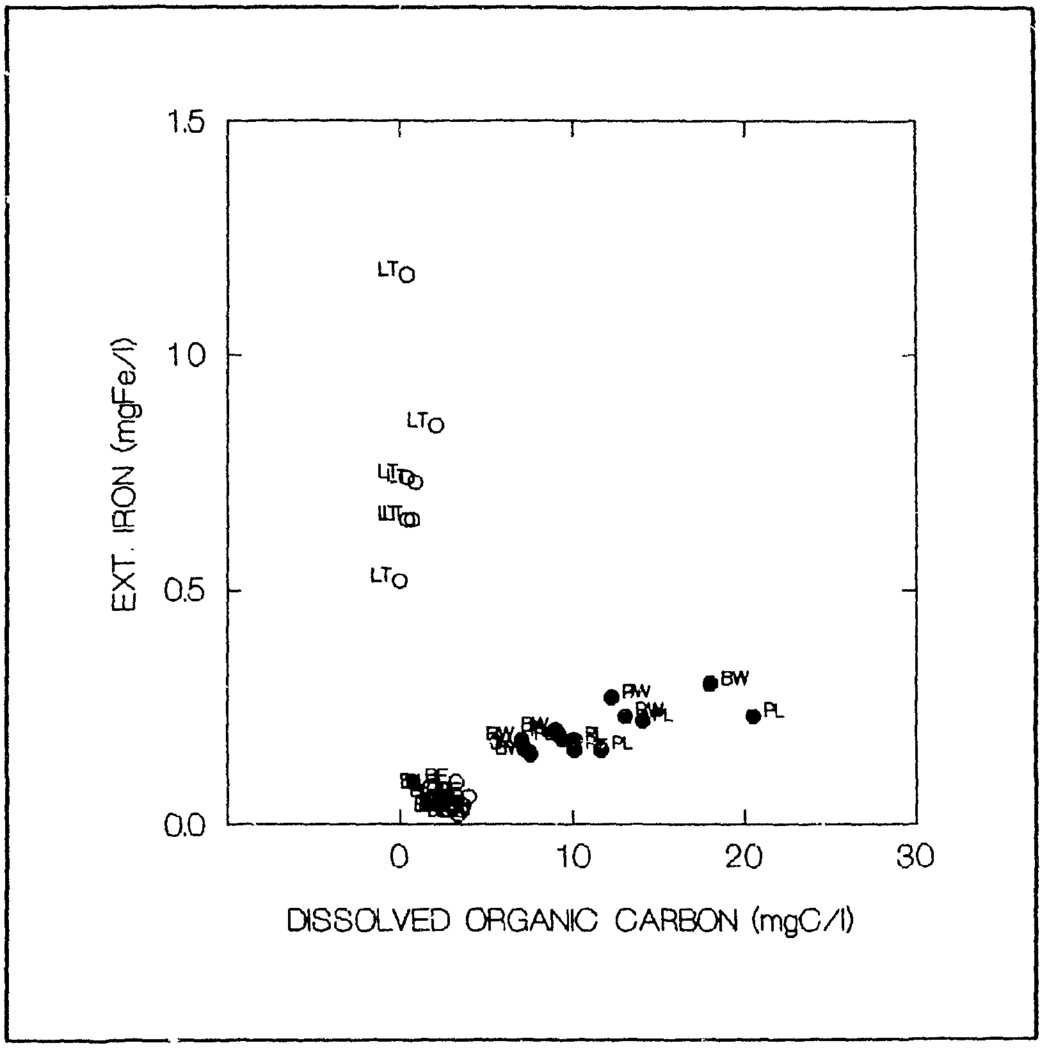
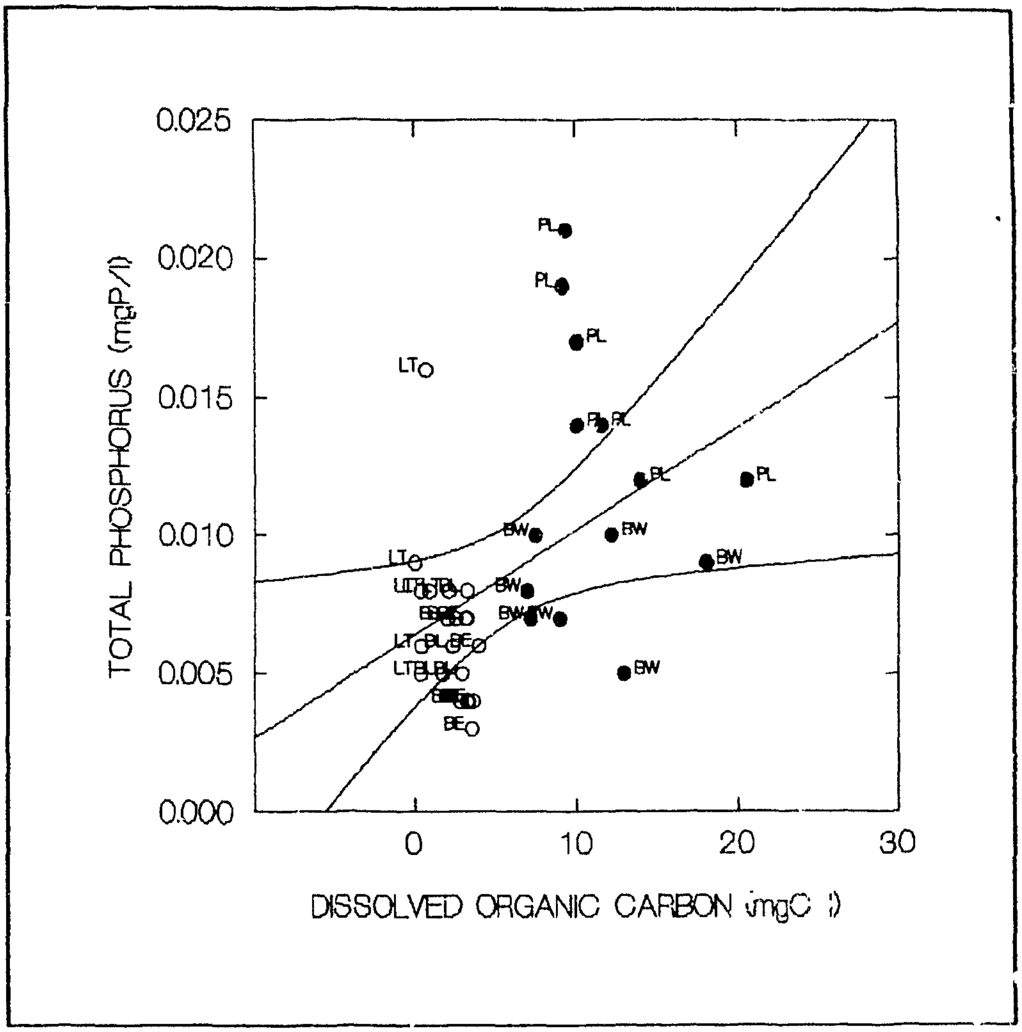

1.5
1.0
0.5
0.0
EXT. IRON (mgFe/l)
0
10
20
30
DISSOLVED ORGANIC CARBON (mgC/l)
LT
BW
PW
PL

Figure 9: Total phosphorus versus DOC concentration (mg·l^{-1}) in 5 lakes (each circle represents a monthly growing season mean (May - November), open circles indicate clear water lakes, dark circles represent coloured lakes; the regression line is presented as the straight line bounded by two lines showing the 95% confidence limits of the regression).

BL = Beaverskin Lake
BE = Big Dam East Lake
BW = Big Dam West Lake
LT = Little Springfield Lake
PL = Pebbleloggitch Lake

FIGURE 9


TOTAL PHOSPHORUS (mgP/l)
0.025
0.020
0.015
0.010
0.005
0.000
0
10
20
30
DISSOLVED ORGANIC CARBON (mgC/l)
PL
PL
PL
PL
PL
PL
PL
LT
LT
LT
LT
BW
BW
BW
BW
BW
BW
BW
BW
BE
BE
BL

Water chemistry data available for Beaverskin and Pebbleloggitch Lakes from 1980 to 1988 were also examined for trends in pH, DOC, Al, Fe, Mn, Ca and TP over this time period. No significant changes over the 8 year period were found for any of the variables in either of the two lakes.

3.2. Sediment Geochemistry

3.2.1. Sediment Heterogeneity. Porewater measurements were found to be relatively consistent within site but varied among different locations within a lake. Beaverskin Lake sediments were used to assess the heterogeneity of lake sediments with respect to conductance and phosphorus fractions by samplingporewaters at different locations in the lake which varied according to water depth (inshore, <3 m; mid-depth, 5 m; and the deepest point, 7.2 m). Conductivity profiles were typically scattered and no clear differences were observed between the three sites. However, both total dissolved and soluble reactive phosphorus profiles showed clear trends with water depth. Sediment total dissolved phosphorus (TDP) concentrations at the 5 m site were slightly greater than those at the 3.0 m site but considerably lower than those in the deeper sediments and closely reflected differences in organic content of the sediments (Figure 10). Shallow sediments were observed to be most coarse consisting of sand and gravel compared with deeper sediments which consisted of a fine organic ooze.

Table 6. Principal components analysis of selected water chemistry variables in 5 lakes based on monthly growing season means (May - November; Appendix B).

ROTATED FACTOR LOADINGS

	1	2	3
MONTH	0.021	0.018	-0.988*
PH	-0.908*	-0.362	0.003
DOC	-0.361	0.781*	-0.230
AL	0.971*	-0.122	0.001
FE	0.942*	0.021	0.008
MN	0.981*	-0.171	0.016
CA	0.973	-0.197	0.019
TP	0.151	0.895*	0.130
	acidity metals	organic nutrients	season

PERCENT OF TOTAL VARIANCE EXPLAINED

1	2	3
58.962	20.330	13.073

* indicates component where variable has its highest loading.

Concentrations of elements measured in sediment core sections were not measured at different water depths but replicates were done at the deep sites in some of the lakes. Concentrations of these constituents in replicate sediment core profiles were not significantly different within individual sites (Appendix C).

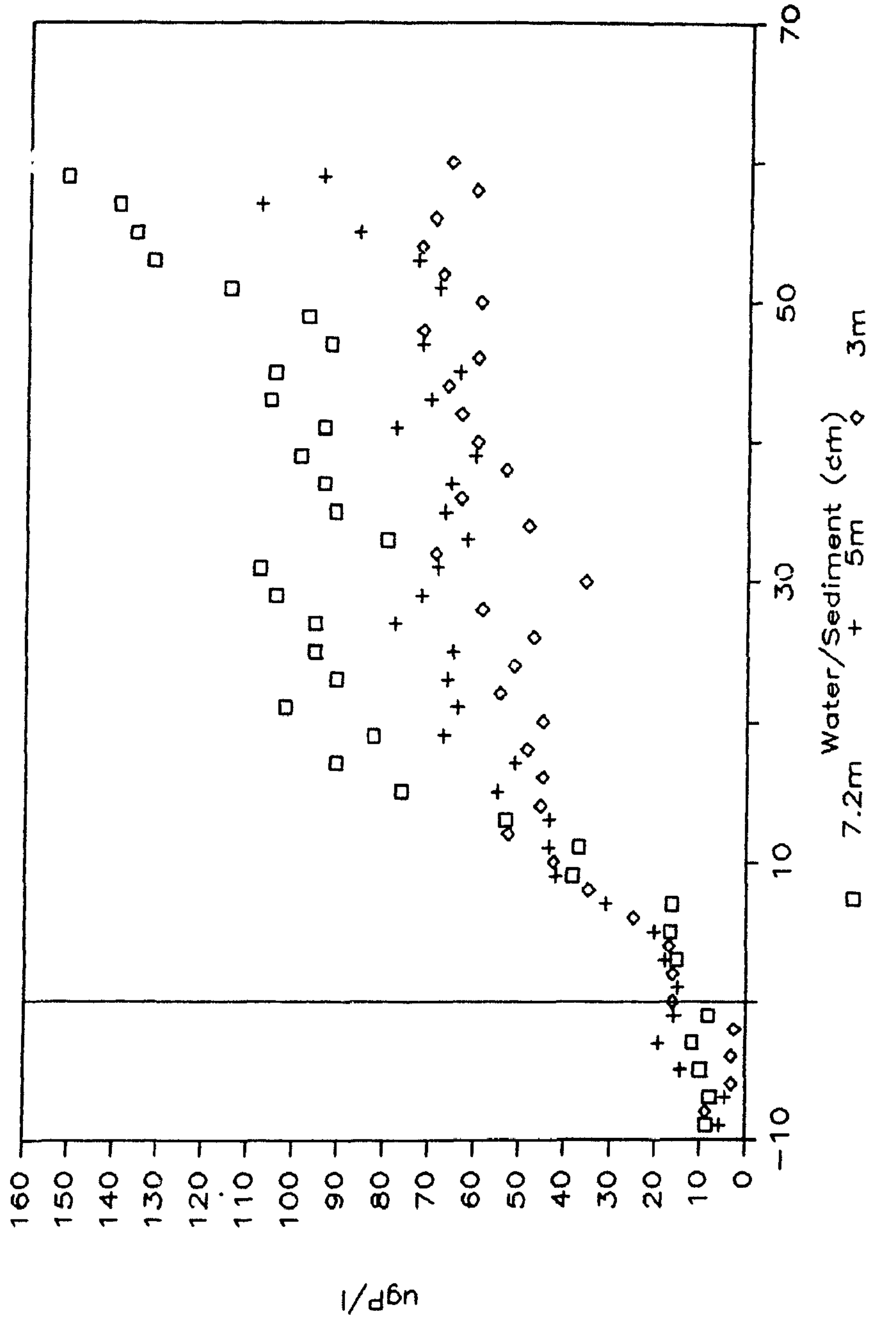
3.2.2. Water, organic and mineral content. Water content, organic and mineral content of sediments from Beaverskin, Big Dam East, Big Dam West, Little Springfield and Pebbleloggitch Lakes are given in Appendix C and illustrated in Figures 11 to 15.

With the exception of Little Springfield Lake, water content was greatest at the sediment surface (80-90%) and decreased with increasing sediment depth. Water content generally stabilized by 3-5 cm. Little Springfield Lake had decreasing water content from 1-3 cm followed by a gradual increase to 6 cm. Deeper sediments in this lake (>6 cm) had constant water content comparable to profiles found in the other 4 lakes.

Organic content of the sediments in the 5 lakes generally ranged between 25% and 30% at or near the surface. Organic content in Beaverskin Lake showed a peak at 13 cm and an increase in the upper 4 cm. Big Dam West Lake showed peaks in organic content at 20 cm and 8 cm and also increased in the upper 5 cm. Organic content of Big Dam East and Pebbleloggitch Lakes did not change substantially

Figure 10: Porewater SRP concentration (ugP·l^{-1}) at 3 depths in Beaverskin Lake.

FIGURE 10


ugP/l
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
10
30
50
70
Water/Sediment (cm)
□ 7.2m
+ 5m
◇ 3m

with depth, while Little Springfield Lake showed a consistent decline in organic content over the entire length of the core. Generally, organic content was closely correlated with water content.

3.2.3. Oxidation-Reduction Potential (Redox). Redox conditions were expressed as electrode potentials (mV) and are presented in Appendix E for each of the five lakes. Redox in lake sediments was zero between 0 and 1 cm in the four Kejimkujik Lakes and at 1.5 cm in Little Springfield Lake indicating the transition zone between the oxidized surface layer and the anoxic, reducing environment below.

3.2.4. Sediment Chemistry. Arsenic (As) and cadmium (Cd) were found to be below detection limits in cores from all 5 lakes and are not discussed further. The remaining chemical constituents along with percent water and organic content are illustrated in Figures 11 to 15.

Beryllium, chromium (Cr), cobalt (Co), copper (Cu), nickel (Ni), lead (Pb), strontium (Sr), tin (Sn), vanadium (V) and zinc (Zn) were all present in low concentrations (generally < 100 $mg \cdot Kg^{-1}$ dwt) relative to aluminum (Al), barium (Ba), calcium (Ca), iron (Fe), magnesium (Mg), manganese (Mn), phosphorus (P) and titanium (Ti). Thus, the latter group of elements were considered to be major constituents and the former as minor constituents. Barium, Cr, Ni, Sr were not considered important within the context of phosphorus dynamics or paleolimnology so these

Figure 11 Sediment geochemistry in Beaverskin Lake.

FIGURE 11

BEAVERSKIN LAKE

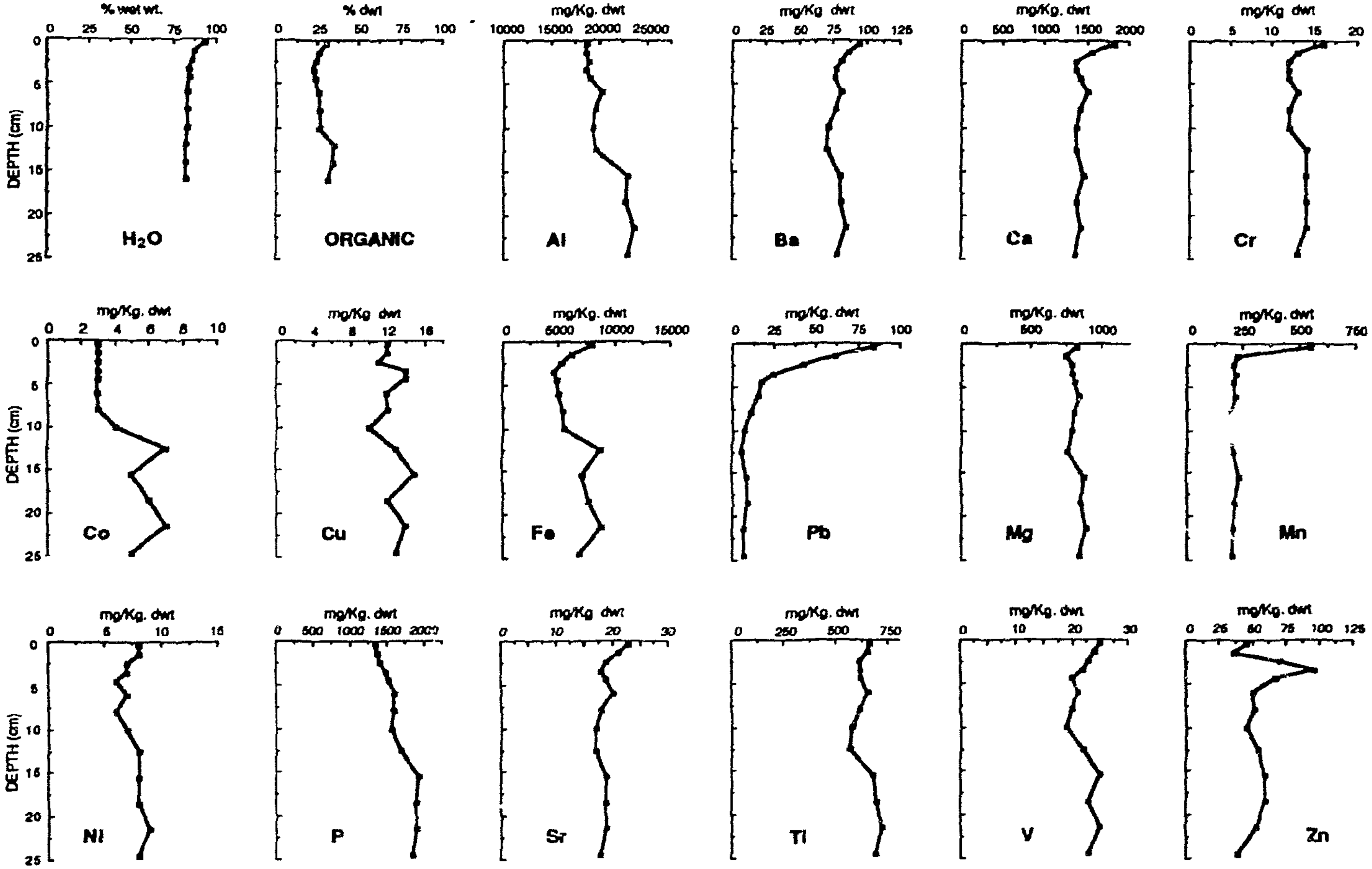


Figure 12 Sediment geochemistry in Big Dam East Lake.

FIGURE 12

BIG DAM EAST LAKE

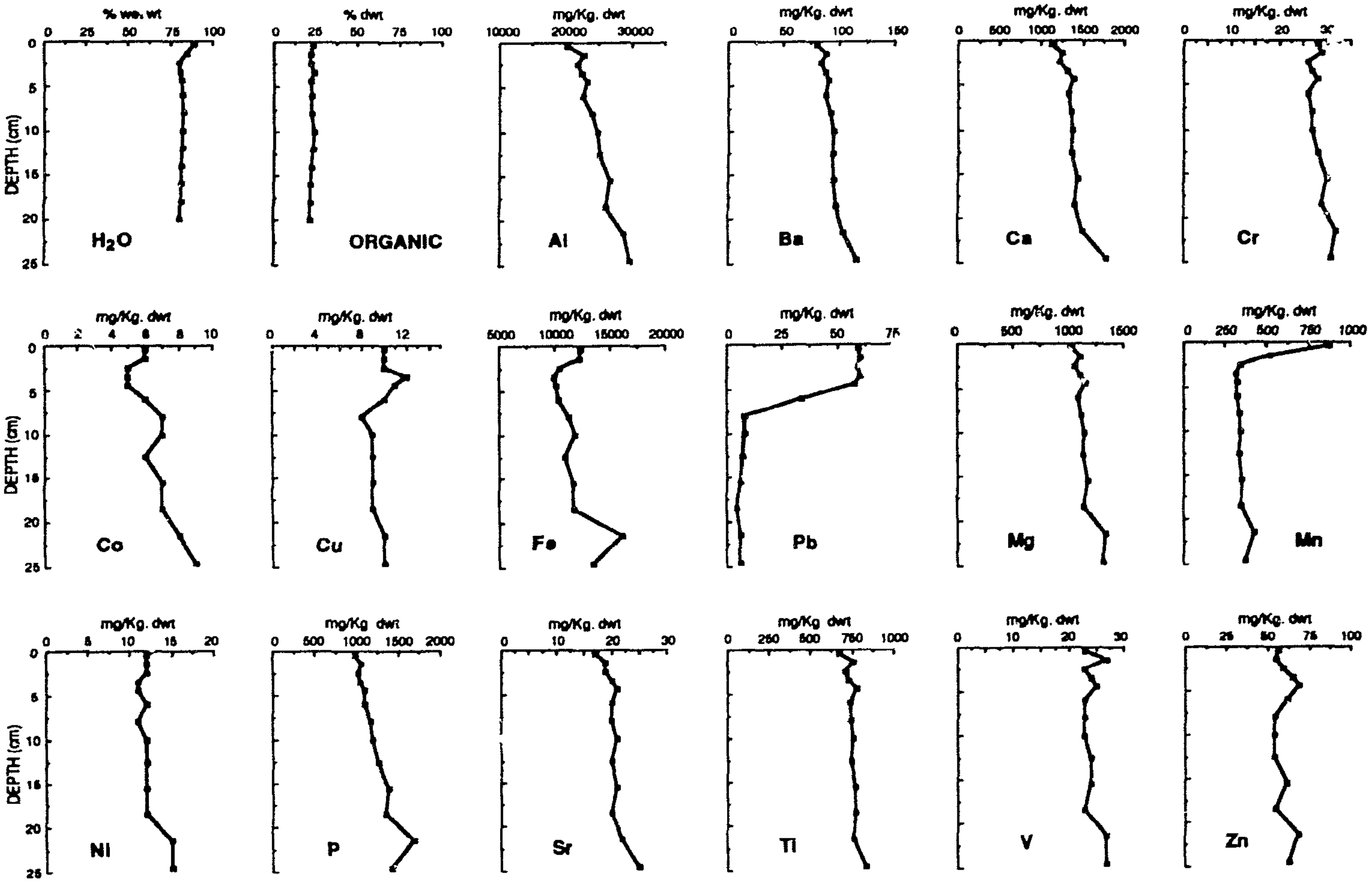


Figure 13 Sediment geochemistry in Big Dam West Lake.

FIGURE 13

BIG DAM WEST LAKE

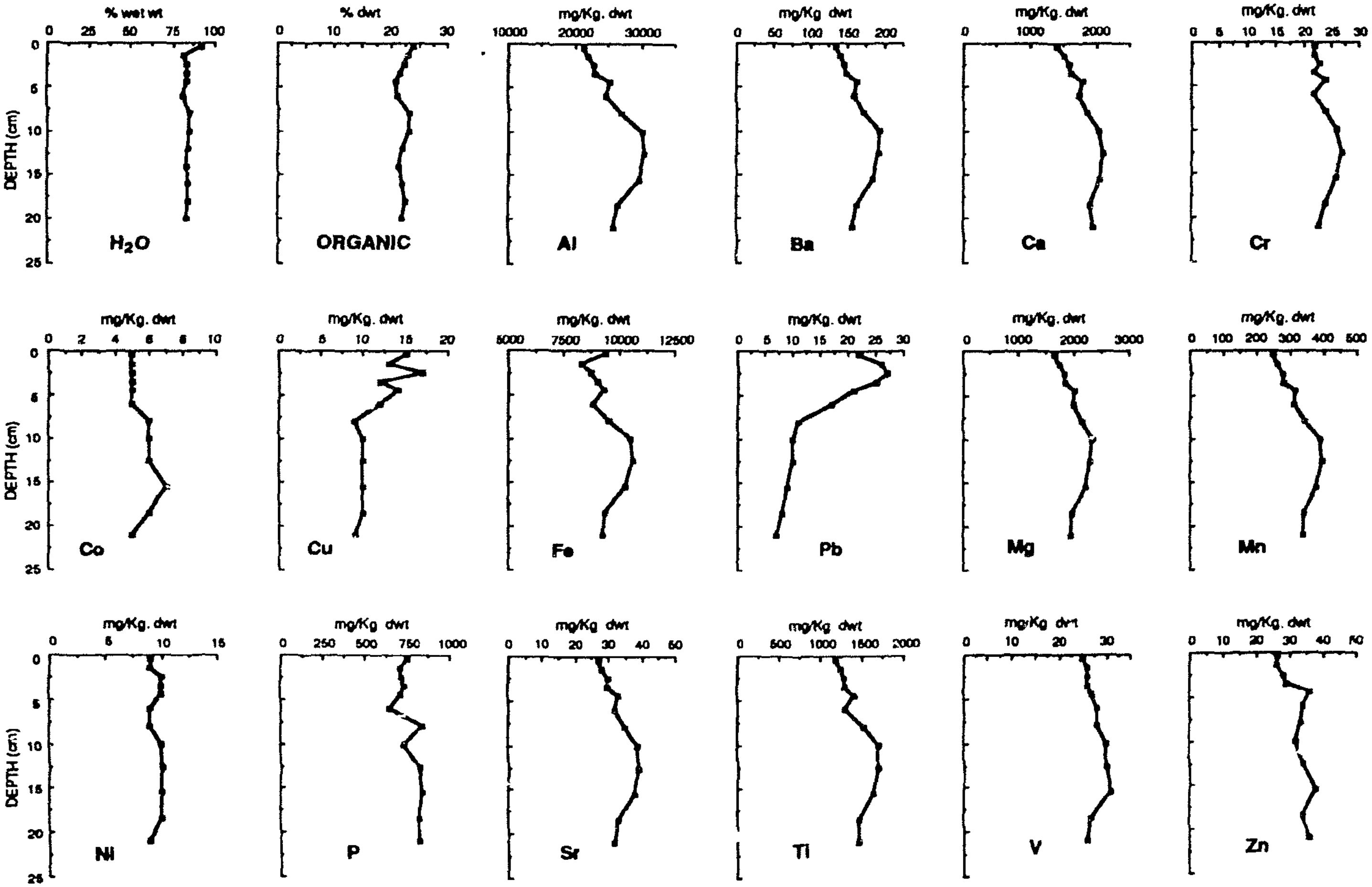


Figure 14: Sediment geochemistry in Little Springfield Lake.

FIGURE 14

LITTLE SPRINGFIELD LAKE

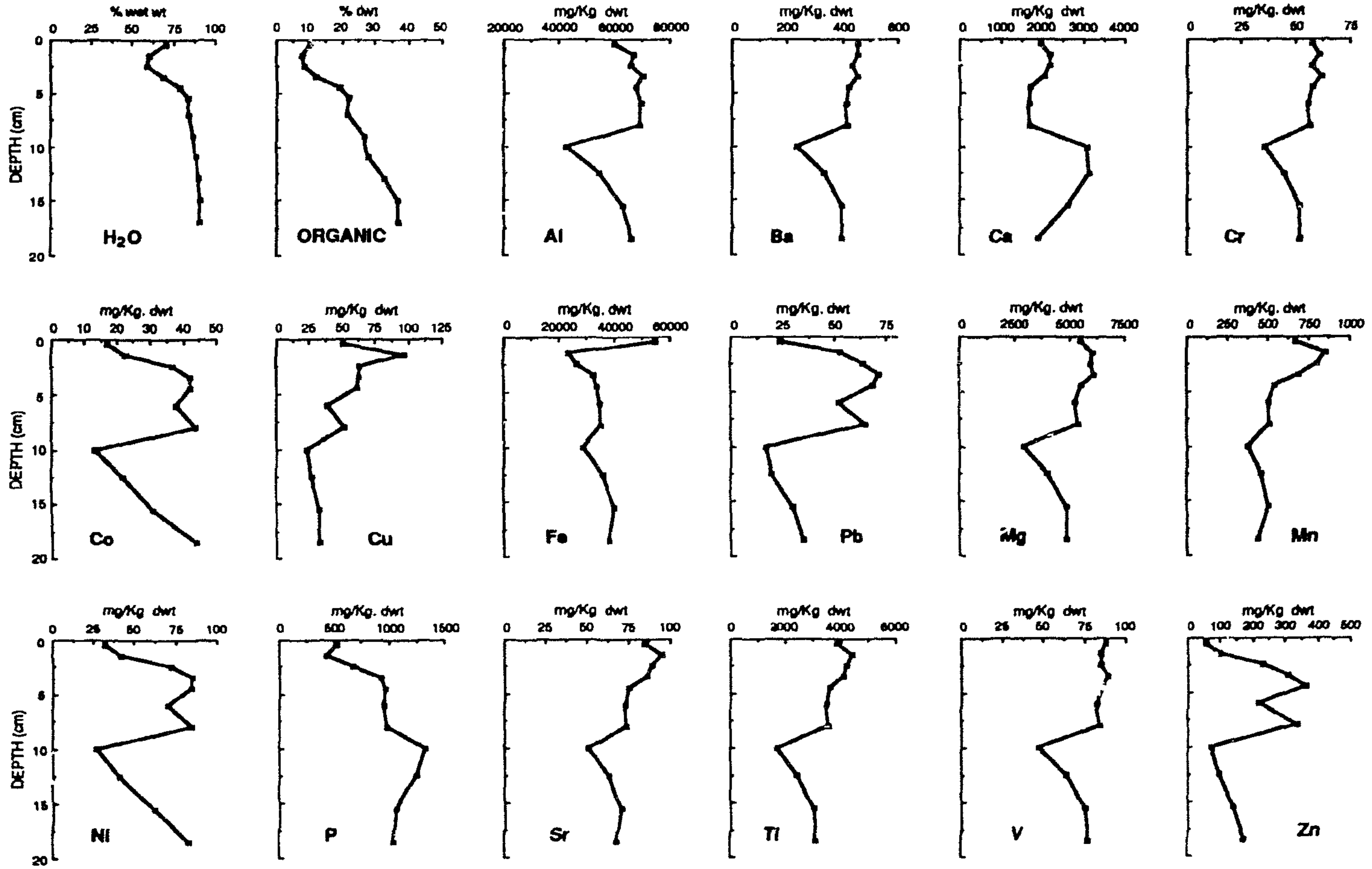
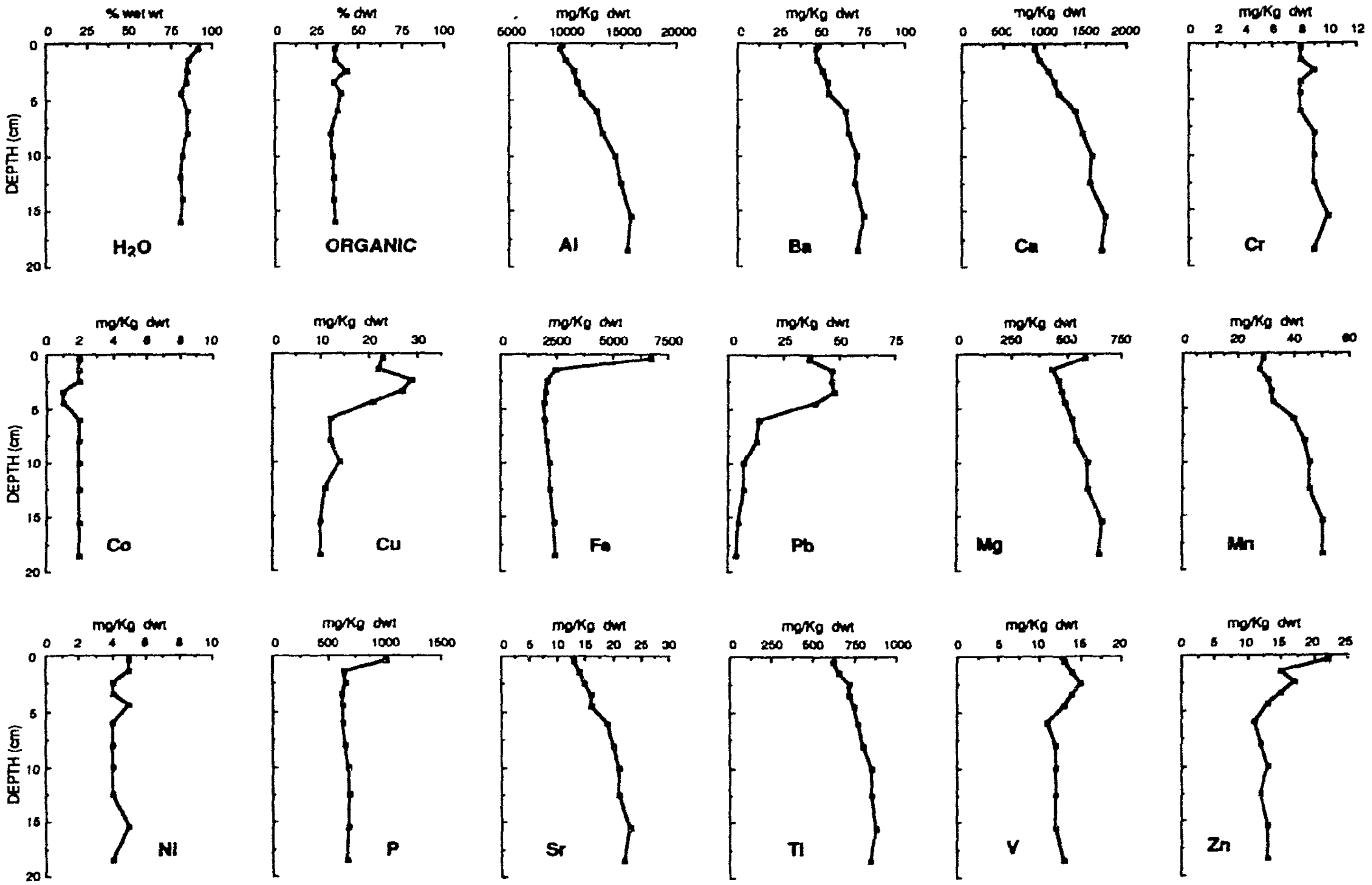


Figure 15: Sediment geochemistry in Pebbleloggitch Lake.

FIGURE 15

PEBBLELOGGITCH LAKE



constituents are not discussed further. Lead, Mn, Ti, V and Zn wereimportant in assessing either diagenetic processes, historical changes within the catchments (primarily land use changes) or anthropogenic influences and discussion was restricted to within one or more of these contexts. The remaining constituents (Al, Ca, Mg, Fe, and P) are important within the above framework but are also important with respect to phosphorus dynamics. Silica (SiO_2) was found to be the most abundant constituent in the sediments of all 5 lakes (> 95%) followed by Al and Fe. Calcium and phosphorus were present in substantially lower concentrations followed by Ti, Mg, Mn and Ba although the order of the latter constituents varied somewhat between lakes.

Sediment Al concentrations were greatest in Little Springfield Lake (40-70 $g \cdot Kg^{-1}$ dwt) compared to between 10 and 30 $g \cdot Kg^{-1}$ dwt found in the 4 Kejimkujik area lakes. Pebbleloggitch Lake had the lowest Al concentration among the 4 Kejimkujik lakes, although it was the most organic lake. Aluminum concentration profiles generally showed declining gradients with more recent sediments although Beaverskin Lake showed a stabilization in Al concentration in the upper 5 cm.

Calcium concentration in lake sediments ranged from 0.93 $g \cdot Kg^{-1}$ dwt in Pebbleloggitch Lake to 3.1 $g \cdot Kg^{-1}$ dwt in Little Springfield Lake. Calcium profiles in Big Dam East, Big Dam West and Little Springfield Lakes showed a decline in Ca concentration in the upper 5 cm. Pebbleloggitch Lake showed a consistent decline in Ca concentration over the entire length of the core. Beaverskin Lake was the only lake to show increased Ca concentration in the surface sediment.

Iron concentrations in sediments of the 5 lakes ranged from 1.97 g.Kg^{-1} dwt in Pebbleloggitch Lake to 54.6 g.Kg^{-1} dwt in Little Springfield Lake. Iron concentration profiles were variable with increasing depth in all lakes except Pebbleloggitch Lake. Diagenetic accumulation of Fe at the oxidized layer was apparent in all lakes (Figures 11 to 15).

Magnesium concentration ranged from 0.49 g Kg^{-1} dwt in Pebbleloggitch Lake to 6.1 g·Kg^{-1} dwt in Little Springfield Lake. Magnesium profiles in each lake closely conformed to those of Ca. Magnesium concentration generally increased with increasing sediment depth except in Beaverskin and Pebbleloggitch Lakes where concentrations decreased over the first few centimetres.

Manganese concentrations ranged from 0.03 g·Kg^{-1} dwt in Pebbleloggitch Lake to 0.87 g·Kg^{-1} dwt in Big Dam East Lake. The manganese concentration profile was uniform in Beaverskin and Big Dam East Lakes except for high concentrations at the surface. Manganese concentrations increased slightly with increasing sediment depth in Big Dam West and Pebbleloggitch Lakes but no increase in concentration was evident at the sediment-water interface. In Little Springfield Lake sediments, Mn concentration showed a subsurface maximum at 1-2 cm with lower concentrations above and below this depth.

Sediment P concentrations ranged from 0.43 $g \cdot Kg^{-1}$ dwt in Little Springfield Lake to 1.9 $g \cdot Kg^{-1}$ dwt in Beaverskin Lake. Beaverskin and Big Dam East Lake showed a gradual decrease in P concentration to about 15 cm after which P concentration stabilized with depth in Beaverskin Lake. Phosphorus concentration in Big Dam West Lake was relatively consistent (0.7 - 0.8 $g \cdot Kg^{-1}$ dwt) over the entire length of the core except for a peak at 8 cm. Phosphorus concentration in Little Springfield Lake sediments increased between 2 and 10 cm but showed a slight decline at the surface and in sediments deeper than 10 cm. Slight increases in P concentration in surface sediments occurred in Big Dam West and Little Springfield Lake sediments. Pebbleloggitch Lake was the only site which showed relatively large increases in P concentration at the sediment surface (Figure 15). The increase in surface P concentration in Big Dam West, Little Springfield and Pebbleloggitch Lakes were coincident with surface Fe enrichment. Sediment P concentration in Beaverskin Lake was weakly correlated with Fe, Mn and Ca concentrations but was strongly correlated to Al concentration ($r^2 = 0.88$). In Big Dam East the correlations between P versus Fe and Ca concentrations were significant at $p < 0.05$ but the strongest correlation was still with Al ($r^2 = 0.87$). In Big Dam West Lake sediment P concentration was weakly correlated to Al, Fe, Mn and Ca concentrations ($r^2 = 0.55$). In Pebbleloggitch Lake total sediment P was significantly correlated only with Fe ($r^2 = 0.98$).

Lead concentrations (Figures 11-15) ranged from 4 mg·Kg^{-1} dwt at the bottom (17-20 cm) of the Pebbleloggitch Lake core to 82 mg·Kg^{-1} dwt at the sediment surface of Beaverskin Lake sediments. Surface sediments of Big Dam West, Little Springfield and Pebbleloggitch Lakes showed slight declines Pb concentrations.

Lead profiles were used to approximate average annual sediment accumulation rates (Table 7). Lead concentrations in deeper sediments of the lakes were low and relatively constant. Sediment Pb concentrations increased markedly in more recent sediments in all lakes (Figures 11 to 15; Appendix D). These increases were coincident with the increased use of leaded gasoline around 1940 (Goldberg et al. 1981; Ouellet and Jones 1983, Ogden et al. 1988). Sedimentation rates were higher in the coloured lakes compared to those estimated for the clearwater lakes.

Titanium concentrations ranged from 670 mg·Kg^{-1} dwt in Pebbleloggitch Lake to 4.4 g·Kg^{-1} dwt in Little Springfield Lake (Figures 11-15). The Ti curve in Beaverskin Lake indicated two periods of disturbance, one at approximately 10 cm (1890) and another at 4 cm (1950). Big Dam East Lake Ti profiles showed only one disturbance at 4 cm (1955). In Big Dam West Lake, Ti concentration profiles showed a shift which began at approximately 17 cm (1927) and another at 6 cm (1967).

Table 7. Depth of initial Pb concentration increase and approximate sediment accumulation rate.

Lake	Depth of Pb Increase (cm)	Accumulation Rate ($cm \cdot yr^{-1}$)
Beaverskin Lake	4-5	0.10
Big Dam East Lake	5-7	0.13
Big Dam West Lake	11-14	0.27
Little Springfield Lake	7-9	0.17
Pebbleloggitch Lake	9-11	0.22

In Little Springfield Lake there was a slow upward decline in Ti concentration until 10 cm when a large increase occurred. This major shift occurred in conjunction with large changes in the concentrations of all other constituents. A smaller shift occurred again at 6 cm. Specific dates were not calculated for Little Springfield Lake because of the highly variable inputs of material and subsequent accumulation rates caused by extensive construction activity within the catchment of this lake. In Pebbleloggitch Lake the Ti concentration profile is relatively constant although there was a tendency for concentrations to increase gradually with increased sediment depth.

Vanadium concentrations were also highest in Little Springfield Lake sediments (50-90 $mg \cdot Kg^{-1}$ dwt) compared to the Kejimkujik lakes (10-30 $mg \cdot Kg^{-1}$ dwt). Vanadium concentrations in Beaverskin Lake sediment showed a consistent increase in the upper 5 cm. This trend was not evident in any of the other lakes (Figures 15-19). Vanadium concentrations in Pebbleloggitch Lake sediments increased between 6 to 3 cm but decreased from 3 cm to the sediment surface.

Zinc concentrations were highest in Little Springfield Lake sediments (61-372 $mg \cdot Kg^{-1}$ dwt) and substantially lower in the Kejimkujik Lakes (11-96 $mg \cdot Kg^{-1}$ dwt). The lowest Zn concentrations were measured in Pebbleloggitch Lake (Figure 15). Zinc profiles in the three Beaverskin Lake cores and two Little Springfield Lake cores showed large Zn peaks at 3-4 cm. Smaller peaks at 4-5 cm were measured in Big Dam East and Big Dam West Lakes while the peak Zn concentration in Pebbleloggitch Lake occurred at the surface.

Calcium:Titanium ratios were calculated for the five lakes in order to assess changes in Ca concentrations normalized to the Ti profile thus removing the effects of changes in watershed weathering processes (see discussion for further explanation). Calcium:Titanium ratios in Beaverskin Lake sediments showed an increased accumulation of Ca in more recent sediments while Big Dam East and Pebbleloggitch Lakes both showed a gradual long term decline in Ca (Figures 16a-d). Calcium:Titanium ratio profiles in Big Dam West Lake showed a gradual decline to 10 cm followed by a rapid increase from 10 to 6 cm (ca. 1953-67) followed by another period of decline toward the sediment surface.

In Little Springfield Lake Ca concentration increased rapidly relative to Ti up to 10 cm. This period of increase was followed by a sudden decline to a ratio of 0.5 which remained constant to the surface. Because of extensive soil disturbance in the watershed of this lake from urban development, Ca:Ti ratios were not plotted. Profiles of sediment Ca:Ti ratios for the other 4 lakes are illustrated in Figures 16a-d.

Since phosphorus was also found to be relatively immobile in sediments (based on flux calculations), P:Ti ratios were calculated to assess changes in phosphorus accumulation rates in sediments normalized for watershed influences in the 4 Kejimkujik lakes (Figures 17a-d). Phosphorus:Ti ratios showed distinct differences when clear (Beaverskin and Big Dam East Lakes) and coloured lakes are compared. In the clear water lakes, P:Ti ratios showed a consistent decline towards the sediment surface in contrast to the coloured lakes where a consistent increase was found nearer the surface.

Aluminum:Titanium profiles were also calculated for the same 4 lakes for similar reasons (Figures 18a-d). In the 2 clear lakes Al:Ti ratio profiles followed a pattern similar

Figure 16a. Ca:Ti ratios in sediments of Beaverskin Lake.

Figure 16b: Ca:Ti ratios in sediments of Big Dam East Lake.

FIGURE 16a and 16b

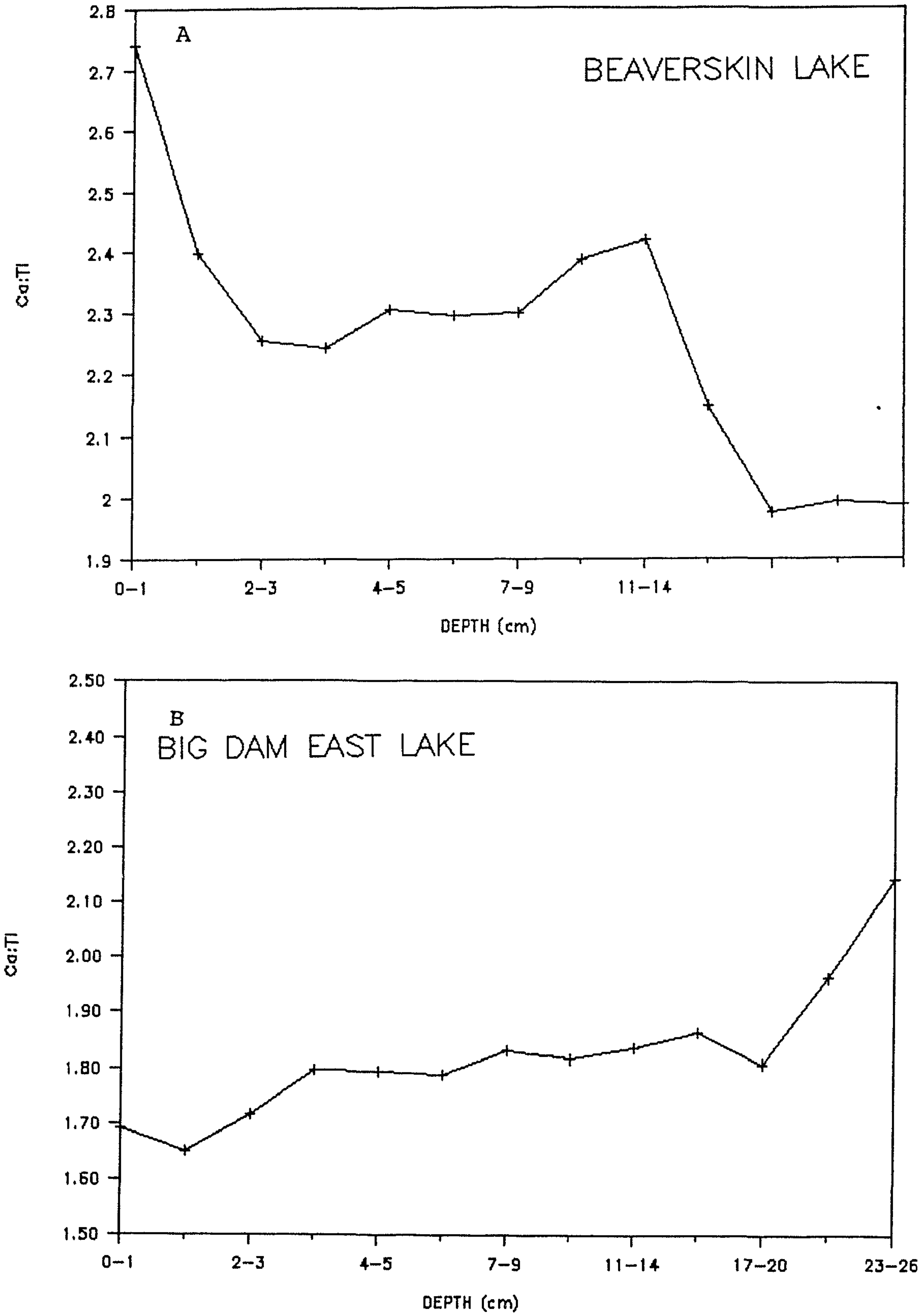


Figure 16c: Ca:Ti ratios in sediments of Big Dam West Lake.

Figure 16d: Ca:Ti ratios in sediments of Pebbleloggitch Lake.

FIGURE 16c and 16d

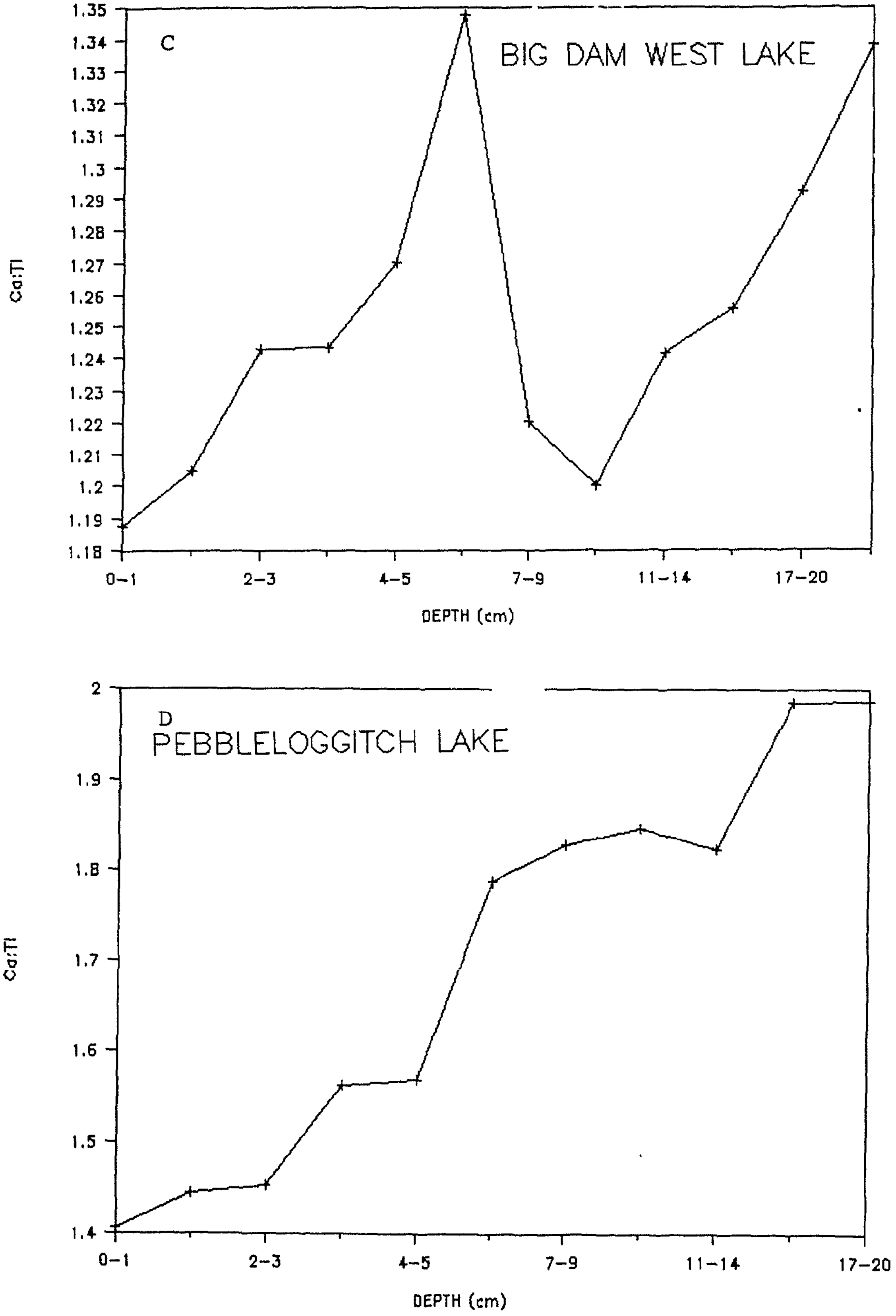


Figure 17a: P:Ti ratios in sediments of Beaverskin Lake.

Figure 17b: P:Ti ratios in sediments of Big Dam East Lake.

FIGURES 17A AND 17B

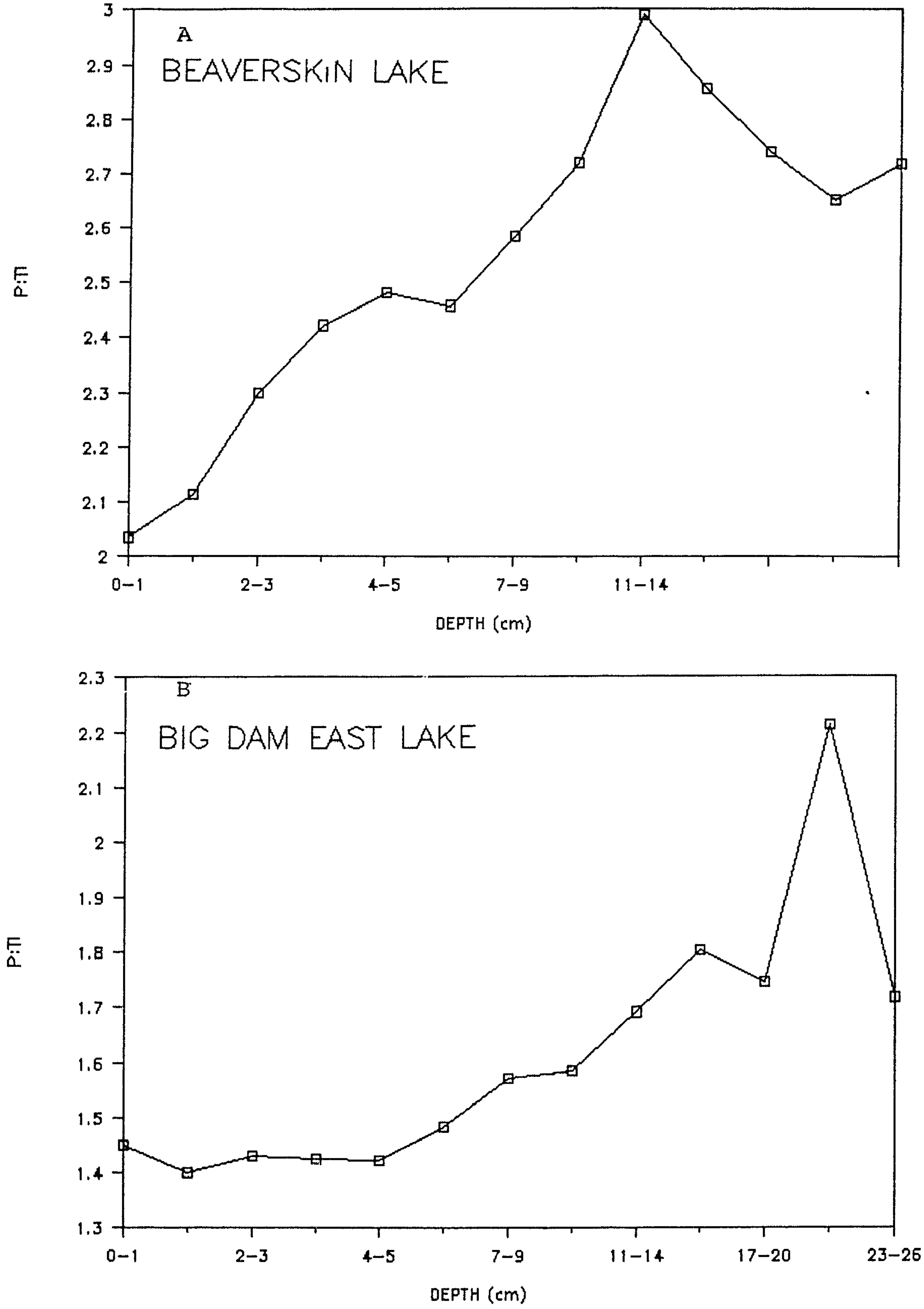
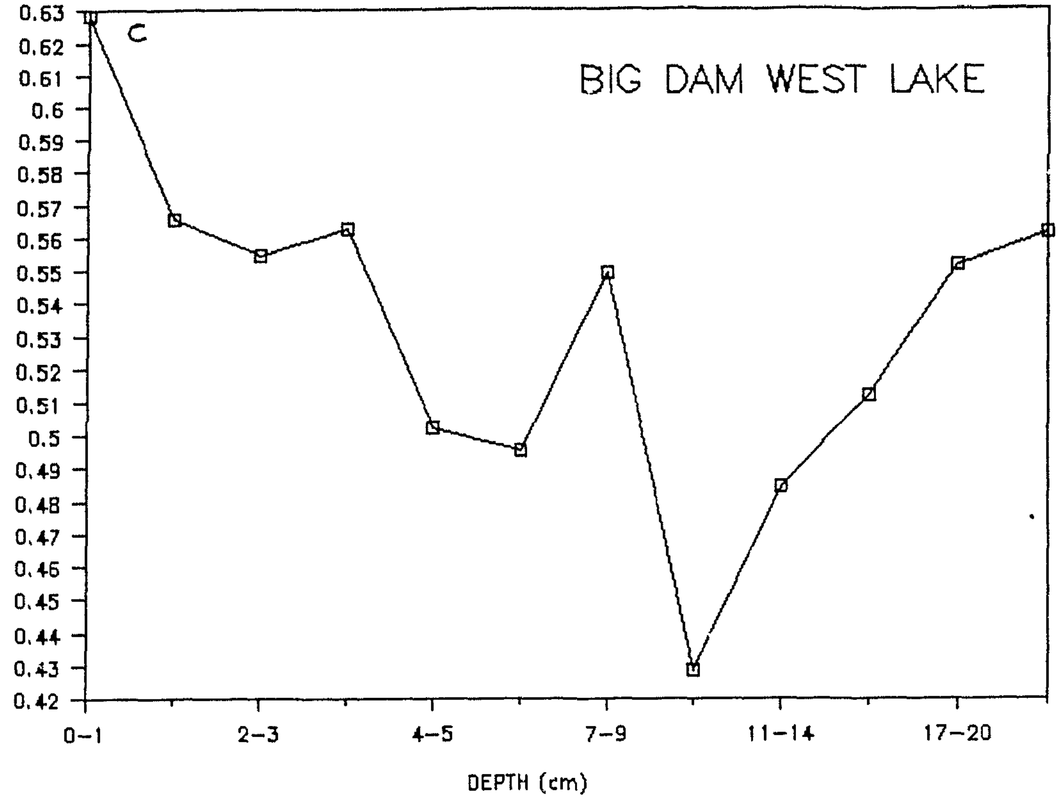


Figure 17c: P:Ti ratios in sediments of Big Dam West Lake.

Figure 17d: P:Ti ratios in sediments of Pebbleloggitch Lake.

Figures 17c and 17d



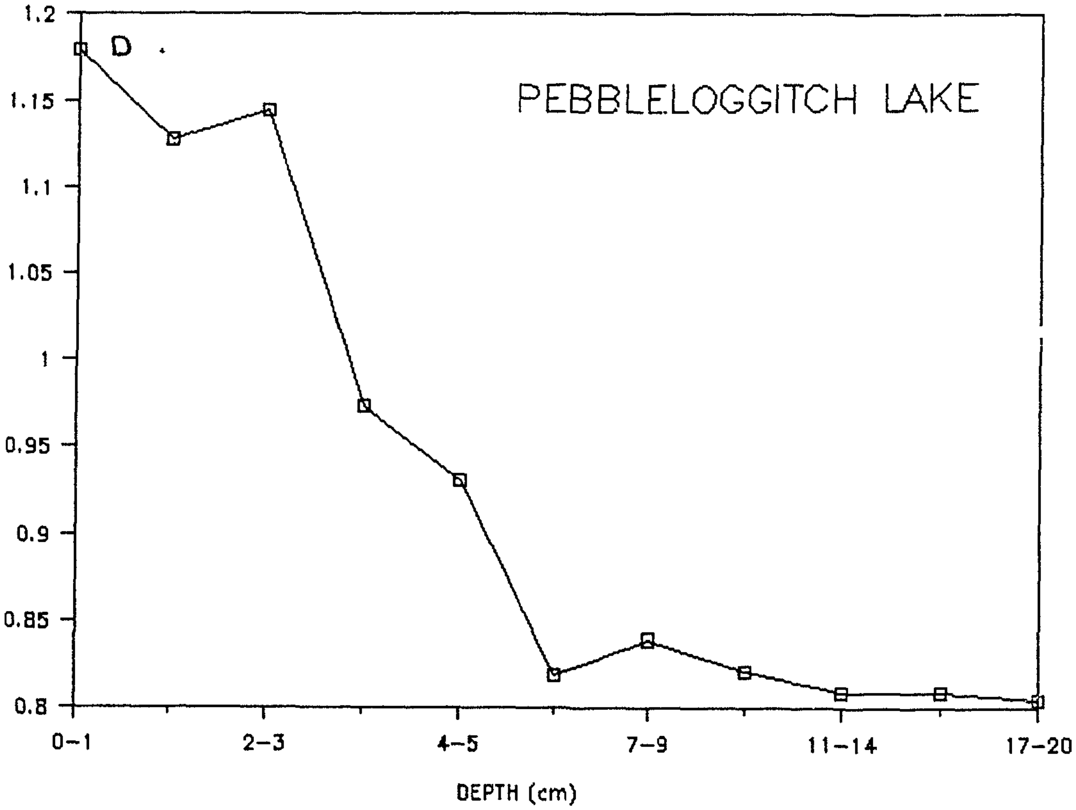
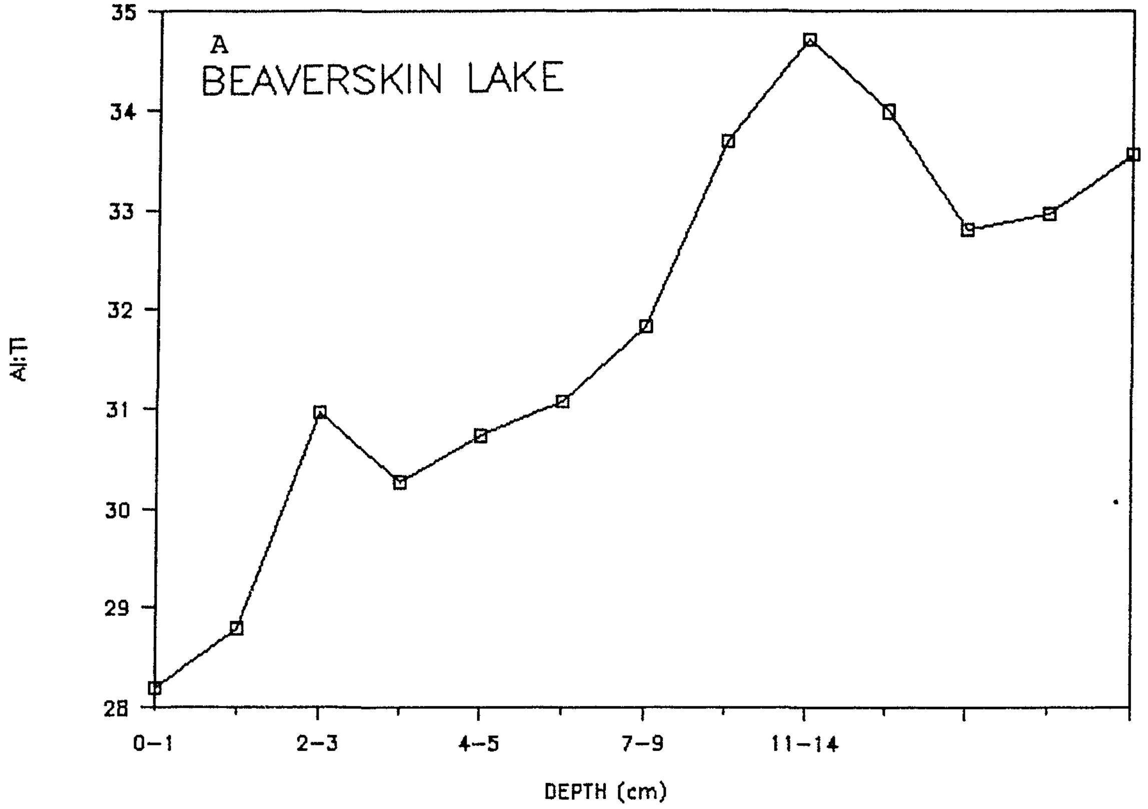


Figure 18a: Al:Ti ratios in sediments of Beaverskin Lake.

Figure 18b: Al:Ti ratios in sediments of Big Dam East Lake.

Figures 18 a and b



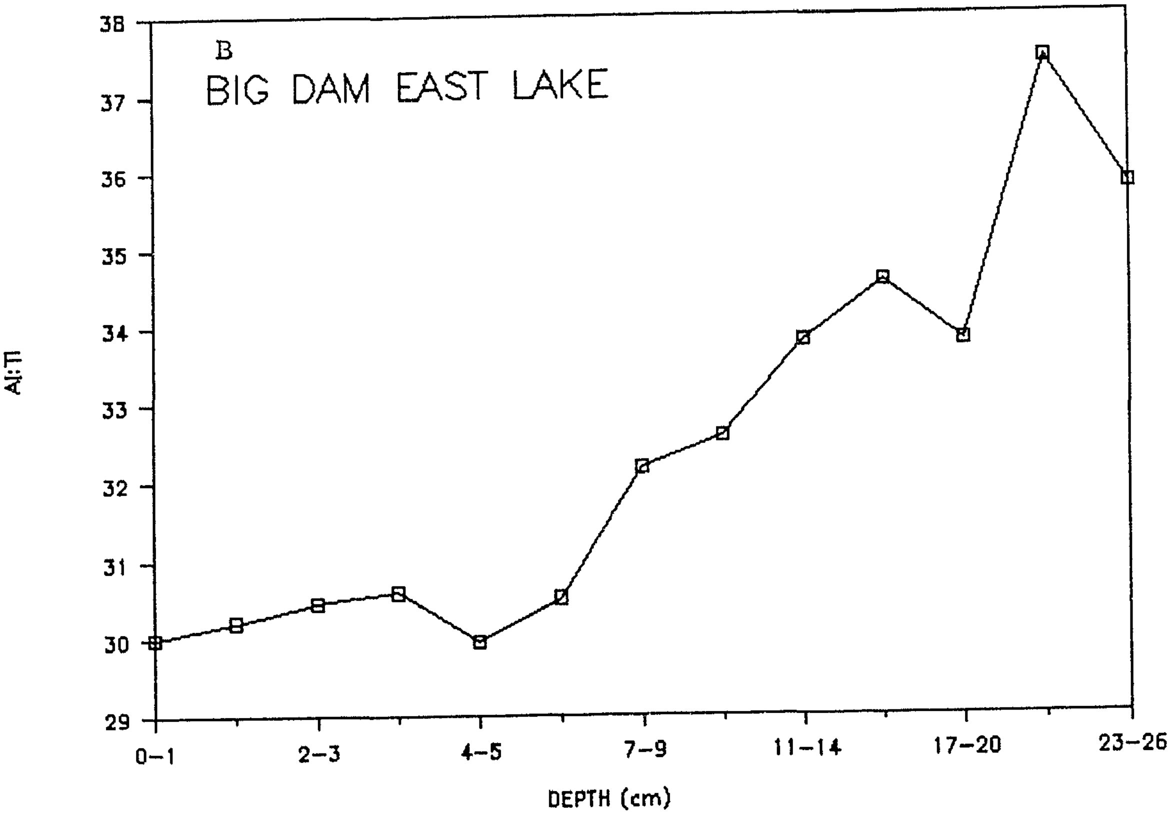
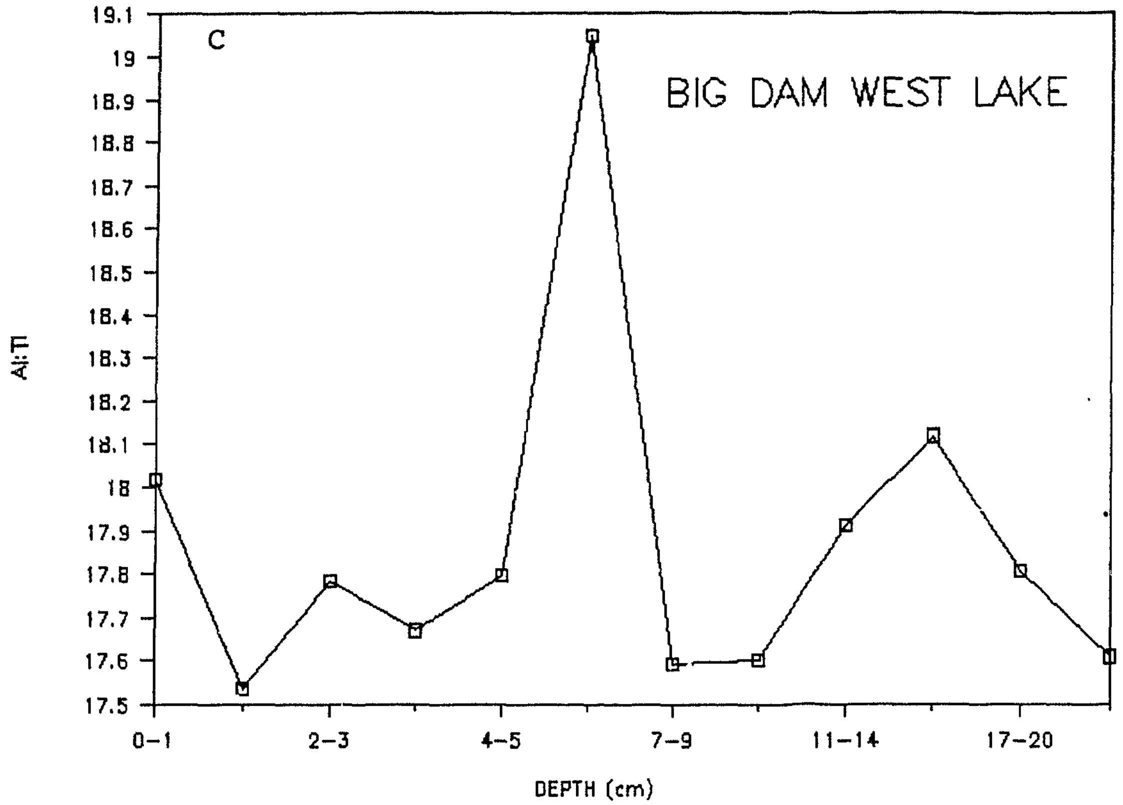
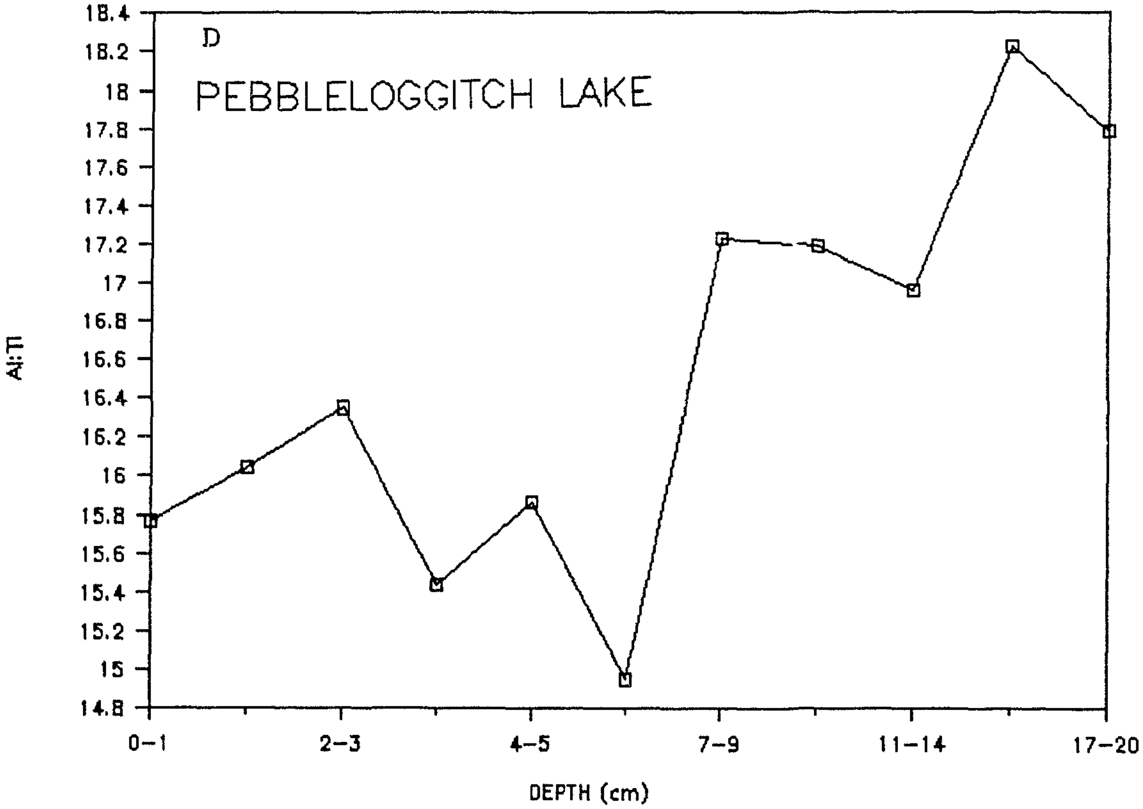


Figure 18c: Al:Ti ratios in sediments of Big Dam West Lake.

Figure 18d: Al:Ti ratios in sediments of Pebbleloggitch Lake.

Figures 18 c and d





to that observed for the P:Ti ratios. However, in the 2 coloured lakes, there was no clear trend in the Al:Ti ratio in either lake.

3.3. Sediment Porewater Chemistry

Sediment porewater profiles of pH, conductivity and TDP and SRP concentrations were measured between 1 and 5 times in the 25 study lakes. Additional measurements of Al, Fe, Mn and Ca concentrations were made in the sub set of 5 study lakes. It was not feasible to present the complete set of data for all 25 lakes due to its length and the number of plots even though some of this data is discussed below for comparative purposes. The complete data is presented for the 5 lakes selected for more detailed analyses. The complete data set for the 25 lakes is presented in Beauchamp and Kerekes (1988). Except as noted below, the data for the 5 lakes presented here is representative of the majority of the 25 lakes sampled.

3.3.1. Methodology Controls. Peeper blanks indicated that there was no contamination evident from any test peepers due to equipment or procedures.

Exposure time for equilibration of constituents across the dialysis membrane was tested by placing peepers *in situ* for periods ranging from 15 to 83 days. No significant differences in pH, specific conductance, TDP or SRP were measured with increased exposure after two weeks. Fourteen days exposure were thus found to be adequate. Shorter periods of placement were not tested, since other studies have indicated a minimum of 7 to 14 days for equilibration (Hesselin 1976; Carignan 1984; Bottomley and Balay 1984).

Concerns regarding changes in pH after removal of peepers from sediments and exposure to air were found to be justified. Measurements of pH from several peepers removed simultaneously from Beaverskin Lake, at 15 min after collection to two days, indicated rapid changes in pH with time. The pH of peeper porewaters increased by as much as 0.5 pH units within 30 min of retrieval, depending on temperature, time of exposure and the chemistry of the lake water being tested. Changes in pH over time following retrieval indicated that the most rapid changes took place soon after retrieval with the rate of change per unit time decreasing with increasing time after exposure. Measurement of pH in peeper cells was generally completed within 15 min of retrieval of the peeper from the lake bottom. The pH was measured in every second peeper cell from the bottom of the peeper up the length of the peeper to the top and in the other cells on the way back down to the bottom of the peeper. Changes in pH within in the lower cells (those deepest in the anoxic sediment) where pH was measured first and last, indicated a pH change, on average, of about 0.2-0.4 pH units during the period in which measurements were being made.

3.3.2. Porewater pH. Profiles of porewater pH for 5 of the study lakes are illustrated in Figures 19 to 23. Many of the lakes studied were either naturally or anthropogenically acidic (Table 3). The most acidic lakes were Drain and Little Springfield Lakes (pH = 4.1 and 3.6 respectively) and the most alkaline lake sampled was Presquile Lake (pH = 7.4).

Acidic lakes generally showed an increasing pH gradient with increased sediment depth although the gradient was strongest in the upper 10 cm. In many lakes pH changed very little after a rapid initial increase in the first 5 -10 cm. Almost all of the acidic lakes had pH values approaching 6.0 to 6.5 by 70 cm sediment depth, including acidic Drain and Little Springfield Lakes. Beaverskin Lake was the only lake which had more acidic water (pH ~ 5.5) overlying sediments and high sediment pH (~6.4), but no gradient in surficial sediments on any of 5 sampling occasions. In this lake, pH at the sediment-water boundary changed abruptly (Figure 19). Circumneutral lakes obviously showed no gradient since sediment and water values were similar. This type of profile was found in the southwest New Brunswick lakes, Fundy lakes and Big Dam East and Laytons Lakes. Only two lakes (McLaren Pond and Presquile Lake) showed pH values in overlying water greater than was measured in the sediment. In both of these lakes the pH gradient in surface sediments

Figure 19: Sediment porewater pH, conductance, total dissolved (TDP) and soluble reactive phosphorus (SRP), aluminum, iron and manganese in Beaverskin Lake.

FIGURE 19

BEAVERSKIN LAKE

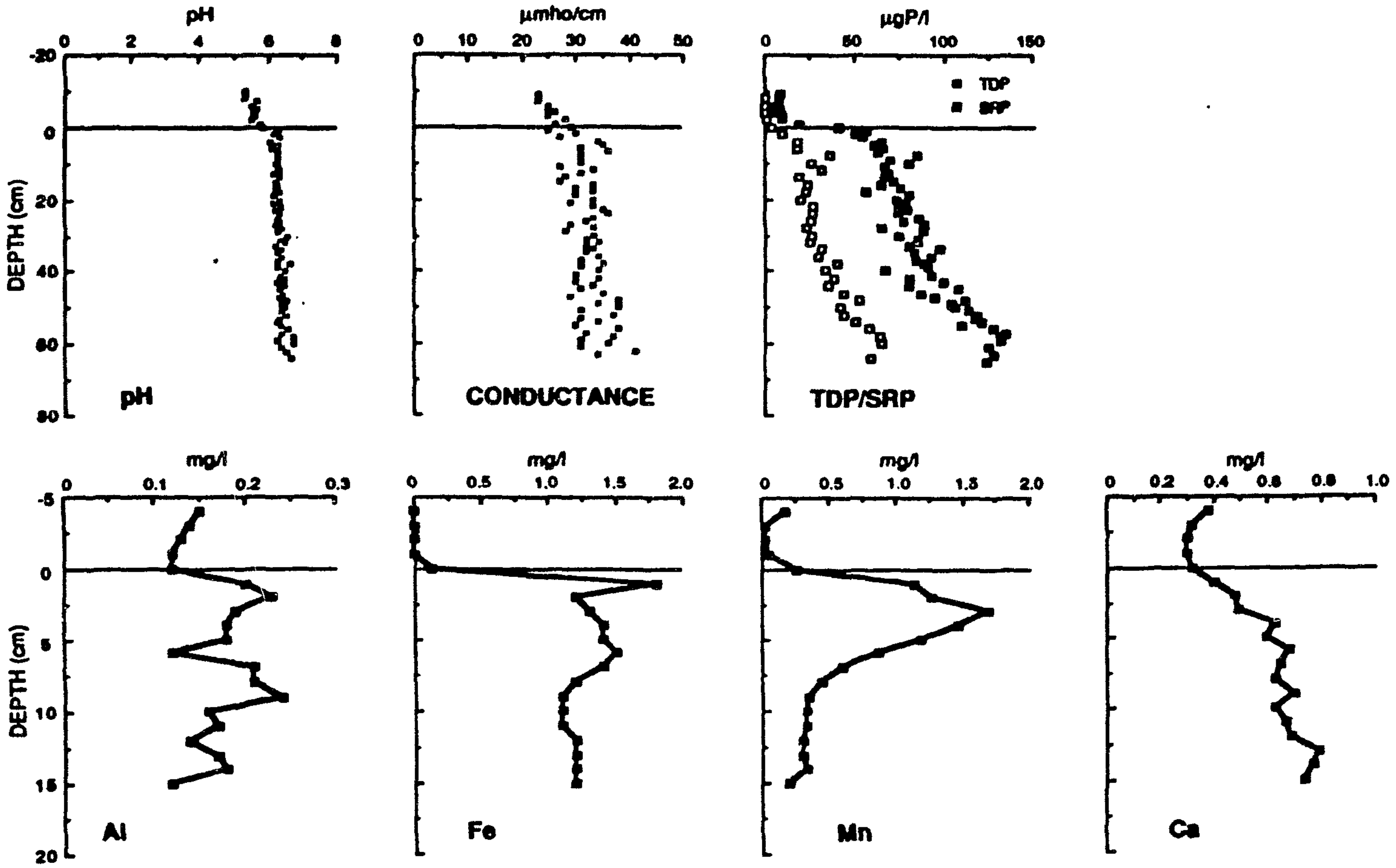


Figure 20: Sediment porewater pH, conductance, total dissolved (TDP) and soluble reactive phosphorus (SRP), aluminum, iron, manganese and calcium in Big Dam East Lake.

FIGURE 20

BIG DAM EAST LAKE

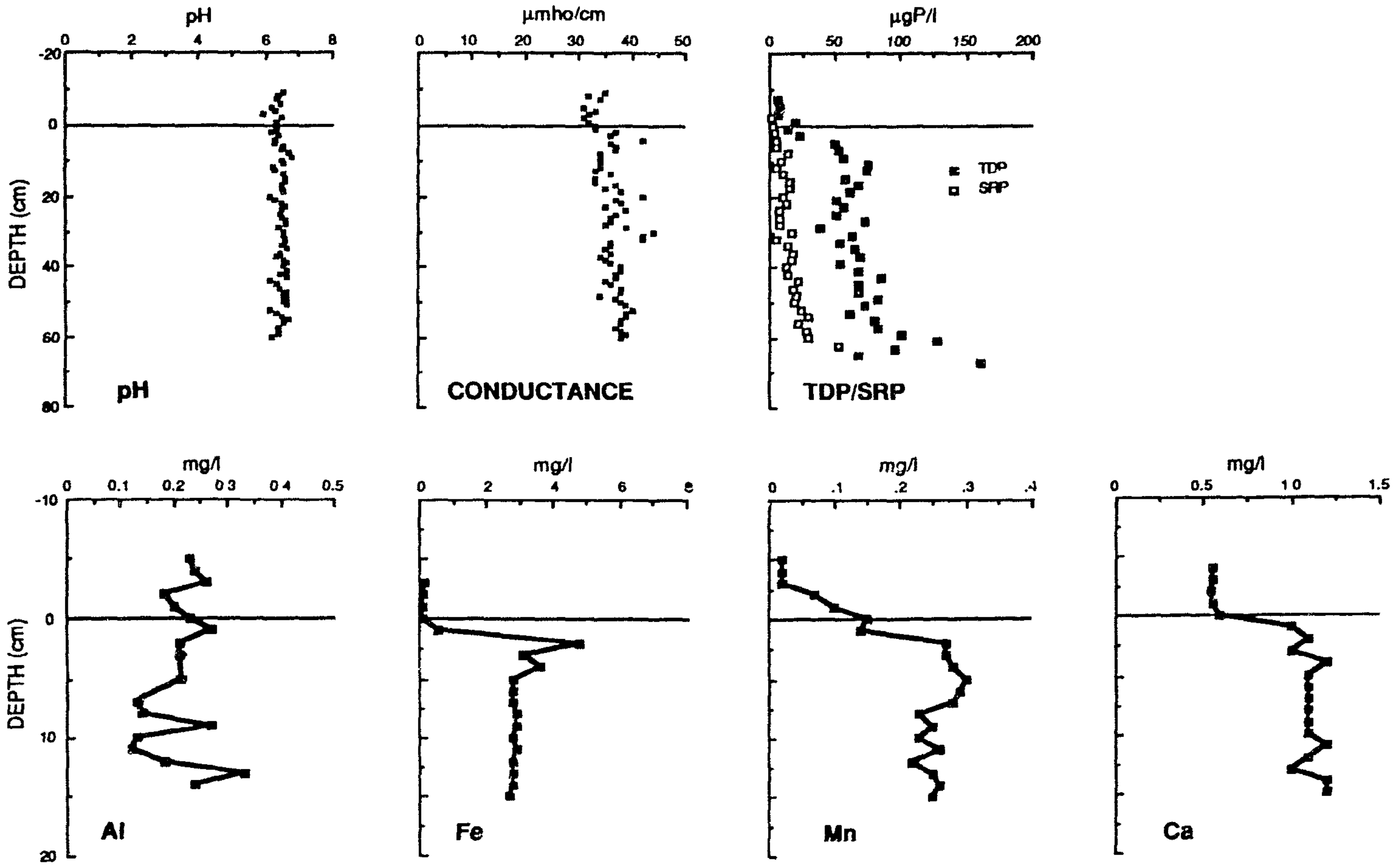


Figure 21: Sediment porewater pH, conductance, total dissolved (TDP) and soluble reactive phosphorus (SRP), aluminum, iron, manganese and calcium in Big Dam West Lake.

FIGURE 21

BIG DAM WEST LAKE

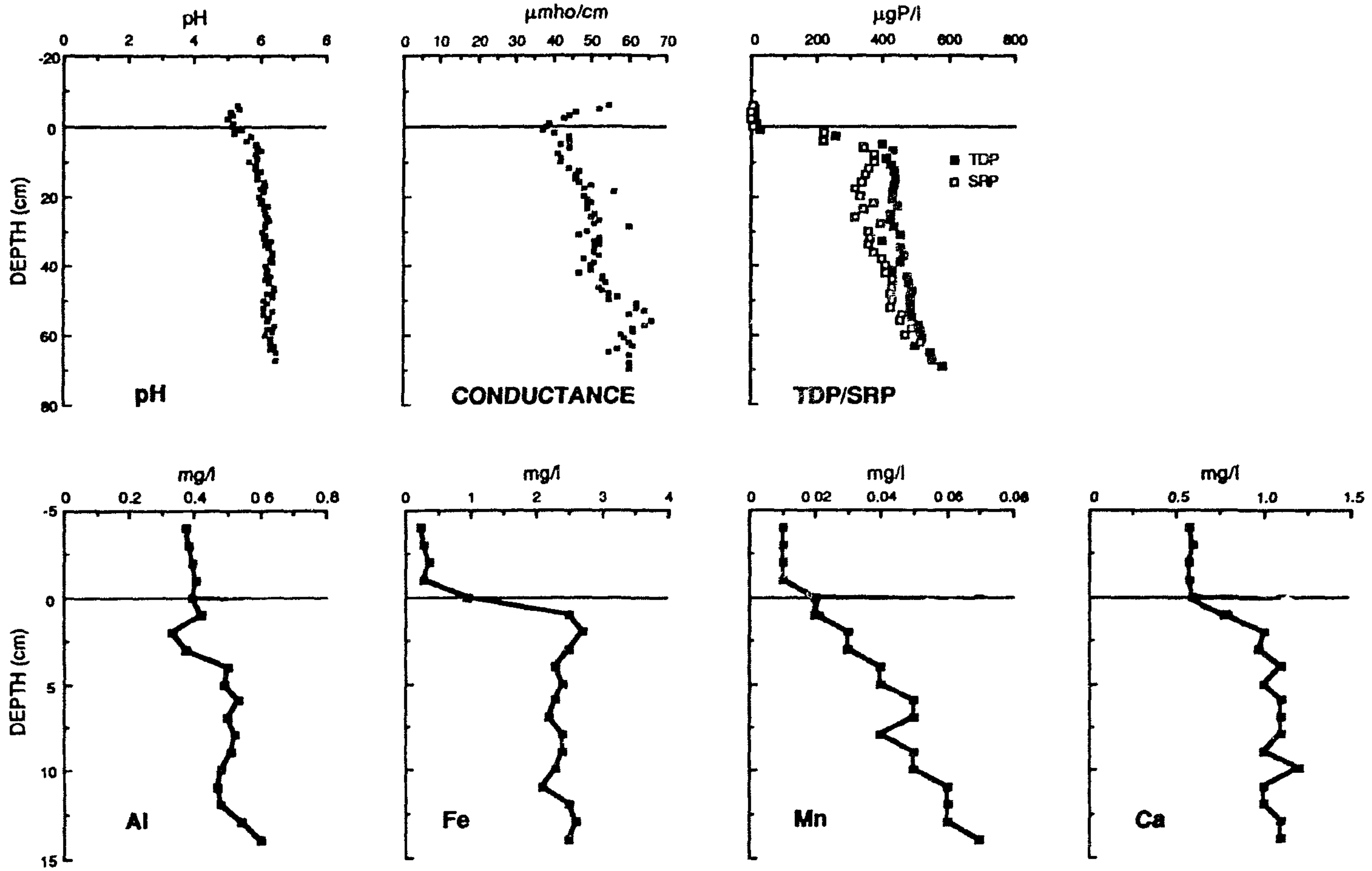


Figure 22: Sediment porewater pH, conductance, total dissolved (TDP) and soluble reactive phosphorus (SRP), aluminum, iron, manganese and calcium in Little Springfield Lake.

FIGURE 22

LITTLE SPRINGFIELD LAKE

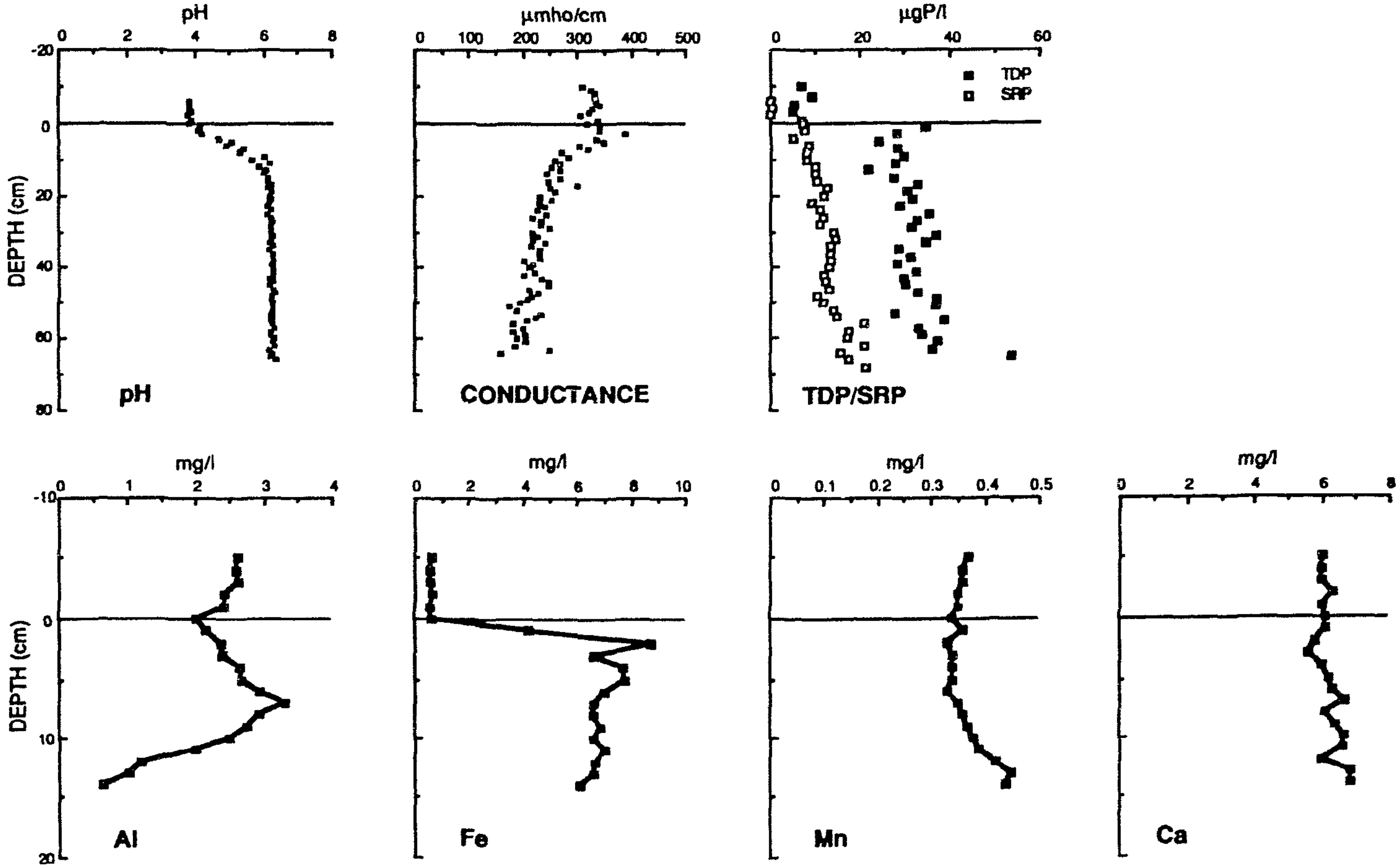
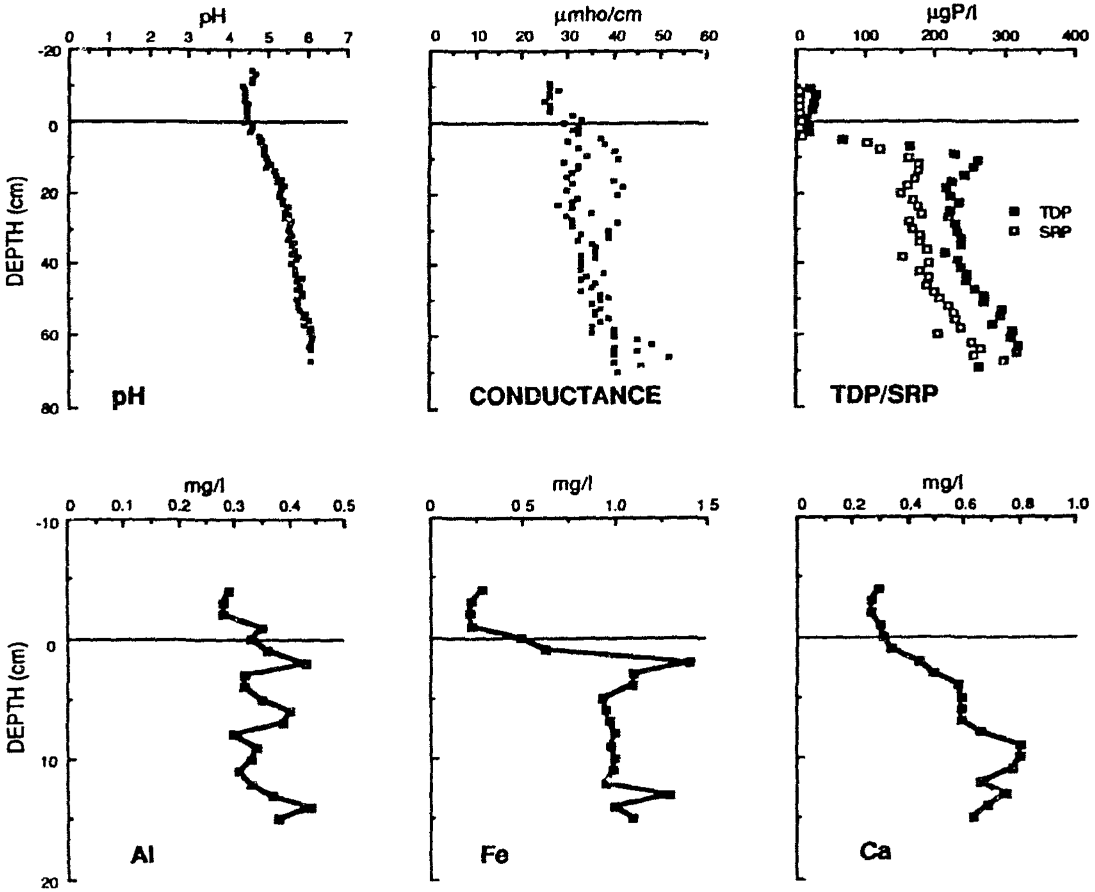


Figure 23: Sediment porewater pH, conductance, total dissolved (TDP) and soluble reactive phosphorus (SRP), aluminum, iron, manganese and calcium in Pebbleloggitch Lake.

FIGURE 23

PEBBLELOGGITCH LAKE



was negative. In Presquile Lake the pH of overlying water was ~ 8.2, however by 10 cm below the interface sediment porewater pH was only 6.9.

The slope of the pH gradient in the upper 10 cm of sediment varied amongst lakes. The steepest gradient was a one pH unit change between 0 and 3 cm, measured in Kejimkujik Lake, compared to the shallowest gradient of one pH unit change between 0 and 30 cm, measured in Pebbleloggitch Lake. This depended, in part, on the pH of overlying water but also sediment mixing. Shallow lakes with sediments actively disturbed by wind and wave action, as in Pebbleloggitch Lake, showed more gradual change throughout the sediment pH profile and lower maximum pH in the upper 70 cm (Figure 23). Pebbleloggitch Lake, Jordan Lake (control), Bog Exhibit Pond and, to a lesser extent, East and West Twin Lakes exhibited this type of profile.

In lakes where repeated measurements were made results were generally consistent, with pH not varying by more than 0.2 pH units between sampling. In shallow lakes the pH of surface sediments was slightly more variable (0.9 pH units).

3.3.3. Porewater Conductance. Specific conductance profiles for 5 study lakes are illustrated in Figures 19 to 23. Specific conductance was highly variable both within and amongst lakes. Porewater conductivity generally reflected conductivity of overlying water although was 2 to 3 times higher in porewaters. Lakes with surface water conductivities of 20-40 umho·cm^{-1}, such as those in southwest N.B., Fundy and the Kejimkujik area, had sediment-porewater conductivities of less than 100 umho·cm^{-1}. Lakes with higher surface water conductivity (i.e. Freshwater, 400-900; McLaren, 250-300; Laytons, 400-2000; Drain, 140-240; Little Springfield, 150-600 and Presquile Lakes, 100-2000 umho·cm^{-1}) also had higher porewater conductivity.

Conductivity profiles usually increased in the upper 10 cm of sediment, although peaks followed by declines were not uncommon. Only two lakes, Drain and Little Springfield, showed a consistent decrease in porewater conductivity as sediment depth increased.

3.3.4. Porewater Phosphorus. Sediment porewater TDP and SRP concentrations for the 5 study lakes are presented in Figures 19 to 23. Porewater TDP and SRP concentrations in sediments were much greater than in overlying waters in all lakes, particularly for SRP. Clearwater lakes on granitic or slate bedrock had the lowest phosphorus concentrations in lake and sediment porewater, followed by coloured lakes on similar substrates. Sediment porewater phosphorus concentrations generally reflected lake trophic status (according to criterion based on total phosphorus concentrations; see Vollenweider and Kerekes 1980), with mesotrophic and eutrophic lakes having progressively higher phosphorus concentrations. The lowest sediment porewater phosphorus concentrations were found in oligotrophic southwest N.B. lakes such as Anthony

Lake, where TDP and SRP did not exceed 40 and 10 ugP$\cdot$l^{-1} respectively. The highest porewater TDP concentration (1100 ugP$\cdot$l^{-1}) was found in eutrophic Laytons Lake followed by 600 ugP$\cdot$l^{-1} in McLaren and Presquile Lakes. Coloured lakes, including Big Dam West, Kejimkujik and Pebbleloggitch Lakes had consistently higher porewater TDP and SRP concentrations than comparable clearwater lakes lying on similar bedrock (i.e.: Big Dam East and Big Dam West Lakes; Figures 20 and 21, respectively).

Most lakes showed a gradient from lower phosphorus concentration in near surface sediment to higher concentrations in deeper sediments, while relative proportions of TDP and SRP remained approximately constant for the different lake types. The relative proportions of porewater phosphorus fractions (TDP and SRP) varied between lake types. Lakes with aerobic surface sediments overlain by oxic water tended to have about 30% of the TDP as SRP compared to almost 90% in sediments overlain by anoxic water for extended periods. The relative proportion of TDP as SRP tended to be consistent over the length of the profile.

Porewater SRP gradients tended to be shallow in clearwater oligotrophic lakes with low sediment phosphorus concentrations. Many of these lakes (Canns, Mud, Anthony, Jake Lee, Newton and Adelaide Lakes) had vertical profiles which gave zero slope and no correlation with sediment depth. Some clearwater lakes with higher sediment phosphorus concentrations such as Beaverskin and Wolfe Lakes had shallow gradients (slope < 0.002). Coloured lakes with progressively higher sediment phosphorus concentrations showed stronger gradients ranging from 0.004 $ugP \cdot l^{-1} \cdot cm^{-1}$ in East Twin Lake (colour = 40 H.u.) to 0.037 $ugP \cdot l^{-1} \cdot cm^{-1}$ in Big Dam West Lake (colour = 100 H.u.). The strongest gradients (0.050 $ugP \cdot l^{-1}$ cm^{-1}) were found in two eutrophic lakes, Laytons Lake and the artificially fertilized Jordan Lake.

Only two lakes showed negative slopes indicating a decrease in porewater SRP with increasing sediment depth. These were Anthony and Little Springfield Lakes which both had a slope of -0.001 $ugP \cdot l^{-1} \cdot cm^{-1}$. Little Springfield Lake and Anthony Lake also had the lowest SRP concentrations in porewaters of any lake sampled. Drain Lake showed a negative slope on one sampling occasion but the average of three measurements used to calculate flux (Table 8) was positive.

3.3.5. Porewater Metals. Porewater Al, Fe, Mn and Ca concentrations measured in Beaverskin, Big Dam East, Big Dam West, Little Springfield and Pebbleloggitch Lakes are given in Appendix H. Selected porewater profiles for these constituent measured in these lakes are also illustrated in Figures 19 to 23.

Porewater Al concentrations in the lakes ranged from 0.12 $mg \cdot l^{-1}$ in Beaverskin Lake to 7.2 $mg \cdot l^{-1}$ in Little Springfield Lake sediments. Porewater Al concentrations in the Kejimkujik lakes tended to be greater in the coloured lakes than the clearwater lakes. Al concentrations in porewater were not substantially greater than those of the overlying water and strong Al gradients were not evident in any of the lakes with the exception of Little Springfield Lake. Flux calculations for Al from surface sediments based on the sediment porewater gradients ranged from 0.7 to 240 mgAL$\cdot$m^{-2}.yr^{-1} which indicated that some Al is being returned to the water column from the lake sediments. Aluminum flux from sediments in Big Dam East Lake was small compared to the other lakes (Table 9). Aluminum flux varied with acidity and water colour. The two coloured lakes showed moderate levels of Al flux while Beaverskin and Big Dam East Lakes showed lower flux. The highest flux was calculated in the most acidic lake, Little Springfield Lake, which also had much greater porewater Al concentrations than were measured in the other 4 lakes.

Porewater Fe concentrations were also highest in Little Springfield Lake (up to 19.0 mg$\cdot$l^{-1}) compared to the Kejimkujik Lakes which generally had ca. 5.0 mgFe$\cdot$ l^{-1}. Iron profiles showed strong subsurface gradients with concentration peaks at the oxidized boundary layer (1-2 cm) followed by rapid declines to stable levels which were relatively consistent over the remainder of the profiles.

Table 8. Lake water dissolved organic carbon (DOC), total phosphorus (TP) concentration, pH and inorganic phosphorus (SRP) flux from sediments to overlying water in 25 lakes in the Atlantic region in order of increasing flux (- indicates a negative flux and increased retention in lake sediments).

LAKE	DOC	TP	PH	SRP FLUX
	--- $mg \cdot l^{-1}$	---		$mgP \cdot m^{-2} \cdot d^{-1}$
Anthony	2.1	3.6	6.00	-0.007
L. Springfield	3.3	10.9	3.70	-0.007
Adelaide	2.6	3.1	6.10	0
Bennet	5.0	7.2	6.63	0
Bog Exhibit	16.5	10.5	4.70	0
Canns	4.4	8.5	6.30	0
French	5.0	11.9	5.80	0
Jake Lee	2.4	7.4	5.60	0
Mud	3.4	5.0	5.30	0
Newton	3.4	5.0	5.60	0
Drain	3.9	25.0	4.18	0.002
Jordan	16.3	4.5	5.50	0.007
Big Dam East	3.6	6.7	5.90	0.007
West Twin	7.5	9.5	5.10	0.007
Wolfe	3.0	5.0	6.52	0.011
Beaverskin	3.3	5.0	5.30	0.014
Freshwater	1.8	7.9	7.10	0.014
East Twin	6.2	9.5	4.90	0.029
Jordan	29.1	11.3	6.60	0.050
Mclaren	3.0	13.7	6.70	0.106
Pebble	13.6	14.0	4.37	0.115
Kejimkujik	10.2	10.0	4.82	0.188
Presquile	3.6	10.5	7.40	0.217
Big Dam W.	9.7	11.3	5.20	0.267
Laytons	3.9	25.4	7.30	0.361

Table 9. Aluminum flux from sediments in the 5 study lakes in order of increasing flux.

Lake	pH	Colour (H.u.)	Al Flux $mgAl \cdot m^{-2} \cdot yr^{-1}$
Big Dam East	6.10	10.0	0.37
Beaverskin	5.30	5.0	4.0
Big Dam West	5.40	80.	17.2
Pebbleloggitch	4.50	80.	18.2
Little Springfield	3.70	5.0	127.1

Porewater Mn concentrations were generally low in all lakes (<0.4 $mg \cdot l^{-1}$). No subsurface Mn peak was measured in Big Dam East, Big Dam West or Pebbleloggitch Lake sediments. However, a large sub-surface Mn peak was measured in Beaverskin Lake (Figure 19). Little Springfield Lake sediments exhibited a generally smooth profile with a small subsurface Mn peak at the 1 cm depth.

Porewater Ca ranged from 0.39 $mg \cdot l^{-1}$ in Beaverskin Lake to 9.2 $mg \cdot l^{-1}$ in Little Springfield. The four Kejimkujik Lakes showed positive Ca gradients with increasing sediment depth while Little Springfield Lake showed no surface gradient.

3.4. Sediment Phosphorus Flux.

Phosphorus flux rates calculated from porewater SRP gradients for 25 sites are given in Table 8. Anthony and Little Springfield Lakes both showed negative flux rates of -0.007 $mgP \cdot m^{-2} \cdot d^{-1}$. Clearwater, oligotrophic lakes (colour < 10 H.u.) showed flux rates ranging from 0 to 0.014 $mgP \cdot m^{-2} \cdot d^{-1}$. Coloured lakes showed substantially higher flux rates ranging from 0.029 $mgP \cdot m^{-2} \cdot d^{-1}$ in Mud Lake (colour 40 H.u.) to 0.267 $mgP\ m^{-2}\ d^{-1}$ in Big Dam West Lake (colour 100 H.u.). The highest flux rates were found in Laytons Lake and the fertilized section of Jordan Lake (0.361 $mgP \cdot m^{-2} \cdot d^{-1}$). A relatively high flux was estimated for McLaren Pond (0.106 $mgP\ m^{-2} \cdot d^{-1}$), one of the few lakes with a periodically anoxic hypolimnion. Kejimkujik and Pebbleloggitch Lakes, both highly coloured lakes, but having oxic surface sediments, had flux rates greater than that of eutrophic and anoxic McLaren Pond (Table 8). Multiple regression analyses of flux rates versus dissolved organic carbon (DOC), lakewater total phosphorus and hydrogen ion concentration indicated a significant relationship only between flux and lake water total phosphorus concentration.

Calculation of the percent contribution of sediment derived inorganic phosphorus to the total annual lake phosphorus load showed that sediments can contribute up to 18% of the lake phosphorus but contributes little or no inorganic phosphorus in most lakes (Table 10). Kejimkujik Lake, a large coloured lake with shallow mean depth (4.5 m) had the highest sediment phosphorus flux but Pebbleloggitch, also coloured but with a much lower hydraulic load, had the highest sediment phosphorus contribution. Oligotrophic, headwater lakes with low DOC concentrations (colour) tended to have very little or no internal phosphorus loading. Wolfe, McLaren and Freshwater Lakes, the only lakes with hypolimnia, had surprisingly low sediment phosphorus loadings.

3.5. Phosphatase Bioassay

3.5.1. Enzyme Kinetics. Enzyme kinetics were approximated using Michaelis-Menten kinetic equations. Enzyme activity closely followed first order kinetics up to an asymptote corresponding to V_{max} after which the reaction was zero order with respect to increased substrate concentration. The greatest phosphatase activity at enzyme saturation (V_{max}) was measured in Pebbleloggitch Lake, the most coloured waterbody (Table 11). Among Big Dam East, Big Dam West, and Little Springfield Lakes, V_{max} was similar, while Beaverskin Lake showed the lowest V_{max}.

The Michaelis-Menten constant, K_m, was determined as the substrate concentration at which the initial rate (v_o) was one-half of that measured at V_{max}. Of the 5 lakes where K_m was measured, it was consistently and substantially greater in the two coloured lakes. In both of these lakes K_m was an order of magnitude greater than was measured in the clearwater lakes (Table 11).

3.5.2. Enzyme-pH Relationships. Acid phosphatase activity was measured in 5 lakes over a pH range from 3.0 to 7.0. Results clearly indicated that enzyme efficiency was highly pH dependant. Figure 24 shows that phosphatase activity profiles were "humped" with distinct pH optima but the optima were different between lakes. With the exception of Little Springfield Lake, the pH where phosphatase activity was maximum closely approximated the actual ambient lake water pH of that particular lake. Little Springfield Lake

Table 10. Lake phosphorus concentration ($[P]_r$), water residence time ($T_{(w)}$), hydraulic load (q_a), estimated inflow phosphorus ($[P]_i$), total (L(P)) and sediment phosphorus load (S(P)) and percent sediment contribution (S(P)/L(P)) in 15 lakes where hydrologic and morphometric data were available.

Lake	$[P]_r$	$T_{(w)}$	q_a	$[P]_i$	L(P)	S(P)	S(P)/L(P) %
Beaverskin	5.0	1.02	2.2	10.1	22.	2.0	9.2
Bennett	7.2	0.05	50.	8.7	432.	0.0	0.0
Big Dam East	6.7	0.62	3.7	12.0	44.	1.1	2.4
Big Dam West	11.3	0.08	32.	14.4	464.	29.2	6.3
Bog Exhibit	10.5	-	-	-	-	0.0	0.0
Canns	8.5	0.16	13.	11.9	150.	0.0	0.0
Drain	25.0	-	-	-	-	0.0	0.0
Freshwater	7.9	0.50	13.	13.5	174.	3.5	2.0
French	10.0	0.08	12.5	12.9	161.	0.0	0.0
Kejimkujik	10.0	0.18	24.	14.3	339.	44.8	13.2
L. Spring	10.9	-	-	-	-	0.0	0.0
McLaren	13.7	0.15	37.7	18.9	713.	30.0	3.5
Pebble	14.0	0.35	4.1	22.3	91.	16.0	17.6
Presquile	10.5	0.07	31.	13.2	408.	14.3	3.5
Wolfe	5.0	0.53	7.3	8.6	62.	2.5	4.0

where $[P]_r$ = average annual concentration of total phosphorus in the lake ($mgP \cdot m^{-3}$).
$T(_w)$ = water residence time in years.
q_a = hydraulic load ($m \cdot yr^{-1}$).
$[P]_i$ = calculated average inflow total phosphorus concentration ($mgP \cdot m^3$).
L(P) = loading of total phosphorus per unit lake surface area ($mgP. m^{-2} \cdot yr^{-1}$).
S(P) = sediment phosphorus input ($mgP \cdot m^{-2} \cdot yr^{-1}$).
- = indicates that these data were not available but were unnecessary since flux was zero anyway. Ten lakes had measurable flux but no data for one or more of the above model inputs.

Table 11. Michaelis-Menten kinetic constants for acid phosphatases in selected lakes.

Lake	Date	V_{max} (nmoles·l^{-1}·min^{-1})	K_m (mmoles·l^{-1})
Beaverskin	8 July 1987	4.4	0.04
Big Dam East	"	38.2	0.02
Big Dam West	"	32.6	0.17
Little Springfield	"	45.1	0.01
Pebbleloggitch	"	100.0	0.14

did not follow this trend. The pH optima for Little Springfield Lake was measured around pH 6.5 compared to its ambient pH of 3.9. The higher optimum pH more closely approximates the historical pH of the lake (based on the pH of similar, adjacent undisturbed lakes) and not its more recently acidified condition.

The magnitude of the effect of pH change on enzyme activity varied between the lakes depending on the magnitude of the change and the proximity to the optimum pH. All the lakes showed rapid declines in enzyme hydrolysis rates below pH 5.5 (Figure 24).

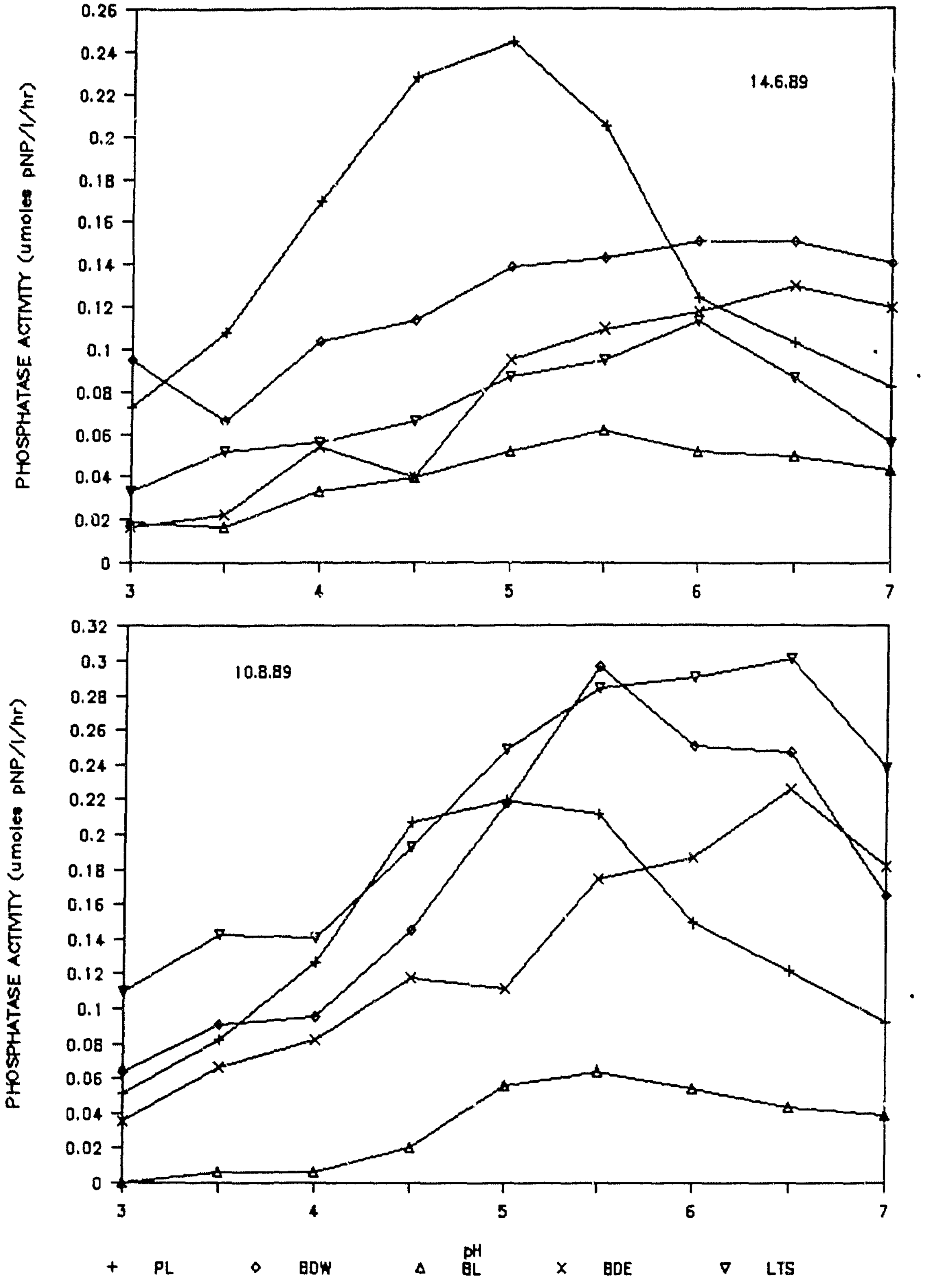
3.5.3. Enzyme Inhibition. Two metals, Al and Fe, known to interfere with phosphatase activity were added to water samples collected from Beaverskin, Big Dam East, Big Dam Westand Pebbleloggitch Lakes to test the direct effects of inorganic, labile forms of these two metals on phosphatase activity. The addition of $AlCl_3$ to freshly collected water samples from the four lakes, showed that phosphatase enzymes had a reduced capability to hydrolyse pNPP substrates in the presence of inorganic aluminum concentrations of 200 $ugAl \cdot l^{-1}$ (Table 12).

In Pebbleloggitch Lake the effect of adding inorganic aluminum was substantial, causing a 68% reduction in phosphatase activity in ambient lake water. In the other

Figure 24: Acid phosphatase activity versus pH in 5 lakes.

FIGURE 24

PHOSPHATASE ACTIVITY vs PH



lakes the effect of the added inorganic aluminum was greater. In Beaverskin and Big Dam West Lakes, the additional labile aluminum completely stopped the hydrolysis of the substrate. Phosphatase activity was reduced by 95% in Big Dam East Lake. Inorganic iron added to water samples from the 5 lakes had no inhibitory effect at Fe concentrations ranging from 100 to 2000 ugFe l^{-1}.

3.5.4. Phosphatase Activity. Simultaneous measurements of pH colour, Al and Fe concentrations and phosphatase activity were carried out in the study lakes on different occasions as shown in Table 13. Beaverskin Lake had consistently lower phosphatase activity compared to the other lakes, especially Big Dam East Lake which had slightly higher pH, comparable metal concentrations but slightly higher organic content (water colour). The highest levels of phosphatase activity were consistently found in the two coloured lakes, Big Dam West and Pebbleloggitch Lakes (Table 13). Phosphatase activity in these two lakes was generally in the order of 2 to 3 times greater than that measured in any of the clear water lakes, including Little Springfield Lake. As indicated previously as well as in this data set, coloured lakes had consistently greater metal concentrations accompanying the greater water colour. Little Springfield Lake had a phosphatase activity comparable to that of Beaverskin Lake on the 14 June survey and a slightly higher

Table 12. Comparison of mean phosphatase activity (in umoles pNP$\cdot l^{-1}\cdot min^{-1}$) in control samples versus samples with the sample inorganic aluminum concentration raised by 200 ugAl$\cdot l^{-1}$. (± st.dev., n=4).

Lake	Control	Treated
Beaverskin L.	0.006 (±0.002)	0 (±0.0)
Big Dam East L.	0.093 (±0.008)	0.005 (±0.004)
Big Dam West L.	0.128 (±0.009)	0 (±0.0)
Pebbleloggitch L.	0.182 (±0.070	0.058 (±0.008)

Table 13. Comparison of pH, colour, phosphatase activity, aluminum and iron concentrations in lake water at selected sites on several dates.

Lake	pH	Colour (H.u.)	Phosphatase Activity (umoles pNP$\cdot$l$^{-1}\cdot$hr^{-1})	Al	Fe
				--- mg$\cdot$l^{-1}	---
22 JULY 1987					
Beaverskin	5.3	5	0.065	0.05	0.04
Pebbleloggitch	4.5	80	0.297	0.22	0.18
23 JUNE 1988					
Beaverskin	5.4	5	0.048	0.03	0.06
Big Dam East	5.9	10	0.121	0.07	0.04
Big Dam West	5.4	80	0.256	0.18	0.18
Pebbleloggitch	4.6	95	0.339	0.25	0.21
14 JUNE 1989					
Beaverskin	5.3	5	0.055	0.04	0.04
Big Dam East	6.3	10	0.130	0.09	0.04
Big Dam West	5.4	65	0.143	0.18	0.18
Pebbleloggitch	4.6	100	0.228	0.47	0.42
Little Springfield	3.9	5	0.054	3.30	0.78
10 AUGUST 1989					
Beaverskin	5.3	5	0.059	0.03	0.08
Big Dam East	6.2	5	0.202	0.04	0.02
Big Dam West	5.6	60	0.296	0.20	0.16
Pebbleloggitch	4.6	90	0.207	0.20	0.18
Little Springfield	3.8	5	0.141	2.20	0.65

phosphatase activity comparable to that of Big Dam East Lake on the 10 August survey. In spite of being substantially more acidic and having exceptionally high Al and Fe concentrations, Little Springfield Lake did not have phosphatase activity as high as was measured in the two coloured lakes.

Bivariate correlations and a factor analysis based on this data set are presented in Table 14. Lake water acidity was, once again, strongly correlated with metal concentrations. The correlation matrix and factor analysis both indicated that phosphatase activity was more closely associated with water colour indicating a possible relationship between enzyme activity and the organic content of the water.

3.5.5. Core Incubations. Results of the core incubation experiments for 4 of the 5 lakes are presented in summary form in Table 15 and in greater detail in Appendix H. The results for Little Springfield Lake incubations were not presented because pH in the cores from this lake could not be controlled without excessive additions of acid and base, possibly due the strong buffering capacity from mineral acids, aluminum or a combination of both of these.

The most visible difference in the treatment cores from the other 4 lakes incubated at the selected pH levels, was the DOC concentration in the water above the sediment after the incubation period.

Table 14. Correlation matrix and principal components analysis of lakewater pH, metal concentrations and acid phosphatase activity (PASEW) for sampling dates where all variables were measured coincidently (n=31).

PEARSON CORRELATION MATRIX:

	PH	COLOUR	PASEW	AL
PH	1.000			
COLOUR	-0.271	1.000		
PASEW	-0.276	0.681*	1.000	
AL	-0.708*	-0.220	-0.010	1.000
FE	-0.826*	0.075	0.202	0.936*

* = $p < 0.01$

PRINCIPAL COMPONENTS ANALYSIS:

ROTATED FACTOR LOADINGS

	1	2
PH	-0.874*	-0.287
COLOUR	-0.024	0.933*
PASEW	0.122	0.891*
AL	0.958*	-0.195
FE	0.979*	0.090
	acidity metals	organic content

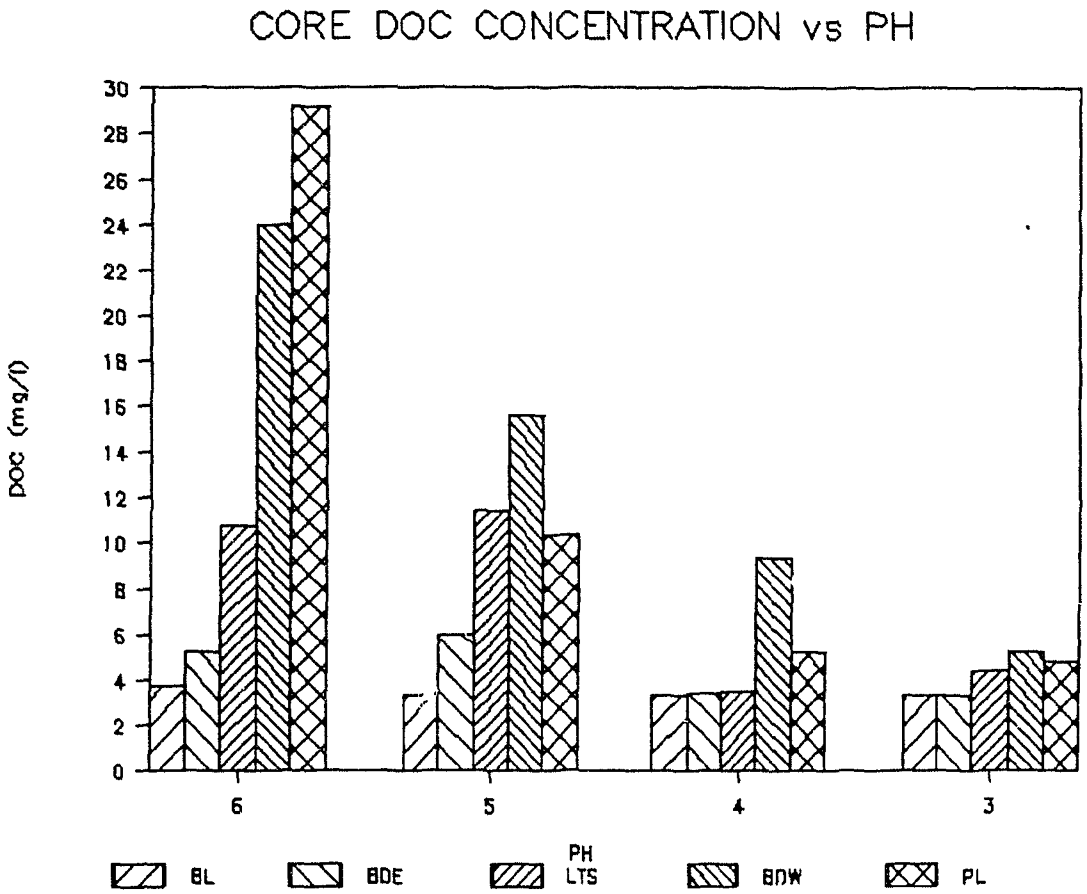
PERCENT OF TOTAL VARIANCE EXPLAINED

1	2
53.106	35.848

* = Component where variable has its highest loading.

Figure 25: Dissolved organic carbon concentrations in control and experimentally acidified cores from 4 lakes.

FIGURE 25


CORE DOC CONCENTRATION vs PH
DOC (mg/l)
30
28
26
24
22
20
18
16
14
12
10
8
6
4
2
0
6
5
4
3
PH
BL
BDE
LTS
BDW
PL

The DOC concentrations in the incubated cores are presented in Table 15 and illustrated in Figure 25. Dissolved organic carbon concentrations were found to be directly related to pH in almost all of the cores although the differences in DOC concentrations were least noticeable in clear water lakes, especially Beaverskin and Big Dam East Lakes where DOC concentrations did not show large differences at higher or lower pH, although the non-parametric ANOVA did show significant differences amongst cores (Table 16). When compared to controls, no significant differences in DOC concentration were found in Beaverskin L. Differences in DOC concentrations in cores collected from Big Dam East L. were significantly lower at pH 4.0 and 3.0 compared to the controls (Table 17). The largest differences in DOC concentrations were measured in cores collected from Big Dam West and Pebbleloggitch Lakes. In Pebbleloggitch Lake, DOC concentrations were reduced by half at pH 4.0. Increasing pH caused DOC concentration in the cores to increase from an average of 10.4 mg l^{-1} under ambient pH conditions to an average of 29.2 mg l^{-1} at pH 6.0. In Big Dam West cores, the differences were similar.

Metal concentrations in the water of most of the cores changed only slightly in the pH 5.0 to 6.0 range. However, when core pH was decreased below 5.0, aqueous metal concentrations increased markedly, reaching maximum values in the pH 3.0 cores. Aluminum and iron showed the largest

Table 15. Mean concentration of DOC, aluminum, iron, manganese, calcium, soluble reactive phosphorus (SRP) and acid phosphatase activity in water (pase-w) and surface sediments (pase-s) in cores incubated at selected pH levels (n=6 for each treatment in each lake).

pH	DOC	Al	Fe	Mn	Ca	SRP	Pase-W	Pase-S
	------------ mg l^{-1} --------					$ugP \cdot l^{-1}$	$umoles \cdot l^{-1} \cdot hr^{-1}$	
Beaverskin L.-								
6.00	3.7	0.24	0.08	0.06	0.60	2.8	0.058	-
c-5.20	3.3	0.29	0.07	0.09	1.20	2.5	0.058	-
4.00	3.3	2.15	0.05	1.21	4.20	1.8	0.055	-
3.00	3.3	24.3	1.30	1.94	8.20	3.4	0.102	-
Big Dam East L.-								
c-6.10	5.2	0.35	0.40	0.43	-	3.2	0.173	0.423
5.00	6.0	0.30	0.41	0.78	-	2.9	0.178	0.310
4.00	3.4	2.58	1.29	4.54	5.70	2.8	0.121	0.197
3.00	3.3	26.4	2.45	5.50	-	4.1	0.230	0.246
Big Dam West L.-								
6.00	24.0	0.50	0.83	0.03	0.77	4.5	0.244	0.340
c-5.50	15.6	0.49	1.53	0.05	-	3.7	0.238	0.236
4.00	9.4	0.92	0.63	0.12	4.22	3.7	0.144	0.262
3.00	5.2	10.6	3.18	0.37	5.80	2.4	0.335	0.412
Pebbleloggitch L.-								
6.00	29.2	0.58	1.28	0.05	0.38	7.3	0.102	0.070
c-4.70	10.4	0.32	0.59	0.06	-	4.4	0.215	0.243
4.00	5.2	1.14	4.51	0.06	3.20	3.2	0.166	0.199
3.00	4.8	8.02	12.7	0.10	6.35	2.5	0.151	0.147

c = control (ambient lake water pH, no treatment).
- = no data.

Table 16. Comparison of differences between metal concentrations, soluble reactive phosphorus concentration and acid phosphatase activity in water (pase-w) and surface sediments (pase-s) in treatment cores held at selected pH levels and control cores using Kruskal-Wallis non parametric ANOVA. (n=6 in all cases).

Lake	DOC	Al	Fe	Mn	Ca	SRP	Pase-W	Pase-S
Beaverskin L.-								
H stat	13.8	19.6	11.4	19.1	19.0	3.73	17.6	nd
D.F.	3	3	3	3	3	3	3	-
Prob.	0.01	0.01	0.01	0.01	0.01	ns	0.01	-
Big Dam East L.-								
H stat	19.3	19.5	15.6	16.2	nd	1.49	12.2	20.9
D.F.	3	3	3	3	-	3	3	3
Prob.	0.01	0.01	0.01	0.01	nd	ns	0.01	0.01
Big Dam West L.-								
H stat	21.6	16.8	2.6	19.	8.2	0.82	10.9	13.8
D.F.	3	3	3	3	2	3	3	3
Prob.	0.01	0.01	ns	0.01	0.01	ns	0.05	0.05
Pebbleloggitch L.-								
H stat	21.4	19.8	11.4	10.1	3.6	10.1	14.1	15.9
D.F.	3	3	3	3	2	3	3	3
Prob.	0.01	0.01	0.01	0.05	ns	0.05	0.01	0.01

n.d. = no data
n.s. = not significant
H Stat = Kruskal Wallis statistic
D.F. = degrees of freedom

Table 17. Comparison of treatment versus control core metal concentration, soluble reactive phosphorus concentration and acid phosphatase activity in water (P-W) and surface sediments (P-S) using Tukey type nonparametric multiple comparison test.

Comparison (A. vs Control)	DOC	Al	Fe	Mn	Ca	SRP	P-W	P-S
Beaverskin L.-								
3.00 vs 5.20 q	0.0	6.6*	5.3*	5.6*	6.5*	na	6.6*	nd
4.00 vs 5.20 q	0.0	3.9*	0.2	3.7*	3.8*	na	4.6*	nd
6.00 vs 5.20 q	3.7*	0.2	1.1	1.5	0.4	na	0.1	nd
Big Dam East L.-								
3.00 vs 6.10 q	4.2*	7.0*	5.8*	6.5*	nd	na	7.4*	9.6*
4.00 vs 6.10 q	3.9*	4.3*	3.6*	6.1*	nd	na	4.3*	7.2*
5.00 vs 6.10 q	1.1	0.5	0.4	1.9	nd	na	0.2	6.6*
Big Dam West L.-								
3.00 vs 5.60 q	8.7*	4.4*	0.6	3.8*	nd	na	3.8*	7.0*
4.00 vs 5.60 q	7.0*	2.5	2.9	1.9	nd	na	6.2*	0.8
6.00 vs 5.60 q	4.1*	0.2	0.6	1.8	nd	na	2.3	3.5*
Pebbleloggitch L.-								
3.00 vs 4.70 q	9.7*	8.5*	6.5*	5.3*	nd	2.5	2.5	4.0*
4.00 vs 4.70 q	9.6*	4.7*	3.2	2.0	nd	1.7	4.9*	2.5
6.00 vs 4.70 q	12.5*	3.2	2.9	0.0	nd	2.9	9.0*	5.9*

* = significant at $p < 0.05$
n.d. = no data
n.a. = not applicable

increases although manganese and calcium were also mobilized from sediments. With the exception of Fe in Big Dam West and Ca in Pebbleloggitch Lake, non-parametric analysis of variance (ANOVA) indicated that pH had a significant overall effect on Al, Fe, Mn and Ca concentrations in the cores (Table 16). Multiple comparison tests of metal concentrations in treated cores compared to the control cores also showed that the largest differences occurred in the most acidic cores (Table 17). Although significant increases in Al, Fe, Mn and Ca concentrations were observed in the cores from the clear water lakes at pH 4.0, this was generally not found to be the condition in the two coloured lakes. Aluminum concentration in Pebbleloggitch Lake was the only constituent to increase significantly in the coloured lakes above pH 3.0.

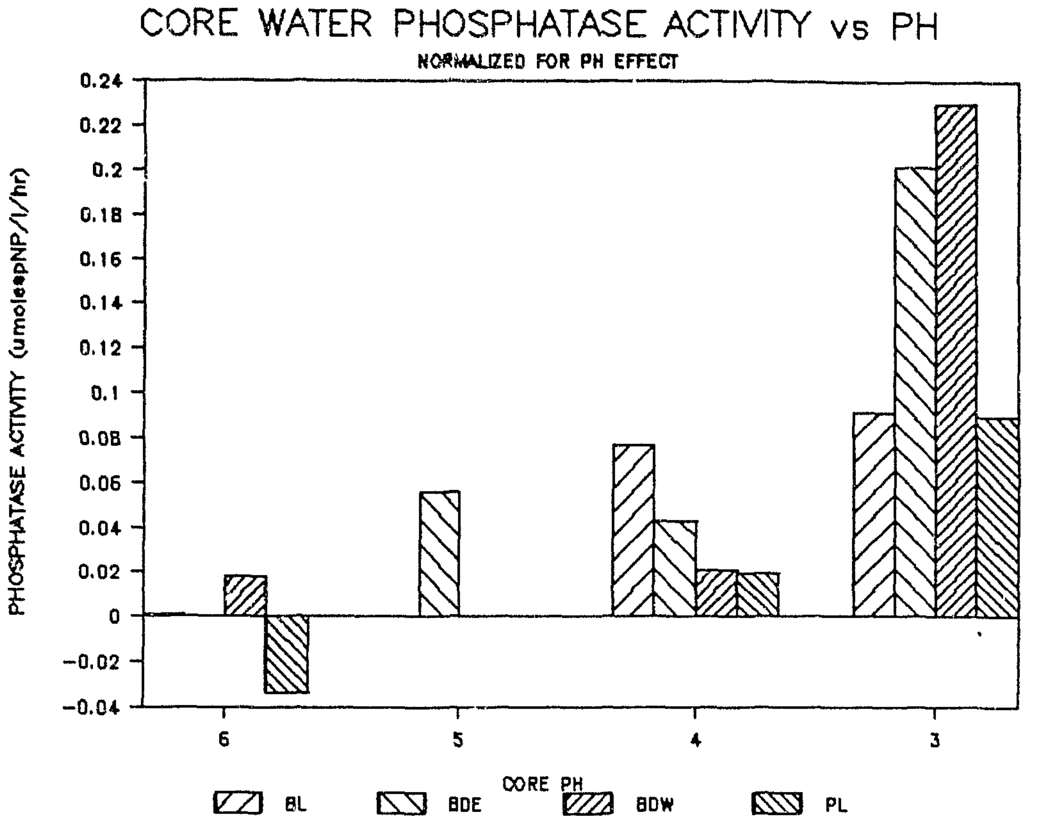
The SRP concentrations were found to decrease with increasing acidity (Table 15), except in Beaverskin and Big Dam East Lakes where SRP concentrations increased in the pH 3.0 cores. Analysis of variance and multiple comparison tests indicated that the increase was not statistically significant at $p < 0.05$.

Phosphatase activity in water and surface sediments of the cores generally showed no consistent relationship with increasing acidity and metal concentrations. Phosphatase activity in the surface water and sediments of the cores generally decreased with increasing acidity although only small differences in enzyme activity were measured in the pH

5.0 - 6.0 range. Significant decreases in phosphatase activity were found in pH 4.0 cores compared to controls from all 4 lakes. A significant decrease was also measured in the pH 6.0 set of cores collected from Pebbleloggitch Lake. In Beaverskin, Big Dam East, and Big Dam West Lakes, significant increases in phosphatase activity in water and sediments were noted in the pH 3.0 cores. No increase in phosphatase activity was measured in pH 3.0 cores from Pebbleloggitch Lake. Phosphatase activity has been shown to be strongly pH dependant and having distinct optima at pH values close to ambient lake pH. Phosphatase activity is known to be depressed by departures from ambient conditions. To illustrate changes in phosphatase activity not related to pH changes, the data were normalized to pH based on the data illustrated in Figure 24. Figure 26 illustrates the difference in phosphatase activity in manipulated cores from those measured in the control cores from the 4 lakes. It was apparent that substantially greater phosphatase activity was observed in increasingly acidic cores.

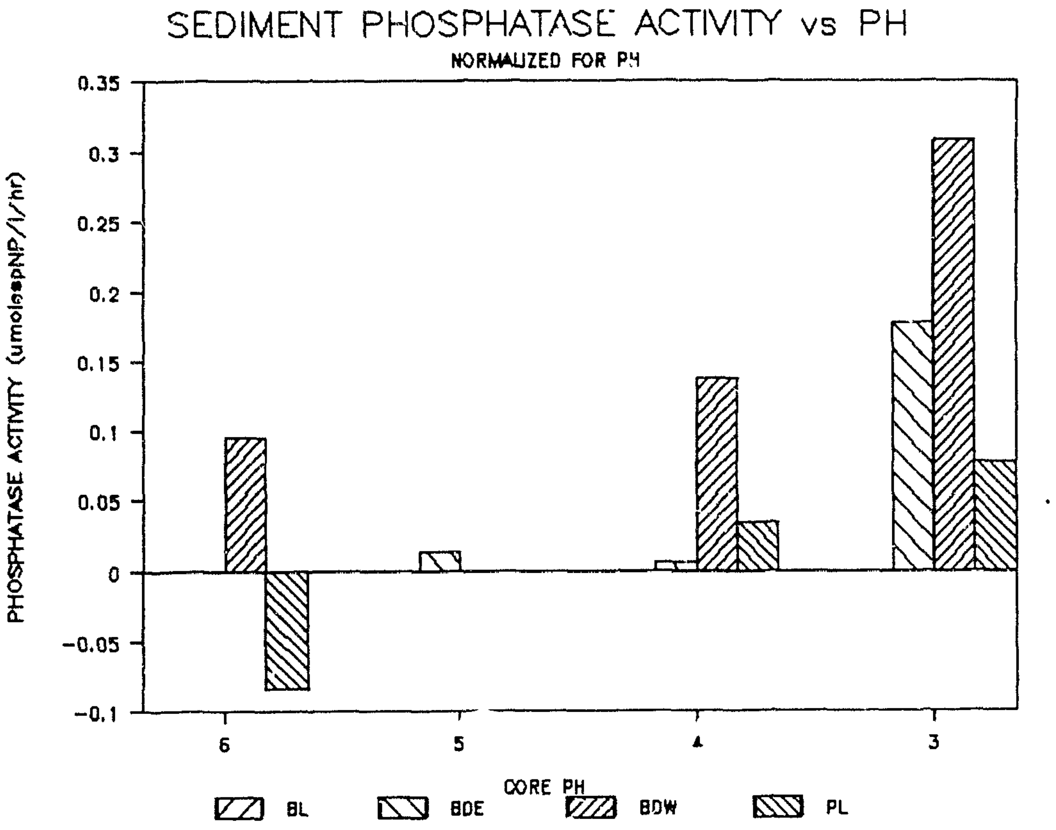
Figure 26: Phosphatase activity in experimental cores illustrated as the difference between activity at ambient (control) pH compared to experimental pH.

FIGURE 26



CORE WATER PHOSPHATASE ACTIVITY vs PH

NORMALIZED FOR PH EFFECT



SEDIMENT PHOSPHATASE ACTIVITY vs PH

NORMALIZED FOR PH

4. DISCUSSION

An understanding of phosphorus dynamics in freshwater requires a knowledge of naturally occurring phosphorus compounds and their biological and chemical transformations. Epilimnetic phosphorus cycling has been intensively researched for some time (eg: Lean 1973) although much of the work has concentrated on more productive (eutrophic) systems. The phosphorus cycle in acidified lakes and the effects of the process of lake water acidification is less well understood.

Several studies have indicated that microbial communities and organic decomposition rates may be adversely affected by increased lake water acidification (Grahn _et_ _al_. 1974; Leivestad _et_ _al_. 1976; Rao 1982; Kelly _et_ _al_. 1984). Indirect evidence has suggested that phosphorus turnover rates and availability may be impeded by lake water acidification indirectly through reductions in organic matter mineralization and directly through phosphorus-metal interactions. Increases in organic accumulation rates and metal concentrations in sediments have been linked to recent increases in acid deposition and increased lake water acidification. Few studies have attempted to examine the effects of lake acidity or acidification on phosphorus supply due to the complex nature of phosphorus chemistry and dynamics in lake water, biota and sediments.

The objective of this study was to examine water chemistry, sediment geochemistry, and phosphatase enzyme activity in order to gain insight into phosphorus compartmentalization, chemical relationships and the effects of acidification on phosphorus cycling and availability in acid and non-acid lakes. Phosphatase activity was also used to investigate one method by which organisms may be able to compensate for any detrimental effects of increased acidity on phosphorus supply. Compensation capacity is also extremely difficult to measure and is often overlooked in ecological studies of perturbations and stress.

Much of the available literature concerning the effects of increased acidity on decomposition rates in lakes has been directed at the lake benthos. In order to determine the importance of lake sediments in lake phosphorus supply and assess potential effects of further lake acidification, inorganic phosphorus flux from lake sediments was measured in 25 lakes (Table 8). Based on pH and organic content, a subset of 5 of these lakes was selected for more detailed study of sediment geochemistry and phosphorus availability.

Most of the study sites are located in areas which receive moderate levels of acid deposition (15-20 kg wet SO_4 ha^{-1}) and are known to be sensitive to acidification (Kerekes et al. 1986), although a few of the lakes are situated on well buffered soils (eg: Laytons Lake). A wide range in lake water pH was measured, even for lakes located on poorly buffered soils. This was largely because of small scale heterogeneity in soil chemistry, drainage characteristics, hydrology and the resulting lake water chemistry.

4.1. Water Chemistry.

Lakes found on poorly buffered soils in the Atlantic region are typically oligotrophic, slightly to moderately acidic, and have either clear or coloured water depending on the extent of bog influence. During the last ice age, all of the Atlantic region was glaciated and presently consists of a low rolling landscape with many lake catchments still having areas of exposed bedrock. Many have areas of poor drainage and varying degrees of bog development. Lakes with high water colour (> 30 H.u.) and concentrations of dissolved organic matter are not uncommon, although water colour can vary widely among the lakes throughout the region (Table 3).

Total phosphorus concentrations in lake water were generally low ($<25\ ugP\cdot l^{-1}$) with greater concentrations usually associated with greater water colour and DOC concentration (Figure 9). Total dissolved phosphorus (TDP) accounted for 20% to 30% of the total phosphorus pool in clear lakes compared with 40% to 60% in coloured lakes. Soluble reactive phosphorus (SRP) accounted for less than 10% of the total phosphorus in the study lakes and, in most cases, was below detection limits ($1.0\ ugP\cdot l^{-1}$). Particulate phosphorus accounted for the remainder of the phosphorus pool. Total phosphorus was significantly ($p < 0.05$) correlated with dissolved organic carbon (DOC). Only a small proportion of the total phosphorus was found in the inorganic fraction with the remainder divided between particulate and dissolved organic phosphorus.

Studies of organic phosphorus budgets in lakes have indicated that organic phosphorus compounds are primarily derived allochthonously (Hobbie and Likens 1973; McDowell and Fisher 1976; Wetzel and Manny 1977; Moeller _et al_ 1979) with the largest fraction of organic phosphorus being comprised of relatively refractory, high molecular weight dissolved organic phosphorus compounds (Bourboniere 1986). The import of phosphorus containing materials and their form depends on several watershed characteristics including drainage area, soil chemistry, forest cover, and land use (Moeller _et al_. 1979; Tate and Meyer 1983; Meyer and Tate 1983).

Although much of the phosphorus imported into lakes is refractory, various abiotic processes and activities of lake biota, can break these down to produce low molecular weight DOP compounds which can be important to algae and bacteria through heterotrophic mechanisms which recover useable phosphorus from refractory organic phosphorus compounds. Low molecular weight DOP compounds can be released from the breakdown of refractory DOP by ultraviolet light (UV sensitive DOP). The relative importance of these regenerative processes varies spatially and temporally depending on a variety of interrelated factors.

Beauchamp and Kerekes (1989) measured rates of planktonic primary production at light optimum (P-max) in 2 lakes with high DOC concentrations and compared these to simultaneous measurements made in a clear water lake. Planktonic primary productivity was found to be consistently higher in the two coloured lakes. This suggests that under certain conditions DOP compounds may constitute an important component of the phosphorus cycle in some lakes. The actual importance may vary depending on the forms of DOP and their sensitivity to UV degradation or enzymatic hydrolysis. The role of DOP is discussed further in the following section on phosphatase activity.

Total phosphorus in lake water was negatively correlated ($p < 0.05$) with lake water pH (Table 5). This negative relationship was related to two mechanisms. Dissolved organic compounds are, to a large extent, comprised of weak organic acids (humic and fulvic acids) and increasing DOC concentrations are generally accompanied by lower pH. Because of the association between DOC and phosphorus, the tendency toward lower pH and increasing DOC concentration is accompanied by increased total phosphorus concentrations. A relationship between pH and total phosphorus was also found in the absence of substantial difference in DOC concentration. When only clear water lakes, those with DOC concentrations less than 30 H.u. (Beaverskin, Big Dam East and Little Springfield Lakes), are considered there is still a significant ($p < 0.01$) negative relationship between phosphorus concentrations and lake water acidity. Total phosphorus concentration increased with increasing acidity in these 3 lakes although the increase could be related to differences in watershed phosphorus loading. Detailed phosphorus budgets necessary to determine these differences in loadings for the 3 lakes were not available.

Metal concentrations in lake water increased significantly with increasing lake water acidity ($p < 0.01$; Table 5). Metals are known to be mobilized from catchment soils and lake sediments in areas impacted by acid deposition (Campbell et al. 1983; Carignan and Nriagu 1985). Arafat and Niragu (1986) found that metal mobilization from lake sediments increased exponentially at pH less than 4.0. It was also evident from core incubations in this study, that metals are mobilized from sediments by increased acidity. The greatest increases were measured in the most acidic cores (Table 15). Organic substances are known to form complexes with Al and Fe which was evident in the relationships observed between DOC and metals in the Kejimkujik area lakes (Figures 7 and 8). The correlations between DOC and metals for the 5 lakes together were weakened by the inclusion of Little Springfield Lake. The strong mineral acidity measured in this lake in the absence of large DOC concentrations but accompanied by elevated concentrations of metals. This biased the regression away from DOC concentration (Table 5). This same bias was also apparent in the principal components analysis (PCA) which indicated that Al concentration is almost exclusively pH dependant. Although Al concentrations and speciation are known to be highly pH dependant (Havas and Jaworski 1986), Al concentrations are higher in coloured lakes than would be expected based on pH alone.

In the presence of large amounts of DOC, much of the Al and Fe are associated with dissolved organic matter and would probably be mainly unreactive (Burrows 1977). In extremely acidic lakes, such as Little Springfield Lake, which has low DOC concentrations (organic complexes flocculate out of solution at low pH), Al is generally found in more reactive forms (Baker and Schofield 1982). Seasonal trends in organic anions and aluminum in Beaverskin and Pebbleloggitch Lakes are discussed by Kerekes et al. (1986). Increased transparency in lakes undergoing acidification has been widely documented (e.g. Effler et al. 1984; Shearer et al 1987). The increase in transparency and extended euphotic zone in acidic lakes has been directly linked to the loss of DOC from the water column (Schindler et al. 1985). Substantial amounts of Al, Fe and organically bound phosphorus are also probably transported to sediments by this process. This process may partially explain long-term decline in total phosphorus measured in Scandinavian lakes by Grahn et al. (1974) although this does not preclude a direct involvement by Al or other metals and the formation of insoluble inorganic precipitates.

4.2. Sediment Geochemistry.

Sediment geochemistry in the 5 lakes was studied to provide information related to phosphorus diagenesis, mobility, and flux. Sediment chemical profiles were also examined for changes which may indicate recent lake water acidification. These data were also examined for evidence pertaining to the extent of watershed and lake water acidification in the region and how various lake types were affected.

The chemistry of sediment at any particular depth is determined by a number of factors including: 1) the chemistry of the material eroded from the lake basin; 2) net sedimentation of material derived from within the lake and; 3) additions, losses or changes in material occurring after deposition by various diagenetic processes (ie: bioturbation, diffusion and leaching). In undisturbed lakes, diagenetic changes are usually greatest near the sediment surface (more recently deposited material) and have no effect by 3 to 5 cm (Berner, 1980; Norton 1984a). Thus, lakes and catchments in long-term steady states (ie: having had no watershed disturbance or change in atmospheric input) should have sediment chemistry which, below about 5 cm, is relatively constant.

Sediment geochronology is commonly determined dated by ^{210}Pb or ^{137}Cs methods corroborated with pollen, charcoal, and diatom stratigraphy (Battarbee 1984; Dickman et al. 1984;

Charles and Norton 1986). Many studies have also included chironomid and mallomonadacean chrysophyte remains as indicators of past limnological conditions (Warwick 1980; Smol et al. 1984a,b; Smol 1986). These data were not available so estimates of sediment accumulation rates and geochronology for the 5 study lakes were based on stable Pb profiles. Lead profiles provide only long-term (decade) estimates of sediment accumulation rates and lack the precision of these other methods since they do not account for short-term (seasonal or annual) variations in sedimentation rates.

Sedimentation rates estimated by this method for the Kejimkujik area lakes (0.10-0.27 cm·yr^{-1}; Table 8) were similar to values reported for other oligotrophic lakes dated using ^{210}Pb, including Kejimkujik Lake (0.20 cm·yr^{-1}; Wong et al. 1989), Big Moose Lake (0.20-0.25 cm·yr^{-1}; Charles et al. 1987) and the Turkey Lakes watersheds (0.2-1.3 cm·yr^{-1}; Johnson et al. 1986). However, accumulation rates estimated for the 5 lakes in this study were lower than those reported for Experimental Lakes Area lakes which ranged from 0.54 to 0.95 mm·yr^{-1} (Anderson et al. 1987) and several lakes in Quebec (0.28-0.33 mm·yr^{-1}; Ouellet and Jones 1983).

The sedimentation rate for Little Springfield Lake was not calculated since this lake has recently been subjected to large influxes of particulate material from extensive watershed disturbance including the development of commercial and residential properties and construction of a major highway. Cultural development has accelerated in the last 10 years and exposure of pyritic slate bedrock has largely been responsible for the high acidity in Little Springfield Lake and other lakes in the vicinity (Kerekes; unpub. data). Sedimentation rates estimated for this lake based on the stable Pb profile would have little interpretive value since accumulation rates have been highly variable between years. Sedimentation rates estimated for the other study lakes were adequate for comparisons between records of known disturbances in lake watersheds and changes in sediment chemistry.

While none of the study lakes had sediment chemical profiles which indicated an absolute steady state, sediments in the four Kejimkujik area lakes showed relatively minor changes over the range measured by the cores. Little Springfield Lake showed the most variability in chemical concentration profiles which reflected extensive disturbance in its watershed. Sediments in this lake showed a major shift in the profiles of most constituents at 10 cm depth which probably corresponded to highway construction within the lake catchment. More recent inputs of sediment from construction activities in the upper portion of the catchment have been observed and sedimentation rates in this basin have continued to be highly variable over time.

Disturbance of pyritic slates within the catchment of Little Springfield Lake and subsequent microbial oxidation of these slates has led to the extreme lake water acidity (pH

3.8) and increased leaching of metals and bas cations from surrounding catchment. Increased acid leaching in the watershed has been the primary cause of the high conductivity and metal concentrations measured in the lake water (Kerekes et al. 1984). Ionic constituents, especially calcium, magnesium, aluminum, iron and manganese, were also found in substantially higher concentrations in Little Springfield Lake than less acidic waterbodies in the region including the other 4 Kejimkujik lakes. The 4 Kejimkujik lakes have also been disturbed in the past but to much less extensively. These lakes are situated on non-pyritic slates and relatively inert igneous bedrock substrates overlain by a thin layer of glacial till. Subsequently, sediment and lake water conductivities and chemical concentrations are lower than those measured in Little Springfield Lake.

4.2.1. Water, Organic and Mineral Content. Sediments in all of the study lakes had a high percentage of the wet weight as water content and low percent organic material which is consistent with the oligotrophic nature of the lakes. Greater water content in surface sediments when compared to deeper sediments was primarily due to less compaction and slightly greater organic content. Norton et al. (1981) found greater water content in the sediments of acidic lakes when compared to similar non-acidic lakes. The greater organic content of sediments in acidic lakes allowed for less sediment compaction. Greater organic content in sediments of the acidic lakes may be related to reduced decomposition rates of organic material and increases in accumulation of organic matter (Kelly et al. 1984). In this study Big Dam East and Pebbleloggitch Lakes did not have higher organic content in the surface sediments compared to deeper in the cores. The absence of any change in the Pebbleloggitch Lake cores was probably related to the shallow depth (< 2.5m) of the lake and the frequency of sediment resuspension, mixing and homogenization by wind and wave action. Beaverskin and Big Dam West Lakes did show increased organic content in surface sediments depth which may be indicative of reductions in organic decomposition rates. Comparisons of the organic content of deeper sections in the sediment cores did not show significant differences between acidic and non-acidic lakes.

Sediments of Pebbleloggitch Lake had slightly greater organic content than did the other lakes which could be explained by the dystrophic nature of this lake. However, Big Dam West Lake which is also dystrophic and more acidic than adjacent Big Dam East Lake which is not dystrophic, did not have an organic content in sediment any greater than the latter lake. Organic content in Little Springfield Lake sediments decreased toward the sediment surface which reflected watershed disturbance and increased loading of inorganic material (minerals and clays) imported from the catchment. At the sediment surface and just below (between 0 and 3 cm) organic content increased. This could reflect increased organic accumulation due to high acidity but corroborative evidence is lacking. Overall, there were no obvious trends in organic content of sediments which could be correlated to lake water acidity although increases in Beaverskin Lake sediments suggests a possibility that there may be recent changes in this lake.

4.2.2. Oxidation-Reduction Potential. Redox conditions are important in regulating phosphorus mobility and interactions between Fe and PO_4. The oxidized or reduced state of many substances, including Fe, determines not only their mobility but reactivity. Under oxic conditions, the exchange of inorganic phosphorus across the sediment water interface is predominantly regulated by redox conditions and interactions with Fe which are dependant on oxygen supply. The depth of the oxidized microlayer in sediments is governed by a number of physical, chemical and biological factors including the oxygen content of the overlying water, sediment porosity, sediment chemistry and bioturbation (Syers et al. 1973; Starkel 1985). All five of the lakes where sediment redox was measured, had oxygen saturated water above the sediment. Since none of the lakes had extensive macrophyte development or obvious macroinvertebrate activity, oxygen diffusion rates relative to consumption was likely the dominant factor controlling the depth of the oxidized layer. Oxygen penetrating into the sediments was quickly consumed by oxidation reactions creating an oxidized microzone averaging from 1 to 1.5 cm in depth (Appendix E). The depth of the oxidized microlayer may vary on a seasonal basis but generally does not penetrate deeper than a few centimetres, even in shallow oligotrophic lakes (Wetzel 1983).

4.2.3. Sediment Chemistry. Concentrations of constituents in lake sediments at depths corresponding to precultural influence (pollution or disturbance) generally reflects the elemental composition of the bedrock surrounding the catchment. Since human expansion and the increased industrialization of North America, the input of many constituents, especially metals, has also increased (Urban et al. (1987). Although Johnson et al. (1986) found that only minor amounts of Al, Fe, Mn, and Ca were derived from direct precipitation, greater inputs of these and other metals have been linked to atmospheric transport (Likens et al. 1984; Hooper and Barrie 1988). This is especially evident in the vicinity of large urban centres or industries such as metal smelting (Crocket and Kabir 1981).

Aluminum was the most abundant metal in the sediments of the five study lakes and, within the context of acidification, is one of the most important due to its potential toxicity and effects on phosphorus mobility. Aluminum concentrations in sediments are dependant on a variety of physical and chemical factors such as input via streams, lake pH, availability of complexing agents such as organic matter or other ligands and subsequent speciation (Driscoll 1980; 1984). Aluminum concentrations generally increase in more recent sediments of acidified lakes due to a combination of increased atmospheric deposition, Al mobilization from acidified watershed soils and retention in lake sediments.

Ouellet and Jones (1983) found that Al concentration did not change with increased sediment depth in non-acidified Lac LaFlamme (pH 6.5), but did increase since 1950 in the sediments of acidic Lac Tantare (pH 4.5). Charles et al. (1987) found that Al deposition rates increased in Big Moose Lake (pH 5.5) sediments until relatively recently. Substantial quantities of Al were also deposited and retained in sediments of Dart's Lake (Schafran and Driscoll 1987).

No increases in the concentration of total Al in recent sediments was evident in any of the study lakes. Sediment cores from the study lakes generally showed higher Al concentrations toward the bottom of the cores compared to the surface sediment. Mobilization of Al by lake water acidity was not likely to have been the cause of declines in Al concentrations surface sediments since Al concentrations also declined in surface sediments in the two least acidic lakes (Big Dam East and West Lakes). Norton et al. (1981) suggests that the mobilization of Al from sediments under acidic conditions would not be reflected by changes in total sediment Al concentration because of the comparatively large size of the sediment Al reservoir. Based on Al flux rates estimated from porewater gradients (Table 9) in relation to the total Al content in sediments, mobilization from sediments could not ccount for the observed declines in the Al profiles. Declines in Al concentrations in surface sediments have been observed in other acidic lakes. Charles et al. (1987) suggested that declining Al concentrations in surface sediments of Big Moose Lake since 1964 may be due to increased lakewater H^+ concentration causing increased competition between Al and H^+ for exchange sites on absorbing surfaces. This competition could be occurring either in the water column or at the sediment water interface but could have the net effect of lowering Al retention. Again, this was not likely to be the cause of lower Al concentrations in the sediments of the study lakes because similar changes in the Al profile occurred in the relatively non-acidic lake.

In order to maintain charge balance, some charged constituents in lake sediments can be attracted or repelled. It has been suggested that changes in Al concentrations near the surface could reflect reciprocal changes in Fe and Pb (Norton and Hess 1980; Norton 1984b). This did not appear to be the case in the 5 study lakes.

It has also been found that aluminum does not tend to accumulate in highly flushed lakes where particulates, to which Al is sorbed, are washed out before they are deposited. Nriagu and Wong (1988) showed that, in relation to import, sediments in Kejimkujik Lake are an inefficient sink for organic carbon and their associated trace metals because they are exported before they can reach the sediments. Flushing rates in the lakes sampled in this study were both lower and greater than that of Kejimkujik Lake (Table 2) ranging from 1 yr^{-1} to 13 yr^{-1} but the Al decline is consistent over this range.

LaZerte (1986) suggested that decreases in the rate of atmospheric deposition of metals to sediments may also be related to declines in surface sediment metal concentrations observed in acidifying lakes. Recent data suggests that acid deposition has declined in recent years due to economic downturns and increasing controls and regulation of emissions (Sirois and Summers 1989; CAPMoN unpub. data). Although this trend would be most evident nearest to large sources, Sirois and Summers (1989) have shown a trend toward decreasing sulphur dioxide concentrations in air and wet excess sulphate deposition in the Kejimkujik area. The decline was small and the length of available data records (8.7 yrs) was too short to establish trends with any certainty but the results did reflect a trend toward lower emissions of sulphur dioxide in eastern North America (Dillon et al. 1988). Since metal mobilization and retention in lakes is directly related to acid deposition, and the fact that acidic and non-acidic lakes showed similar profiles, it is possible that the decreasing trend in Al profiles in more recent sediments could reflect changes in deposition patterns. However, changes in deposition patterns have been relatively recent and relatively small. In comparison to the gradual declines in total sediment Al observed in the study lakes has occurred over a long time period (50+ yrs), therefore, recent changes in deposition do not explain these changes. Aluminum concentrations in the study lakes was found to track closely with Ti concentrations suggesting that some of the change in sediment Al concentrations the lake sediments may be the result of long term changes in watershed erosion patterns.

In Nova Scotia, the long range transport of air pollutants (LRTAP) has input metals via wet and dry precipitation (Hopper and Barrie 1988) although sampling frequencies have been insufficient to accurately determine loadings of various metals in this area. Elevated concentrations of Cu and Zn from atmospheric deposition have also been found in the Adirondack lakes (Galloway and Likens 1979; Norton et al. 1981). Most of the trace metals in the sediments of the Kejimkujik area lakes (Pb, Cu, Zn, Ni) are derived from long range atmospheric transport and deposition (Hopper and Barrie 1988) since they are not present in large quantities within the watersheds or produced locally. Other metals, including Al and Fe, may derived from atmospheric transport as well as from weathering and mobilization from soils within lake catchments since they are also abundant in soils and bedrock.

In order to distinguish between chemical changes in sediments resulting from activities within the watershed and those resulting from outside influences such as acid deposition, concentration profiles of constituents which are mobilized by acidification can be compared to relatively inert materials which enter lakes primarily through natural weathering processes or disturbances within the lake watershed and not long range atmospheric transport.

Titanium is a trace constituent in bedrock which is released through natural weathering processes and physical disturbance within watershed. Titanium is extremely immobile in lake sediments and changes in sediment Ti concentration profiles have been used to estimate changes in the fluxes of materials from the drainage basin of the lake through mechanical erosion. Comparison of Ti profiles against other, relatively non-mobile constituents such as Al, provides a means to differentiate between long range atmospheric transport and deposition versus local influences such as watershed disturbance or natural weathering processes (Norton 1984). Titanium is present in measurable concentrations in precipitation falling in Kejimkujik National Park (Hopper and Barrie 1988) but the amount derived from atmospheric deposition was small when compared to the size of the sediment reservoir, indicating that most of the Ti in sediments is derived from within the lake catchments. It is also likely that much of the Ti in precipitation is associated with locally derived dust and not necessarily long range transport.

Constant Ti concentration with increasing sediment depth represents a lake in a relatively steady state over the time interval represented by that portion of the profile the core. Several elements including Al, Ba, Ca, Cr, Mn and Sr, normally track very closely with the Ti profiles. Any change in the concentrations profiles of these elements accompanied by a similar change in the Ti profile indicate changes in erosion patterns occurring within the watershed. Changes in the concentration profiles of these substance which deviate from the Ti profile indicate the effects of external influences such as LRTAP.

In Beaverskin Lake, the two shifts were observed in the Ti concentration profile which probably correspond to changes in land use activities within the lake watershed. The dates of these two disturbances were estimated from sediment accumulation rates to have occurred around 1900 and again around 1950. This area was extensively logged at the turn of the century and again about 50 years later (Moyes 1987).

The Ti concentration profiles in Big Dam East and Big Dam West Lakes showed small shifts in the upper 5-10 cm and again in the latter lake at the 17 cm. These shifts also corresponded to logging activity in both watersheds in the mid 1950's and once previously in the 1920's in the watershed of Big Dam West Lake. As discussed above, Ti profiles in the sediments of Little Springfield Lake indicated substantial disturbance within the catchment of the lake. This disturbance was reflected by marked changes in sediment elemental composition at 10 cm depth corresponding to highway construction (Kerekes _et_ _al_. 1984). The effects of acidification on lake sediments have been examined by looking at changes in the ratio of Ca:Ti in order to remove the confounding effects of watershed disturbance. Lake acidification is generally indicated by a decline in the Ca concentration of surficial sediments relative to Ti (Charles _et_ _al_. 1987). The decreased Ca concentrations results from acid leaching of base cations causing a decrease in the Ca:Ti ratio.

All of the study lakes, except Beaverskin Lake showed declines in Ca and Ca:Ti ratios in recent sediments. In Beaverskin Lake, Ca:Ti profiles did not indicate increased Ca leaching but rather, and increase in Ca concentration relative to Ti. Possible explanations of this anomalous increase include a dramatic increase in beaver activity in the lake in the last 5 years and the use of lime in experimental enclosures in this lake during the study period.

Calcium and Ca:Ti ratios in Big Dam East, Big Dam West and Pebbleloggitch Lakes declined toward the sediment surface, which lends support to the acidification hypothesis. Calcium and Ca:Ti profiles in Big Dam West Lake showed a peak in Ca and Ca:Ti ratio between 5 and 7 cm which, based on a concurrent shift in the Ti profile, would appear to be related to watershed disturbance (probably logging activities).

Decreases in Ca concentrations in this lake could indicate a natural recovery from this disturbance. Norton (1984a) has suggested that diagenetic enrichment of Fe near the surface of sediments could cause a reciprocal decrease in base cations (Ca and Mg) concentrations which could falsely give the impression of acid leaching. In the study lakes, no significant correlations between Fe and Ca were found ($p > 0.05$).

Phosphorus:Ti ratios were plotted to examine historical changes in the accumulation rates of phosphorus in lake sediments (Figure 17a-d). The results indicated that in the two clear water lakes (Beaverskin and Big Dam East Lakes), there has been a consistent decline in the amount of phosphorus deposited in the sediments of these lakes which is not explained by changes in weathering processes in the watershed as indicated by changes in Ti concentrations. The phosphorus profiles normalized for Ti indicated that another process is responsible for declining phosphorus concentrations in these lakes. Broberg (1984) and Broberg and Persson (1984) investigate phosphorus budgets and phosphorus removal in an acidified lake and its catchment and found that substantial amounts of phosphorus were removed in the B-horizon of terrestrial soils. The mechanism by which this removal occurred was closely related to Al mobilization in acidified soils. Apparently, Al was mobilize in a reactive form which combined with phosphorus but was precipitated in deeper soil layers reducing the natural export of phosphorus into the lake. This removal mechanism may, in part, be responsible for long-term declines in lake phosphorus concentrations described by Grahn et al. 1974.

If Al was involved in the removal of phosphorus in the catchments in Beaverskin and Big Dam East Lakes, there should be a corresponding decrease in Al in the sediments of these lakes. Aluminum:Titanium ratios for the two lakes (Figures 18a,b) shows patterns similar to those observed for P:Ti ratios (Figures 17a,b) which supports concept of a relationship between Al and phosphorus. The greater slope of the P:Ti and Al:Ti profiles in Beaverskin Lake (pH 5.3) compared to that of Big Dam East Lake (pH 6.2) also suggests that these Al-phosphorus precipitation may increase with increased acidity.

Both P:Ti and Al:Ti profiles in the coloured lakes (Big Dam West and Pebbleloggitch Lakes) were distinctly different from those observed in the clear water lakes. In the coloured lakes P:Ti ratios increased since about 1950 corresponding to the period of increased acid deposition (Figure 17c,d). As acidity increases, DOC compounds are known to flocculate out of solution (Bourbonniere 1986) which has largely been responsible for the increase in transparency observed in acidified lakes (Schindler et al. 1985). The close association between DOM and phosphorus has already been discussed and it is not unreasonable to speculate that acidification of coloured (high DOC) lakes would result in an increase in the transport of organically bound phosphorus to the sediment. As discussed later, the organic matrix tightens with increased acidity causing phosphorus to be retained more tightly within this matrix (Bourbonniere pers. com.) and more resistant to subsequent mineralization and release. This removal process is supported by core experiments conducted in this study, which is also discussed in later sections. Although Al was also closely associated with DOM, Al:Ti profiles did not show increases in sediments corresponding to the increases observed for phosphorus. In coloured water, phosphorus tend to be more closely correlated with Fe but Fe:Ti ratios cannot be calculated because of the mobility of Fe in lake sediments during diagenesis.

Changes in P:Ti and Al:Ti profiles in both clear and coloured lakes did provide evidence of possible mechanisms for phosphorus removal as a result of acidification although distinctly different processes might be involved. However, these data do suggest that acidification of these lakes is occurring and that phosphorus supply may be impeded during acidification. Unfortunately, ^{210}Pb data was not available so the changes in phosphorus accumulation rates into the sediments could not be calculated accurately.

Other chemical constituents in lake sediments are more easily related to anthropogenic activity. Lead, Zn and V loadings have been closely correlated to anthropogenic activity and appear to be retained in the sediments, generally causing peaks in these constituents. Relatively low Zn concentration in near surface sediments was observed in all lakes except Pebbleloggitch Lake. Although lower Zn concentrations in surface sediments have been linked to lakewater acidification (Kahl and Norton 1983), differences in the concentration profiles in the study lakes probably resulted from diagenetic processes and the downward migration of Zn (Carignan and Tessier 1985). Norton (1984b) suggested that, if the subsurface peak in Zn was due to diagenetic processes, Cu concentrations should behave similarly. Figures 11 to 15 show that Cu concentrations in lake sediments were enriched between 2 and 5 cm and that the zones of Zn, Pb and Cu enrichment appeared to be linked. Therefore, this strongly suggests that patterns in atmospheric trace metal deposition for more mobile species, such as the latter constituents, may not be easily interpreted from the sediments record. Sulphate concentrations in the sediments of the study lakes were not measured, but pH profiles indicated that alkalinity was produced in this region (also see Carignan 1985), further indicating that the Zn and Cu enrichments were probably diagenetic and not related to acidification. Johnson _et_ _al_. (1986) also found that Pb, Zn were enriched in sub-surface sediments of the Turkey Lakes.

In this study, Mn showed post-depositional mobility in the sediments of the clearwater lakes, but this was not evident in the two coloured lakes. The upward mobility of Mn in sediments has been widely documented and may not be correlated to acidification (e.g. Carignan and Flett 1981; Johnson et al. 1986).

4.3. Sediment Porewater

4.3.1. Porewater Phosphorus. Dissolved and soluble reactive phosphorus concentrations in sediment porewater were measured in 25 lakes. Porewater phosphorus concentrations generally reflected lake trophic status (based on inlake TP concentration; Vollenweider and Kerekes 1982) with one exception. The exception was in highly acidic Drain Lake, a lake recently eutrophied by domestic sewage input. Sediments in this lake were found to have low porewater TDP and SRP concentrations indicative of pre-eutrophication and similar to those measured in upstream Little Springfield Lake.

Sediments in coloured lakes had greater TDP and SRP concentrations than clear water lakes because of the additional organic input associated with bog drainage. An example of this contrast are Big Dam East (colour 5 H.u.) and Big Dam West Lakes (colour 80 H.u.). These lakes lie adjacent to each other with the former flowing into the latter. Big Dam West has bog drainage within its catchment while Big Dam East has negligible bog influence. As a consequence of the organic influence, sediment porewaters in Big Dam West Lake have TDP and SRP concentrations 5 to 6 times greater than those measured in Big Dam East Lake. Porewater TDP and SRP concentrations were also high in other coloured lakes, including Pebbleloggitch and Kejimkujik Lakes. However, within the group of 25 study lakes, sediment phosphorus concentrations were only weakly correlated ($p < 0.05$) with water colour even when eutrophic lakes were removed from the analysis. This suggests that other factors such as lake morphometry, lake order, catchment characteristics, sediment chemistry and flushing rate may also have a substantial influence on porewater phosphorus concentrations and diffusive flux.

4.3.2. Porewater Metals. The chemical partitioning of aqueous Al compounds into various organic, inorganic and colloidal forms in lake water has been extensively studied and reviewed (eg. Campbell et al. 1983; LaZerte 1984; Havas and Jaworski 1986). The speciation of Al in sediments and porewaters is strongly dependant on pH and the form and concentration of organic matter or other ligands (Driscoll 1984).

In addition to being a sink for Al imported from the surrounding catchment or from the atmosphere, sediments may also have an important role as a source. Wong et al. (1989) compared Al downflux to Al upflux from sediments in two lakes (one clear and one coloured). Aluminum downflux (sedimentation) in the coloured lake was estimated to be 8800 $mg \cdot m^{-2} \cdot yr^{-1}$ which was substantially greater than that of an adjacent clear water lake (700 $mg \cdot m^{-2} \cdot yr^{-1}$). Return of Al to overlying water from the sediments of these two lakes based on diffusion coefficients and porewater gradients showed that sediments tend to accumulate Al, but Al upflux was substantial (480 and 100 $mg \cdot m^{-2} \cdot yr^{-1}$, respectively). They concluded that, although Al accumulation rates were high, sediments in the two lakes were an important source of dissolved Al to the overlying water. In addition, these authors found that a fraction of the Al species in organic rich waters can be reactive although reactivity is dependant on the concentrations and characteristics of organic ligands.

Wong et al. (1989), also found that although flux rates in the coloured lake were greater, all of the total reactive monomeric Al in porewaters in the coloured lake was associated with organic matter compared to only 60-70% in the clear water lake. They further concluded that lowering lake pH may enhance the release of monomeric Al species believed to be more toxic to biota. In the clear water lake, total Al flux rate from sediments was lower but the proportion of bioavailable Al was greater.

In this study, porewater Al concentrations in the 4 Kejimkujik lakes were between 100 to 600 $ug \cdot l^{-1}$ which was similar to values from 125 to 850 $ug \cdot l^{-1}$ reported by Wong et al. (1989) for the clear and coloured lakes. Porewater Al concentrations in the were substantially greater in Little Springfield Lake (500 to 3500 $ug \cdot l^{-1}$) due to the high acidity and high total sediment Al concentrations measured in this lake. In the 4 Kejimkujik lakes, porewater Al concentrations tended to be higher in the coloured lakes (270 to 600 $ug \cdot l^{-1}$) compared to clear water lakes (140 to 280 $ug \cdot l^{-1}$) which probably reflects the close association between Al and DOM in the water column.

Porewater Al profiles showed a negative gradient towards the sediment surface suggesting that Al may be returned to the water column by diffusion processes. Aluminum flux from the sediments of the five lakes showed that flux rates increased with both water colour and acidity (Table 9). The smallest Al flux rate was measured in Big Dam East Lake (0.37 $mg \cdot m^{-2} \cdot yr^{-1}$), the least acidic clearwater lake. Aluminum flux in Little Springfield Lake was much greater than that of any of the other lakes (127 $mg \cdot m^{-2} \cdot yr^{-1}$). The greater flux in Little Springfield Lake was probably due to the combined effects of acidity and the large concentrations of Al measured in sediments (Figure 14) and porewaters (Figure 22). Of the four Kejimkujik lakes, Pebbleloggitch Lake had the highest Al flux (18 $mg \cdot m^{-2} \cdot yr^{-1}$). The relatively high flux in Pebbleloggitch and Big Dam West Lakes was, once again, related to the greater organic content of these lakes compared to the clear water lakes and the association between organic matter and Al in both water and sediments. This association is particularly evident if Big Dam West and Beaverskin Lake flux rates are compared. Big Dam West Lake had a lake water pH comparable to that measured in Beaverskin Lake, but Al concentrations in sediments and porewaters, as well as Al flux, were 2-4 times greater in the former lake.

The substantial differences in Al flux estimates between lakes with similar pH indicates that differences in organic matter and Al speciation are important factors in sediment Al mobility and flux and that Al flux from lake sediments cannot be considered in relation to pH alone. Overall, the amount of Al released to overlying water was relatively small when compared to the Al reservoir in sediments.

4.4. Sediment Phosphorus Flux.

Sediment and porewater concentrations of Al, Fe, Mn, and Ca are potentially important in relation to phosphorus flux because these constituents, particularly Al and Fe, are known to form complexes to which inorganic phosphorus may be adsorbed (Nur and Bates, 1979). Under oxic conditions, inorganic phosphorus tends to be adsorbed to some chemical forms of these constituents resulting in the formation of a variety of phosphorus containing hydrous-oxide and organo-metallic complexes (Syers et al. 1973).

Inorganic phosphorus may be found in discrete phosphorus compounds such as those mentioned above, or adsorbed on the surface or within the matrices of sediment Fe, Al, and Ca compounds. The solubility of discrete compounds is influenced by ionic strength of the solution and pH which can be predicted by solubility product relationships.

A variety of organic phosphorus compounds, such as phosphate esters, can be sorbed by similar mechanisms (Syers et al. 1973). Sorbtion-desorbtion mechanisms play a dominant role in the uptake and release of inorganic phosphorus from lake sediments. The affinity between inorganic phosphorus and various sediment constituents, especially Fe, is responsible for the high net retention of phosphorus by lake sediments. Many studies have shown that sorbtion processes, as opposed to precipitation, dominate inorganic phosphorus mobility in sediments (Wetzel 1983).

Phosphorus mobility in relation to sorbtion reactions is a function of the relative concentrations of these substances in the sediment, the nature and availability of sorbtion sites as well as the degree of saturation of these sites. Oxic sediments in oligotrophic lakes have generally been found to have a high sorbtion capacity with respect to inorganic phosphorus (Meyer and Kramer 1986). This explains the low flux rates measured in shallow oligotrophic lakes such as those sampled in this study.

Iron is a constituent which is widely recognized to be important in sediment phosphorus dynamics. Inorganic phosphorus in sediments is known to have a strong tendency to interact with ferric iron to form ferric hydroxy-phosphate complexes (Stumm and Morgan 1970). Phosphorus may also be present in discrete compounds including viscarite [$AlPO_4$], strengite [$FePO_4$], and hydroxyapatite [$Ca_{10}(PO_4)_6(OH)_2$] but these compounds are not common in sediments and are relatively insoluble at pH levels found below the first few centimetres of sediment (Syers et al. 1973).

In this study, porewater Fe concentrations were found to be strongly influenced by redox conditions and diagenetic processes. In the 5 lakes where porewater Fe concentrations were measured, it was evident that reduced Fe migrated upwards but was precipitated at the oxidized boundary layer. This resulted in an accumulation of total Fe between the sediment surface and 1-2 cm (Figures 19 to 23). Declines in porewater Fe concentrations were balanced by increases in total sediment Fe indicating a change from the aqueous to the solid phase. Accumulations of upward migrating Fe were found just below the oxidized layer in all 5 lakes. Near-surface enrichments of sediment Fe and Mn are common in lakes and are sometimes accompanied by higher phosphorus concentrations (Bortelson and Lee 1974; Carignan and Flett 1981). Iron-phosphate complexation can lower porewater SRP concentrations in the oxidized layer causing a chemical gradient which could be mistaken for a diffusion gradient. In Beaverskin and Big Dam East Lakes, peaks in total and porewater Fe and Mn concentrations near the sediment surface were not accompanied by increased phosphorus concentrations. In Big Dam West Lake, a small Fe increase in near surface sediments was accompanied by a small increase in total sediment phosphorus. In Pebbleloggitch Lake, coincident increases in total sediment Fe and phosphorus indicate that some SRP mobilized from deeper sediment layers was being immobilized near the sediment water interface. The comparatively, high SRP flux calculated for the two coloured lakes but accompanied by an increase in total sediment phosphorus at the oxidized boundary layer, suggests that the SRP fluxes in these lakes may be overestimated because of co-precipitation with Fe in the oxidized layer. This also indicated that phosphorus mobility may be regulated by somewhat different processes in clear versus coloured lakes. In coloured lakes, phosphorus was more closely associated with Fe. This did not appear to be the case in the clear lakes.

Aluminum and Al compounds in sediments and their role in the sorbtion/desorbtion of inorganic phosphorus has not received as much attention as the role of Fe. Harter (1968) found that Al did affect the mobility of inorganic phosphorus either by direct formation of Al-PO_4 compounds or indirectly due to the presence of aluminosilicates which are capable of phosphorus sorbtion. In Beaverskin and Big Dam East Lakes (two clearwater lakes), sediment Al concentrations were correlated with total sediment phosphorus concentration (Beauchamp and Kerekes 1988). In the latter lake, Fe was also significantly correlated with phosphorus concentration although the relationship was not as strong as that for Al. In the two coloured lakes (Big Dam West and Pebbleloggitch Lakes), total sediment phosphorus concentrations were not significantly correlated with Al but were significantly correlated with Fe.

Manganese and Ca were not significantly correlated with phosphorus in any of the study lakes although Ca may play a role in phosphorus mobility (Syers et al. 1973; Wetzel 1983; Ogburn and Brezonik 1986). Manganese has also been implicated in sediment phosphorus dynamics but more through its association with Fe rather than any direct relationship. Manganese can form reddingite [$Mn_3(PO_4)_2$] under some conditions but this reaction and the formation of discrete phase Mn-phosphorus compounds is uncommon (Niragu and Dell 1974).

Flux rates measured in the 25 lakes in this study were low but generally within the range of SRP releases measured aerobic sediments of other lakes (Table 18). In this study, sediments were found to be a net phosphorus sink which, based on phosphorus flux rates, indicated that only a small percentage of the incoming phosphorus is being returned to the water column. Estimates of the contribution of sediment derived phosphorus to overlying lake water indicated that, on average, sediments did not contribute a large proportion to the annual lake phosphorus budget. In all but two of the fifteen lakes sampled, $<$ 10% of the annual phosphorus budget was derived from sediments (Table 10). In 6 of these lakes, no inorganic phosphorus was released from sediments. Sediment phosphorus loading estimates were consistent with other studies indicating that aerobic sediments have a high sorbtion capacity and contribute little or no inorganic phosphorus to the water column in these types of lakes (Table 18).

Given the importance of phosphorus supply in maintaining primary production, even in acidic lakes (Dillon et al. 1979; Shellito and DeCosta 1981; Kerekes et al. 1984), the relationship between flux and lake water acidity was examined.

Statistical analysis of lake water DOC, TP and H^+ concentrations did not reveal significant correlations between phosphorus flux rates and lake water acidity for the 25 lakes. Lakes with relatively high pH had low phosphorus flux rates while acidic lakes, such as Pebbleloggitch (pH 4.4) and Kejimkujik (pH 4.8) had relatively high flux rates. Big Dam West and Kejimkujik Lakes both had comparable sediment porewater SRP concentrations, ranging from approximately 300 $ugP\cdot l^{-1}$ in surface sediments to approximately 600 $ugP\cdot l^{-1}$ in deeper layers. The flux rate in Big Dam West (pH= 5.2; flux rate= 0.267 $mgP\cdot m^{-2}\cdot d^{-1}$) was significantly higher than that of Kejimkujik Lake (pH= 4.8; flux= 0.188 $mgP\cdot m^{-2}\cdot d^{-1}$), which may indicate a relationship with acidity. Drain and Little Springfield Lakes, the two most acidic lakes (pH 3.6 and 4.0 respectively) had very low SRP flux rates with the latter having a negative flux. Acidic lakes such as Big Dam West, Kejimkujik and Pebbleloggitch have much higher flux rates than do many less acidic lakes (which also usually had much lower porewater SRP concentrations).

Table 18. Literature estimates of SRP flux from aerobic lake sediments.

Lake	Trophic Status[a]	Method[b]	Flux ($mgP \cdot m^{-2} \cdot d^{-1}$)	Reference
Beaverskin	oligo	core	0.0	Andrews 1980
Mendota	eut	core	1.0-5.0	Holdren 1976
Mendota	eut	core	0.0-9.0	Gallepp 1979
Mendota	eut	core	-1.9-8.3	Holdren Armstrong 1980
Wingra	eut	core	-0.6-3.4	Holdren Armstrong 1980
L. John	eut	core	0.02-1.1	Holdren Armstrong 1980
Esrom	eut	core	-8.0-16.11	Kamp-Neilson 1975
Esrom	eut	core	-1.4	Kamp-Neilson 1975
Fureso	eut	core	-2.0	Kamp-Neilson 1974
Warner	eut	core	0.65	Neame 1977
Warner	eut	lab	1.2	Fillos & Swanson 1975
Constance	eut	core	1.2	Fillos & Swanson 1975
Erie	eut	mass	3.51	Banoub 1975
Erie	eut	in situ	0.68	Burns & Ross 1972
Ontario	meso	core	0.68	Burns & Ross 1975
Ontario	meso	pore	0.8	Bannerman et al. 1974
Michigan	meso	core	0.17	Quigley & Robbins 1986
Michigan	meso	pore	1.12	Quigley & Robbins 1986
Minocqua	meso	core	0.02-0.41	Holdren Armstrong 1980
Langso	oligo	core	0.1-0.6	Kamp-Neilson 1974
Gribso	dys	core	0.02-0.2	Kamp-Neilson 1974
Doboy		core	0.031	Pomery et al. 1965
Muddy		lab	9.6	Fillos & Swanson 1975
Norriviken		lab	5.0	Ahigren 1972

[a] eut = eutrophic
meso = mesotrophic
oligo = oligotrophic
dys = dystrophic

[b] core = core incubation
lab = laboratory incubation of sediment (usually mixed)
pore = calculated from porewater gradient in situ= chamber
mass = mass balance calculation

The relationship between sediment SRP flux and lake water TP concentration was significant at $p < 0.05$ indicating that higher flux rates occurred in more productive lakes.

Mayer and Kramer (1986) examined the effect of lake acidification on phosphorus immobilization and retention by sediments in several Canadian Shield lakes ranging in pH from 4.4 to 8.5. In this study, the effect of pH on the sorption of inorganic phosphorus by sediments from lakes of different geology and pH was assessed using the Langmuir model to determine equilibrium constant adsorption and adsorption capacity. Retention was assessed by the reversibility of adsorption. Non-calcareous sediments exhibited a significantly higher adsorption capacity than did more calcareous sediments indicating a greater availability of adsorption sites in the former type of sediment. Mayer and Kramer (1986) suggest that adsorption of phosphorus is due to the combined availability of Al and Fe oxide adsorption sites in the sediments. Lowering the pH of the sediment matrix by 1.5 pH units from 7.0 to 5.5 caused an increase in adsorption of 4% in one lake while a decrease in pH of 2.5 units (from pH 7.0 to 4.5) in another lake caused a 17% increase in adsorption. Measurement of the desorbtion of added inorganic phosphorus indicated that the sediments which adsorbed more phosphorus (non-calcareous) desorbed the least amount of phosphorus added (0.3 - 4%) compared to more calcareous sediments where 10-30% of the added inorganic P was desorbed.

This suggests that adsorption processes in non-calcareous sediments (typical of lakes in the Atlantic region as indicated by geology and surface water chemistry) are not readily reversible and sediments have a high net retention of inorganic phosphorus.

This is supported by the low inorganic phosphorus flux rates measured in this study. The majority of lakes where phosphorus flux was sampled are known to lie on substrates low in calcium and have low dissolved calcium concentrations in surface waters (unpub. data) and, presumably, sediments. Mayer and Kramer (1986) concluded that sorbtion-desorption parameters indicated that sediment mineralogy and chemistry were primarily responsible for phosphorus absorbtion and retention capacity. By comparison, the pH of lake water was relatively unimportant.

In a similar study, Ogburn and Brezonik (1986) used sediment-water slurries and undisturbed sediment cores collected from the littoral zone and mid-lake to examine inorganic phosphorus sorbtion and release by sediments at pH values ranging from 3.6 to 7.0. Very little SRP was released from the littoral sediments at any pH. No SRP was released from mid-lake sediments at pH 3.8 to 5.5. However, SRP was released in increasing amounts from mid-lake sediments at pH > 5.5. Inorganic phosphorus enrichments (1 $mg \cdot l^{-1}$ SRP addition) to sediment-water slurries and undisturbed sediment cores were used to examine sorbtion properties of sediments over the same pH range. Binding capacity of sediments was similar from pH 3.5 to 4.2 but decreased markedly at pH > 5.0. This indicated that sediments could retain more inorganic phosphorus as pH decreased down to pH 5 which supports the oligotrophication hypothesis as lakes are acidified to this pH. However, further acidification would have little effect on sediment phosphorus sorbtion.

Sediment phosphorus release rates in the sample of lakes measured in this study varied independently from pH supporting the results of the above studies which concluded that sediment chemistry played a dominant role in the determination of flux rates and not lake water acidity. In all cases, it was further determined that flux rates of inorganic phosphorus from aerobic lake sediments is low.

4.5. Phosphatase Bioassay.

Planktonic autotrophs generally prefer phosphorus in the form of orthophosphate and are unable to metabolize organic phosphorus compounds directly (Rigler 1964; Berman 1970; Lean and Nalewajko 1976). However, ambient orthophosphate concentrations in oligotrophic lakes are often insufficient to account for estimates of planktonic phosphorus uptake (Cembella 1984). Franko (1986) identified three distinct orthophosphate regenerative mechanisms which can release inorganic phosphorus from various organic phosphorus containing compounds which could account for the observed differences between demand and availability. These are: (1) displacement and release of available phosphorus from high molecular weight colloidal phosphorus (HMWP) compounds, (2) hydrolysis of dissolved, low molecular weight phosphate esters and HMWP by phosphatase enzymes, and (3) ultraviolet (UV) radiation induced release of inorganic phosphorus from ferric iron-dissolved humic material (DHM) complexes (UV sensitive phosphorus complex; Franko and Heath 1982, 1983). The relative abundance of other substances (ie: DHM and Fe concentrations) can influence the relative magnitude and importance of the contributions made by these regenerative processes which partially explains why the relative importance of these processes has been found to vary between lakes (Wetzel 1983).

Certain DOP compounds may be indirectly used as sources of phosphorus by planktonic organisms (Johannes 1964; Kuenzler 1970; Cembella et al. 1984). As indicated above, the ability of plankton to metabolize organic phosphorus compounds is closely related to the chemical nature of these substances (Franko and Heath 1982; Franko 1984). Understanding the chemical nature of the DOP pool in lake water is, in itself, problematic. Only a fraction of the organic phosphorus compounds found in lake water have been described and the chemical terminology and analytical methods have often been inconsistent. Operationally defined compounds or classes of compounds are not easily comparable or examined in a functional context (Downes and Paerl 1978). The group of enzymes primarily responsible for enzymatic hydrolysis of organic substrates in lakes are the phosphatases. Phosphatases are the most studied group of extracelluar enzymes in aquatic ecosystems (Feder 1973). They are extracelluar enzymes with their primary role directed toward the hydrolysis of certain exogenous phosphorus containing compounds. The production and excretion of phosphatase enzymes by organisms, including algae, confers a competitive advantage to producers by allowing them to mineralize organic phosphorus to supplement their metabolic requirement for inorganic phosphorus when supply of the latter is limited (Fitzgerald and Nelson 1966; Berman 1969; Jones 1972; Berman 1970; Healey 1973; Jansson 1976; Bierman et al. 1980; Rifkin and Swift 1980; Konopka 1982).

Low molecular weight phosphorus (LMWP) compounds are secreted by a variety of planktonic organisms (Fog and Miller 1958; Pomeroy et al. 1963; Corner 1973; Lehman 1980; Sondergaard and Schierup 1982; Fogg 1983). Low molecular weight compounds, such as condensed polyphosphates, certain colloidal phosphorus compounds and phosphate esters, are substrates which can used to derive additional inorganic phosphorus through enzyme hydrolysis (e.g. Ituriga and Hoppe 1977; Paerl and Downes 1978). Phosphatase substrates may comprise a substantial portion of the dissolved organic phosphorus (DOP) pool in some lakes (Herbes 1974; Heath and

Cooke 1975; Wetzel 1983). However, their availability is known to be spatially and temporally variable (Wetzel 1983). Preferred phosphatase substrates are rapidly metabolized making their measurement and contribution to lake productivity difficult to assess (Wright and Hobbie 1966; Wright 1970). Berman (1970) and Bierman et al. (1970) found that a substantial amount of inorganic phosphorus was released from DOP compounds by phosphatase activity and that enzyme mediated release of orthophosphate can be important in phosphorus (and plankton) dynamics in some, but not necessarily all lakes.

4.5.1. Enzyme Kinetics. Enzyme kinetics were measured in the 5 study lakes to provide information on how the basic properties of phosphatase enzymes differed between the lakes. Michaelis-Menten theory assumes that the enzymes react with only one substrate although many enzymes are known to react with a complex of substrates. There is a wide degree of variability in substrate specificity in that some enzymes will react with only one substrate and not others which may be very similar in molecular structure, while other enzymes react with many different substrates. Phosphatase enzymes can react with a variety of phosphate esters (Lehninger 1975) although they are known to prefer esterfied phosphorus compounds (especially phosphomonoesters). The substrate (p-nitrophenylphosphate; pNPP) used in this study is a phosphomonoester and was present in high concentrations compared to natural substrates so that single substrate kinetics would provide a useful approximation of phosphatase kinetics in the different lakes.

It was found that the maximum initial velocity (V_{max}) reached by phosphatases was lowest in Beaverskin Lake (4.4 nmoles$\cdot l^{-1}\cdot min^{-1}$; Table 11) which was substantially lower than V_{max} measured in Pebbleloggitch Lake (100 nmoles$\cdot l^{-1}\cdot min^{-1}$). The other lakes had V_{max} values between 30 and 50 nmoles$\cdot l^{-1}\cdot min^{-1}$. V_{max} is a function of the enzyme concentration and the rate constant for the dissociation of the enzyme-substrate complex (k_{+2}). Assuming that k_{+2} was similar in the different lakes, V_{max} would then be proportional the concentration of phosphatase enzymes. If it is assumed that the rate constants were similar, Beaverskin Lake would appear to have had the lowest enzyme concentration while Pebbleloggitch Lake had the greatest on the particular day sampled. However, V_{max} can vary with enzyme type, substrate, temperature and pH. Since the temperature and substrate was the same for all the sites, it was possible that the differences in V_{max} were also due to between lake differences in the structure enzyme pool or pH.

The Michaelis constant (k_m) is the substrate concentration where the enzyme is half saturated (the substrate concentration where v_0 is one-half of V_{max}). K_m varies with different substrates, but individual substrates usually have a characteristic k_m for a particular enzyme. Since the same substrate was used in all assays, examination of k_m values provides some interesting insights into the differences in the enzyme kinetics between the different lakes. The three clearwater lakes had substantially lower k_m values than the two coloured lakes (Table 11). While it is difficult to compare lakes with widely different values for V_{max}, comparisons of k_m in lakes with similar V_{max} does provide evidence of how the enzymes behave with respect to substrate concentrations. Lakes with low k_m in lake water (where V_{max} is similar) indicates that the enzymes in these lakes have a greater affinity for the substrates and are capable of more rapid substrate hydrolysis and low substrate concentrations. When substrate concentrations are naturally low, a high k_m is advantageous. Low k_m values in the clear water lakes may indicate an adaptation to low substrate concentrations in these lakes. From the data in Table 11, it would appear that phosphatases in Big Dam East and Little Springfield Lakes have a much greater affinity for the pNP substrate than was found in Big Dam West Lake (coloured).

4.5.2. Enzyme-pH Relationships. Phosphatase activity in lakes is dependent on a variety of environmental factors such as lake water pH. Reichardt et al. (1967) found that acid phosphatase activity was maximum at a lake water pH of 5.6. Lehninger (1975) states that pH versus enzyme activity plots usually are usually (but not always) bell shaped. Berman (1970) found that pH optima, substrate specificity and enzyme kinetics all varied substantially on a seasonal basis. Seasonal and spatial variability of these variables was not examined in this study but it was evident that phosphatase activity is highly pH dependant.

Results of this study showed pH optima were distinctly different among the five study lakes but similar within individual lakes on two sampling dates (Figure 24). The pH optima for phosphatase enzymes in the four of the five study lakes was within 0.5 pH units of the ambient lake water pH in a particular lake. There was also a tendency for pH optima to be slightly higher (approximately 0.5 pH units) than the actual lake water pH. However, the optimum pH for phosphatase enzymes in Little Springfield Lake (6.5) was not close to the ambient lake water pH (3.8). Assuming that the pH optima measured for Little Springfield Lake phosphatase enzymes reflects pre-acidification conditions, it appears that the isozymes in this lake have not adjusted in response to acidification.

Reductions in phosphatase activity by increased lake water acidification could effectively reduce the ability of planktonic organisms to mineralize organic phosphorus substrates in the water column. Ogburn and Brezonik (1986) used three sets of limnocorrals to assess the effects of pH on phosphorus cycling in a moderately acidic freshwater lake. Two enclosures were acidified to pH 3.6 and 4.1, respectively, while the third was left as a control at the ambient lake pH of 4.7. Inorganic phosphorus enrichments (SRP additions to approximately 20 $ugP \cdot l^{-1}$ or 10x background) to these enclosures as well as 12 l carboys filled with lake water (the latter maintained in a laboratory at the same pH's), showed that SRP loss rates were independent of pH. It was concluded that planktonic uptake of SRP was not affected by pH. However, they did find that the mineralization of soluble organic phosphorus (SOP) to SRP was slower at lower pH.

Reductions in phosphorus regeneration from organic substrates by enzyme hydrolysis under increasingly acidic conditions would be a short term effect if organisms could quickly adapted the enzyme pool to accommodate changes in pH. Data from Little Springfield Lake suggested that this modification has not occurred over a period of several years. Given the high turnover rates of major phosphatase producers such as bacteria and algae and the species shifts which generally lead to the development of acidophilic species suited to more acid conditions, it was surprising that plankton in Little Springfield Lake did not appear to be more suitably adapted to ambient conditions.

It could be argued that the phosphatase enzymes in Little Springfield Lake were derived elsewhere (i.e. forest soils and inflow streams). Stevens and Parr (1977) measured high phosphatase activity in lake inflows and suggested that stream inputs during high flow periods could account for up to 40% of the phosphatase activity measured in their lakes. However, they also noted that peak flow periods occur over only a small portion of the year and generally did not coincide with peaks in phosphatase activity. Jansson _et al_. (1981) found that, on an annual basis, the influx of phosphatase from streams was negligible since low phosphatase activity coincided with high flow periods. It has also been shown that free phosphatases in lake water are short lived and persist only for a matter of hours or a few days (eg: Pettersson 1980) suggesting that what is found in lakes during low flow periods is what is produced _in situ_. Since pH optima for phosphatases in Little Springfield Lake were measured during low flow periods (June - August), it was not likely that the observed differences were related to phosphatase enzymes derived externally.

4.5.3. _Enzyme Inhibition_. Acidification is known to mobilize metals from lake sediments and the surrounding catchment (Dickson 1978, Cronan and Schofield 1979). Inorganic Al (Al^{3+}) can bind with orthophosphate (Huang 1975; Dickson 1980) and thus may remove inorganic phosphorus under "natural" conditions rendering it unavailable to biota. Acidic lakes in Scandinavia have shown long-term declines in lake water total phosphorus concentrations and lake oligotrophication (Grahn _et al_. 1974; Jansson _et al_. 1986). Jansson _et al_. (1986) have suggested that greater phosphatase activity measured in acidified lakes is due to phosphorus removal by metal complexation resulting in an increase in the severity of phosphorus limitation followed by a corresponding increase in phosphatase production. This hypothesis is supported to some degree by the results of studies concerning the direct effects of aluminum on $^{32}PO_4$ uptake and photosynthetic activity. It has been found that both $^{32}PO_4$ uptake and photosynthetic activity were significantly reduced at Al concentrations from 0.1 and 0.4 $mg \cdot l^{-1}$ although the magnitude of the effect was dependant on lake water pH and organic content (Paul 1984; Nalewajko and Paul 1985; cited in Havas and Jaworski 1986). Dickson (1980) found that orthophosphate added to clear lake water in the presence of Al was quickly adsorbed to the Al. However, in humic lake water, no adsorption of phosphorus by Al occurred.

It is apparent that the effect of Al on phosphorus availability can occur indirectly. Enzyme hydrolysis of dissolved organic phosphorus (DOP) substrates can be suppressed by the addition of Al^{3+} and, to a lesser extent, Fe^{3+} in laboratory experiments. Jansson (1981) found that metal ions bind to the phosphate group on the substrate which is probably the same site attacked by the phosphatase enzymes. Most enzymes, including phosphatases, are relatively site-specific and are unable to attack substrates if the binding site is already occupied. Both the enzymes and metals appear to have an affinity for the same substrate sites, and will compete for them. Jansson (1981) showed that the ratio of phosphatase, phosphatase substrates and metal concentrations were critical in determining the rate of organic phosphorus hydrolysis at low substrate concentrations.

Lehninger (1975) describes three types of reversible enzyme inhibition as well as irreversible inhibition. Reversible inhibition includes competitive inhibition which involves a direct combination of the inhibitor with the enzyme in such a way that the inhibitor competes with the normal substrate for binding at the active site. Uncompetitive inhibition occurs when the inhibitor combines with the enzyme-substrate complex to yield an inactive enzyme-substrate-inhibitor complex which does not yield a product. Noncompetitive inhibition occurs when the inhibitor combines with either the free enzyme (usually somewhere other than at the active site) or the enzyme-substrate complex interfering with formation of the enzyme-substrate (ES) complex and the decomposition of the ES complex to yield products. Irreversible inhibition usually involves the chemical modification of the enzyme such that the enzyme becomes inactivated. Note that all of these types of inhibition involve the enzyme whereas Jansson (1981) suggested that Al blocks the substrate binding site and give no indication of involvement of the inhibitor with the phosphatase enzymes. The three types of reversible inhibition are easily tested for using the Michaelis-Menten formulation although irreversible inhibition is not easily tested. Since k_m is intrinsic to a particular enzyme and substrate, the Al inhibition mechanism could have been examined by addition of different forms and concentrations of Al and measuring k_m. Any change in k_m would indicate that the enzyme was affected. Unfortunately, no testing was done in this study to verify the type of inhibition occurring, the mechanisms involved or the effects of different chemical forms (in terms of reactivity) of Al, (although, in retrospect, this would have been a worthwhile exercise) so no conclusions can be made concerning the mechanisms by which Al inhibition occurs.

Although Fe^{3+} did not affect the hydrolysis of the p-nitrophenylphosphate (pNPP) substrate in this study, additions of Al^{3+} had a variable effect on substrate hydrolysis depending on the organic content of the lake water. Al had a reduced capability for suppressing phosphatase activity in the presence of increasing DOM concentrations (Table 12). It appeared that Al was sequestered by DHM reducing its competitive ability to bind with the phosphatase substrates. The reason for the differences between the effects of Fe measured by Jansson (1981) and those measured in this study are not known. They may be related to differences in the substrates used in these two studies. Jansson (1981) used the phosphomonoester substrate 3-methylumberiferryl phosphate (MUP) while p-nitrophenylphosphate (pNPP) was used in this study. Although no effect from Fe was observed in this study using pNPP, it does not mean that other substrate types are similarly unaffected by inorganic Fe.

Assuming that both Al and Fe could have an effect on phosphatase activity the metal having the greatest influence on the substrate will depend on the relative concentration of the metal, phosphatase enzymes and the substrates. In this study Al and Fe were generally found in similar concentrations and could potentially have similar effects. In Little Springfield Lake, Al concentrations were 4 times that of Fe and Al would be more likely to have a greater effect on substrate hydrolysis. In several Scandinavian lakes, Al was also present in greater concentrations than Fe. Since certain metals, particularly Al, have an affinity not only for inorganic phosphorus, but for certain organic phosphorus compounds as well, these metals may not only sequester inorganic phosphorus but may also reduce the capacity for enzyme hydrolysis of certain DOP compounds and, thereby reduce the mineralization rate of available phosphorus from these compounds.

4.5.4. Phosphatase Activity. Greater phosphatase activity was consistently measured in the two coloured lakes (Big Dam West and Pebbleloggitch) compared to the clear lakes (Table 13). As discussed earlier, dissolved humic substances readily adsorb inorganic phosphorus and form dissolved humic-iron-phosphate complexes. The introduction of high concentrations of dissolved humic matter (DHM), the sequestering of orthophosphate by DHM and reduced phosphorus availability have been implicated in the depression of primary production in lakes and reservoirs (Jackson and Hecky 1980; Stewart and Wetzel 1982). The high phosphatase activity measured in

Pebbleloggitch and Big Dam West Lakes may also be related to a reduction in phosphorus availability due to sorbtion of inorganic phosphorus with DHM. Franko (1986) found that additions of DHM and Fe strongly repressed phosphorus uptake and stimulated phosphatase activity when DHM was added to lake water samples under laboratory conditions. Auclair et al. (1985) added DHM to lake water samples and also reported stimulations in community alkaline phosphatase activity related to the increased DHM concentrations. Brassard and Auclair (1984) examined orthophosphate uptake rate constants in the presence of different DHM molecular weight fractions and found that DHM could mediate orthophosphate uptake rates. In all cases, low molecular weight DHM was more effective in altering metabolic rates than high molecular weight DHM. Thus, the overall effect of DHM can vary in relation to the relative concentrations of individual chemical components of the DHM pool. These data indicate that greater DHM concentrations measured in organic lakes reduces inorganic phosphorus availability which stimulates phosphatase production. Whether increased phosphatase production is simply a response to depleted intracellular phosphorus or whether there is a feedback mechanism between extracellular DOP availability is uncertain although to former is most likely.

Under natural conditions, organic phosphorus compounds in coloured lakes may play a dual role by also providing an additional source of phosphorus. Mechanisms such as the breakdown of UV sensitive phosphorus complexes can contribute to increased rates of planktonic primary production in coloured lakes. Total phosphorus concentration and planktonic primary productivity (at light optimum; Pmax) were consistently greater in Pebbleloggitch Lake compared to Beaverskin Lake (Beauchamp and Kerekes 1989). The relative importance of enzyme versus UV mediated hydrolysis may be determined by the relative concentrations of phosphatases and UV-sensitive substrates. This two mechanisms may also work in concert where complex DOM can be broken down into phosphatase substrates such as phosphomonoesters.

Phosphatase activity has only recently received attention as a potentially useful index of environmental perturbations which can affect phosphorus cycling (Jansson 1981). The third objective of this study was to test for relationships between lake water acidity and phosphorus availability (directly and through DOP mineralization). The 5 lakes selected for study covered a wide range in pH (3.8-6.1), DOC (2.0-21 $mgC \cdot l^{-1}$), Al (0.5-3.3 $mgAl \cdot l^{-1}$) and Fe (0.06-0.76 $mg \cdot l^{-1}$) concentrations. Bivariate correlations gave no indication of a relationship between lake water acidity or metal concentrations and acid phosphatase activity. Phosphatase activity was significantly correlated with organic content ($p < 0.01$; Table 14). Greater Al and Fe concentrations were measured with increasing acidity but, overall, increased metal concentrations were not accompanied by increased phosphatase activity. This was largely due to the inclusion of Little Springfield Lake in these analyses. Phosphatase activity remained low in Little Springfield Lake in spite of high Al and low DOC concentrations. In the coloured lakes, metals could be complexed with organic matter reducing their effect on phosphorus availability. This would not be the case in Little Springfield Lake where Al was likely to be in a more reactive form. Aluminum would be expected to sequester inorganic phosphorus under these conditions and induce more severe phosphorus limitation and greater phosphatase activity. The low phosphatase activity in Little Springfield appeared to reflect the effect of pH on enzyme kinetics and the difference between the enzyme pH optima and ambient lake water pH in this lake.

4.5.5. Core Incubations. Lakes are spatially and temporally variable in relation to chemistry, hydrology, and planktonic community structure, all of which can alter or influence phosphatase activity and obscure the understanding of the processes in question. Laboratory bioassay techniques were used in order to examine phosphorus-metal-pH interactions under more controlled conditions. Cores consisting of sediments and overlying water were collected from five lakes and incubated in the laboratory at different pH levels depending on the pH of the lake under ambient conditions. Cores were incubated at pH 6.0, 5.0, 4.0 and 3.0.

Little Springfield Lake core experiments were eliminated from the results because of problems manipulating pH in the cores. The daily additions of acid and base to core "microcosms" required to reach the desired pH failed to maintain that pH for 24 hours over the entire 14 day incubation period. It was probable that the strong mineral acidity in this lake and possibly aluminum buffering prevented an equilibrium to a new pH level from being easily maintained. Although the processes governing the buffering reactions were not specifically tested, Little Springfield Lake water has high H^+, and Al concentrations (251 and 267 $ueq \cdot l^{-1}$, respectively) and a high alkalinity deficit (Kerekes et al. 1986a). It is also possible that the presence of lake sediments may have played a substantial role in pH regulation of the overlying water.

In cores from the remaining four lakes, Al, Fe, Mn and Ca were mobilized from the sediments by increasing the acidity. Increased metal concentrations were generally accompanied by decreasing SRP concentrations suggesting that inorganic phosphorus was immobilized by the metals. Nalewajko and O'Mahoney (1988) found that additions of Al and Fe to lake water samples increaed the amount of phosphorus lost from solution as pH was rapidly decreased. They suggest the phosphorus concentration minima, which occured between pH 5.2-5.6, corresponded to the combined effects of the formation of iron-phosphate and aluminum-phosphate complexes. Iron-phosphate complexes show maximal formation at pH 5.1 compared to aluminum-phosphate co-precipitation which is maximal at pH 6.0 (Stumm and Morgan 1970). Nalewajko and Paul (1985) measured Al-$^{32}PO_4$ binding in Plastic Lake in relation to pH and found that maximum binding occurred also occurred at pH 6.0. However, minimal phosphorus concentrations in the two lakes described above occurred nearer pH 5.0 than 6.0 indicating that iron-phosphate interactions were dominant. The differences in SRP concentrations between core treatments were not statistically significant overall except in Pebbleloggitch Lake where consistently lower SRP concentrations were measured over the whole pH range (Table 16). Ogburn and Brezonik (1986) used three sets of limnocorrals to assess the effects of pH on total phosphorus concentrations in lake water. Two enclosures were acidified to pH 3.6 and 4.1, respectively, while the third was left as a control at the ambient lake pH of 4.7. After being held for 4 weeks at these pH levels, total phosphorus concentrations were found to be significantly lower in the pH 3.6 enclosures ($p < 0.05$, ANOVA) than at higher pH values.

In this study, the lack of significant differences in SRP concentration between treatments was largely due to low SRP concentrations and the relatively small magnitude of change in relation to within and among treatment variances. Soluble reactive phosphorus concentrations tended to decline from pH 6.0 to 4.0. However, in Beaverskin and Big Dam East Lakes, SRP concentrations increased in pH 3.0 cores. The increase in SRP concentration in Beaverskin and Big Dam East Lakes indicated that in clear water lakes, some phosphorus may be in a form which can be more easily mobilized from sediments by acidity. In the coloured lakes, sediment phosphorus was more tightly bound to organic compounds and was not released by increased acidity, even under extremely acidic conditions. Bourbonniere (pers. com.) indicated that the lack of response in coloured lakes may be due to the fact that the organic matrix tends to physically tighten up (fold or coil) with increased acidity and this tightening may further prevent acid hydrolysis. The trend toward reduced inorganic phosphorus concentrations in the core water accompanied by elevated metal concentrations could also indicate a reduction in available phosphorus due to metal complexation.

Phosphatase activity decreased in cores incubated at pH 4.0. The declines in phosphatase activity measured at pH 4.0 were partially due to the effect of pH on enzyme activity. Phosphatase activity in pH 3.0 cores from Beaverskin, Big Dam East and Big Dam West Lakes showed a recovery to values greater than were measured in control cores (Table 15). When normalized for the effects of pH on enzyme activity, phosphatase activity was found to increase in all cores incubated below the ambient lake pH (Figure 26). The overall increase in normalized phosphatase activity was significant at $p < 0.01$. Comparisons between controls and individual treatments based on non-parametric multiple comparison tests indicated that the increase in normalized phosphatase activity was significant in water and sediments of the cores of all 4 lakes at pH 3.0 and 4.0. but was not significant at $p < 0.05$ in any of the lakes at higher pH values. This suggests that compensation by organisms may not take place until a relatively high level of environmental stress is reached (pH > 5.0).

As previously indicated, organic content and the availability of suitable organic substrates is critical in determining the amount of SRP which can be regenerated from DOC compounds. Acidification of experimental cores was shown to result in a decrease in DOC concentrations with increasing acidity (Table 15; Figure 25). Dissolved organic compounds flocculate under acidic conditions and the removal of DOP compounds by acidification could result in lower phosphatase substrate availability as well as a reduction in organic complexes capable of binding metals such as Al thus increasing the potential for increased metal toxicity without increases the metal concentration, simply its chemical form. Al may also have a direct effect on phosphatase enzymes by blocking enzyme hydrolysis of suitable organic substrates. Increased concentrations of Al and lower concentrations of phosphatase substrates may provide a mechanism which could result in further declines in phosphorus regeneration from organic phosphorus compounds.

5. Summary and Conclusions

Phosphorus cycling in lakewater is complex (Lean and Rigler 1974; Richardson and Marshall 1986) and there is a need for more information in order to better understand how acidity and other factors interact to influence lake productivity. Increased acidity, greater transparency, lower chlorophyll-*a*, total phosphorus concentrations, and reductions in the rates of organic matter decomposition measured in acidified lakes have led to the hypothesis that acidification induces lake oligotrophication. The objective of this study was to examine the oligotrophication hypothesis by examining phosphorus compartmentalization, sediment phosphorus mobility, mineralization, and availability in various lake types. Historical changes in 5 study lakes were assessed by examination of the sediment chemical record.

The results of this study indicated that total phosphorus and metal concentrations were greater in the water column of coloured lakes compared to similar clear water lakes and that both phosphorus and metals were closely associated with DOC concentration. However, this does not provide any evidence of historical changes in water chemistry with respect to acidification. In relation to the first objective of the study concerning evidence of lake acidification examined through changes in the sediment record, there were three findings suggesting that acidification of the watersheds may be occurring. Firstly, decreasing P:Ti ratios toward the sediment surface in the 2 clear water lakes was indicative of the loss of phosphorus in the watersheds of these 2 lakes. In the 2 coloured lakes, the opposite pattern appeared. It would appear that acidification of these lakes may result in a reduction of organic phosphorus from the watershed or flocculation of organic phosphorus in the lakes themselves. Secondly, declining sediment Al profiles were found in the clear lakes, symptomatic the co-precipitation of phosphorus and Al in the soils of the catchment. Sediment Al profiles were not correlated with phosphorus in the sediments of the coloured lakes suggesting that this phosphorus removal process was not occurring in these basins, as would be expected if flocculation was the dominant removal process in coloured lakes. Lastly, Ca profiles declined in the surface sediments of 4 of the 5 lakes sampled. Declining Ca profiles are known to be indicative of cation denudation accompanying acidification due to acid deposition.

The second objective of this study concerned the relative importance of inorganic phosphorus flux from lake sediments in the lake phosphorus budgets and whether there was any indication of differences in flux with respect to acidity. In a sample of 25 lakes varying in pH, total phosphorus and DOC concentration as well as morphometry and hydrology, sediment phosphorus flux rates were correlated with trophic status (inlake total phosphorus concentration) and DOC concentration. Lake water pH was not significantly correlated with flux in this sample of lakes. Most of the lakes sampled showed little or no evidence of phosphorus release from the lake sediments illustrating that oxidized sediments are a phosphorus sink. Calculations based on a simple model indicated that even for the largest fluxes measured, sediments play a minor role in the phosphorus budget of these lakes.

The third objective of this study was to examine inorganic phosphorus availability and mineralization of inorganic phosphorus from DOP compounds in relation to acidity. This was done by measurements of phosphatase enzyme activity and kinetics in a sub set of 5 lakes. Enzyme kinetics showed low k_m values in clear water lakes indicating a higher substrate affinity of phosphatases in these lakes. Low k_m is advantageous since it is indicative of more rapid substrate hydrolysis at low substrate concentrations.

Consistently greater phosphatase activity in coloured lake waters suggests that phosphorus may be sequestered by DOC and less available. Previous studies of primary production in two of the lakes sampled in this study (Beaverskin and Pebbleloggitch Lakes) have shown that primary productivity at light optimum was greater in the coloured lakes. Greater productivity may indicate that greater phosphatase activity can mineralize DOP substrates and enhance rates of planktonic primary production. Additions of inorganic Al were found to inhibit the rate of hydrolysis of the enzyme phosphomonoester substrate, even at relatively high substrate concentrations.

Reactive Al species can enter lakes through surface runoff and from lake sediments suggesting that lake acidification may affect phosphatase activity and DOP mineralization.

Cores consisting of sediments and overlying water were artificially acidified to examine changes in SRP and metal concentrations with increasing acidity and investigate compensatory mechanisms. Increased Al concentrations with increased acidity of core waters showed that metals were mobilized from sediments while coincident decreases in SRP concentrations suggested that Al may act directly on inorganic phosphorus and decrease its availability to biota. Given that Al can block DOP hydrolysis and sequester inorganic phosphorus it is apparent the metal mobilization could potentially pose a serious threat to trophic dynamics in lakes. However, this would depend largely on the relative concentrations of reactive forms of Al, phosphatases and substrates. Increased phosphatase activity with increasing acidity in the test cores suggested that organisms do have some compensation capacity in response to the changes (either directly or through reductions in mineralization rates) in SRP availability. Further research effort would be required to assess the importance of phosphatase mediated hydrolysis of DOP compounds in inorganic phosphorus supply in these lakes and the actual quantative ability of increases in phosphatase production in compensating of SRP losses. This compensation mechanism may partially explain the fact that decreases primary productivity has generally not been found to accompany lake water acidification.

Another question raised in this study concerns the ability of the plankton community to modify the phosphatases to ambient conditions. In 4 of the 5 lakes studies, the optimum pH for phosphatase enzymes was within 0.5 pH units of the ambient lake pH. The phosphatases in these 4 lakes were adapted to ambient conditions over a range in pH from 4.6 to 6.3, which is considerable. In Little Springfield Lake, the most recent and severely acidified lake, the phosphatase pH optima was found at 6.5 compared to the lake pH of 3.9. Although enzyme modification rates were not addressed in this study, the lack of response in Little Springfield Lake was still surprising. Bacteria are known to be major producers of phosphatase enzymes in lakes and play an important role in the breakdown of organic material. Bacteria typically have rapid turnover times and rapid modification or adaptation by bacterial communities to alterations in environmental conditions could be anticipated. Algae might respond more slowly but turnover in algal communities would still be expected in a matter of days or weeks. Many studies have examined and compared planktonic community structure in lakes varying in acidity and found that communities in lakes with substantially different acidities tend to be distinctly different (eg. Blouin 1989; Beauchamp and Kerekes 1989). Various studies have inferred changes in lakewater pH based on the relative abundance phytoplankton remains found in lake sediments (eg. Charles and Norton 1986; Charles et al. 1987). Experiments with artificial acidification of manipulated mesococosoms (Blouin 1985) have typically shown rapid response by planktonic communities to changes in pH water acidity (days to weeks) with alkaliphilic species being quickly replaced by acidobiontic or acidophilic species. Considering the rapid turnover of most phosphatase producing species (i.e. bacteria) and the pH preferences exhibited by dominant (presumably acidophilous) species, this discrepancy was surprising and remains unexplained. Sediment geochemistry profiles indicated that the four Kejimkujik area lakes have remained in a relatively steady state over the period described by the length of the cores (averaging about 100 yrs for the 4 lakes) suggesting that the rate of acidification may be important in determining effects.

Since phosphatase enzyme activity was found to be highly pH dependant, any change in ambient pH would have immediate effects on enzyme activity and DOP mineralization rates. Acid deposition episodes are known to occur frequently in the Atlantic region (Beattie and Whelpdale 1989). The implications of short term effects of episodic events (also pH depression during snowmelt) would be spatially and temporally quite variable but could also be important in trophic dynamics in poorly buffered lakes. Nalewajko and O'Mahony (1988) collected water samples from two Ontario lakes, one acidic and one circumneutral, and subjected them to rapid decreases in pH. Inorganic phosphorus concentration were found to decline initially with minimal concentrations at pH 5.2-5.6 after which concentrations increased. Increased concentrations of both Fe and Al were found to exacerbate inorganic phosphorus loss although the effects over a pH range of 4.0 to 6.0 were slightly different for the two. These data showed that not only can phosphorus availability can be affected by metals but episodicity may be important as well.

As previously discussed, sediment analyses have suggested that DOC was lost either in the watershed or in the lake itself of a combination of both. Core incubation experiments clearly showed that DOC concentrations decreased dramatically with increased acidity. While DOC losses are particularly evident in coloured waters, similar losses probably occur in clear waters as well though they are less evident. Given that DOC concentrations decrease as pH decreases, the impact of these losses on phosphatase substrate availability can only be speculated upon. Further research on the effects of pH change on DOP chemistry with special emphasis on phosphomonoesters should be undertaken.

In conclusion, the results of this study did indicate the potential for reduced phosphorus availability which supports the oligotrophication hypothesis. Evidence presented suggests that lake acidification is occurring in the region may have negative effects on nutrient cycling processes. Therefore, the null hypothesis stating that acidity does not affect phosphorus mineralization or availability is rejected. However, these effects may be subtle and highly variable spatially and temporally within and between lakes depending on a myriad of physical and chemical factors which could directly or indirectly enhance or mitigate these effects. There is also evidence that modifications of enzymes or changes in production can compensate for detrimental effects of acidification. Given the spatial and temporal variability and complexity of aquatic ecosystems, the effects would be difficult to quantify but certainly warrant further investigation.

6. Appendices

Appendix A. Results of phosphatase method calibration.

Appendix B: Mean monthly pH, DOC, aluminum, iron, manganese, calcium and total, total total dissolved and soluble reactive phosphorus.

Appendix C. Percent water, organic and mineral content of sediments in five lakes.

Appendix D. Concentrations of selected metals in sediments of five lakes.

Appendix E. Oxidation reduction potential in the sediments of 5 lakes (expressed as electrode potential in mV).

Appendix F. Porewater metal concentrations in selected lakes.

Appendix G. Enzyme kinetic calculations in sediment and water of 5 lakes.

Appendix H. Phosphatase activity and metal concentrations in cores incubated at selected pH's.

Appendix I. Phosphatase activity in water samples treated with inorganic aluminum.

Appendix J: Changes in dissolved organic carbon concentration in cores following incubation at selected pH levels.

Appendix A. Results of phosphatase method calibration.

1) Effect of incubation time:

Incubation Time (min)	PL - pNP conc (ugpNP·ml^{-1})	BL - pNP conc (ugpNP·ml^{-1})
0	0.000	0.000
10	0.046	0.014
30	0.123	0.022
60	0.231	0.050
90	0.297	0.065
120	0.431	0.078
150	0.483	0.091

2) Effect of extract volume:

Extract Volume (ml)	PL - pNP conc (ugpNP·l^{-1}·hr^{-1})	BL - pNP conc (ugpNP·l^{-1}·hr^{-1})
0.03	0.005	0.001
0.05	0.015	0.002
0.1	0.051	0.008
0.2	0.118	0.020
0.4	0.185	0.031
0.8	0.298	0.038
1.2	0.389	0.052
1.6	0.354	0.056
2.0	0.395	0.065

3) P-nitrophenol concentration vs absorbance:

pNP conc (ug·ml^{-1})	absorbance
0	0
2	0.252
4	0.504
6	0.751
8	1.004
10	1.231

Regression output:	
Constant	-0.041
Std err of y est	0.066
R squared	0.9997
No. of Observations	6
Degrees of freedom	4
X coefficient(s)	8.0829971
Std err of coef.	0.0637465

Appendix B: Mean monthly pH, DOC, aluminum, iron, manganese, calcium and total, total total dissolved and soluble reactive phosphorus.

Lake	M	pH	DOC	Al	Fe	Mn	Ca	TP	TDP	SRP
BL	5	5.5	3.1	0.05	0.04	0.01	0.37	0.007	0.001	0.001
BL	6	5.3	3.2	0.05	0.06	0.02	0.37	0.008	0.002	0.000
BL	7	5.3	2.3	0.07	0.06	0.02	0.35	0.006	0.002	0.000
BL	8	5.4	1.7	0.03	0.08	0.03	0.33	0.005	0.001	0.000
BL	9	5.3	2.0	0.04	0.08	0.02	0.33	0.007	0.002	0.000
BL	10	5.4	2.5	0.03	0.03	0.02	0.35	0.007	0.003	0.001
BL	11	5.5	2.9	0.04	0.04	0.01	0.36	0.005	0.003	0.001
BDE	5	5.9	3.6	0.09	0.04	0.01	0.71	0.004	0.000	0.000
BDE	6	5.8	3.9	0.10	0.06	0.02	0.68	0.006	-	0.000
BDE	7	6.0	3.5	0.06	0.03	0.02	0.64	0.003	-	0.000
BDE	8	6.0	3.3	0.04	0.02	0.01	0.73	0.004	-	0.000
BDE	9	6.1	2.8	0.05	0.03	0.00	0.60	0.004	-	0.000
BDE	10	5.9	3.2	0.06	0.04	0.01	0.69	0.004	-	0.000
BDE	11	5.9	3.2	0.06	0.09	0.01	0.80	0.007	-	0.002
BDW	5	5.0	7.5	0.19	0.15	0.02	0.62	0.010	-	0.003
BDW	6	5.3	7.0	0.20	0.18	0.02	0.67	0.008	-	0.002
BDW	7	5.2	9.0	0.30	0.20	0.02	0.72	0.007	-	0.001
BDW	8	5.3	7.2	0.19	0.16	0.02	0.67	0.007	-	0.001
BDW	9	5.2	18.0	0.18	0.30	0.02	0.75	0.009	-	0.002
BDW	10	5.2	12.2	0.25	0.27	0.02	0.85	0.010	-	0.003
BDW	11	4.8	13.0	0.24	0.23	0.02	0.80	0.005	-	0.001
LTS	5	3.7	2.1	3.7	0.85	0.30	6.6	0.008	0.005	0.002
LTS	6	3.7	0.9	3.7	0.73	0.33	6.8	0.008	0.002	0.000
LTS	7	3.6	0.4	2.4	1.17	0.31	6.4	0.005	0.003	0.000
LTS	8	3.6	0.4	2.2	0.65	0.30	6.3	0.008	0.003	0.001
LTS	9	3.5	0.7	3.1	0.65	0.33	6.3	0.016	0.010	0.002
LTS	10	3.5	0.0	3.9	0.52	0.35	6.4	0.009	0.006	0.002
LTS	11	3.5	0.4	3.6	0.74	0.33	6.1	0.006	0.003	0.001
PL	5	4.5	10.1	0.18	0.16	0.03	0.42	0.014	0.004	0.001
PL	6	4.5	11.6	0.2	0.16	0.01	0.34	0.014	0.006	0.003
PL	7	4.6	9.4	0.22	0.18	0.03	0.41	0.021	0.005	0.002
PL	8	4.5	10.1	0.20	0.18	0.01	0.34	0.017	0.004	0.001
PL	9	4.6	9.2	0.22	0.19	0.01	0.33	0.019	0.006	0.002
PL	10	4.6	14.0	0.25	0.22	0.01	0.39	0.012	0.005	0.002
PL	11	4.4	20.5	0.34	0.23	0.01	0.42	0.012	0.005	0.001

Appendix C. Percent water, organic and mineral content of sediments in five lakes.

Beaverskin Lake.

DATE: 26/7/87

DEPTH (cm)	% WATER	% ORGANIC	% MINERAL
0-1	91	33	67
1-2	88	26	74
2-3	86	27	73
5-7	88	24	76
7-9	86	27	73
9-11	84	27	73
11-13	85	29	71
13-15	88	31	69
15-17	89	31	69

DATE: 17/9/87

DEPTH (cm)	% WATER	% ORGANIC	% MINERAL
0-1	89	29	71
1-2	88	26	74
2-3	85	24	76
3-4	85	25	75
4-5	84	25	75
5-7	83	25	75
7-9	84	26	74
9-11	82	28	72
11-13	85	29	71
13-15	87	30	70
15-17	87	32	68

DATE: 24/7/87

DEPTH (cm)	% WATER	% ORGANIC	% MINERAL
0-1	93	30	70
1-2	87	26	74
2-3	86	24	76
3-4	84	23	77
4-5	84	24	76
5-7	83	26	74
7-9	83	26	74
9-11	83	26	74
11-13	82	35	65
13-15	82	35	65

Appendix C. cont'd.

Big Dam East Lake cont'd

DATE: 20/8/87

DEPTH (cm)	% WATER	% ORGANIC	% MINERAL
0-1	89.3	23	77
1-2	84.4	22	78
2-3	80.4	22	78
3-4	81.1	24	76
4-5	81.4	23	77
5-7	82.4	22	78
7-9	82.5	23	77
9-11	82.2	24	76
11-13			
13-15	81.6	23	77
15-17			
17-19	81.4	22	78
19-21			

Big Dam West Lake.

DATE: 4/11/87

DEPTH (cm)	% WATER	% ORGANIC	% MINERAL
0-1	92	24	76
1-2	88	23	77
2-3	85	22	78
3-4	83	21	79
4-5	82	21	79
5-7	80	20	80
7-9	79	19	81
9-11	76	21	79
11-13	77	19	81
13-15	78	22	78
15-17	78	23	77
17-19	79	23	77
19-21	80	23	77
21-23			

Appendix C: cont'd.

Big Dam West Lake cont'd

DATE: 20/8/87

DEPTH (cm)	% WATER	% ORGANIC	% MINERAL
0-1	92	24	76
1-2	82	23	77
2-3	83	22	78
3-4	83	22	78
4-5	83	21	79
5-7	82	21	79
7-9	84	23	77
9-11	84	23	77
11-13	84	22	78
13-15	83	21	79
15-17	84	22	78
17-19	84	23	78
19-21	84	22	78
21-23	83	22	78

Little Springfield Lake.

DEPTH (cm)	% WATER	% ORGANIC	% MINERAL
0-1	70	9	91
1-2	60	7	93
2-3	60	8	92
3-4	69	12	88
4-5	79	18	82
5-6	84	21	79
6-8	84	22	78
8-10	86	25	75
10-12	89	28	72
12-14	90	29	71
14-16	91	38	62
16-18	91	35	65

Appendix C. cont'd

Little Springfield Lake

DATE: 10/8/87

DEPTH (cm)	% WATER	% ORGANIC	% MINERAL
0-1	68	10	90
1-2	60	8	92
2-3	64	9	91
3-4	73	12	88
4-5	81	19	81
5-6	84	22	78
6-8	83	22	78
8-10	86	27	73
10-12	88	28	72
12-14	89	33	67
14-16	90	37	63

DATE: 10/8/87

DEPTH (cm)	% WATER	% ORGANIC	% MINERAL
0-1	66	8	92
1-2	60	7	93
2-3	68	11	89
3-4	79	17	83
4-5	81	19	81
5-6	79	20	80
6-8	81	18	82
8-10	81	21	79
10-12	85	27	73
12-14	88	31	69
14-16	88	33	67

Pebbleloggitch Lake.

DEPTH (cm)	% WATER	% ORGANIC	% MINERAL
0-1	92	35	65
1-2	86	36	64
2-3	85	43	57
3-4	85	35	65
4-5	82	40	60
5-7	86	37	63
7-9	85	33	67
9-11	82	34	66
11-13	81	35	65
13-15	82	35	65
15-17	81	36	64

Appendix C. cont'd.

Pebbleloggitch Lake

DATE: 17/9/87

DEPTH (cm)	% WATER	% ORGANIC	% MINERAL
0-1	90	35	65
1-2	87	36	64
2-3	86	35	65
3-4	84	35	65
4-5	83	35	65
5-7	83	34	66
7-9	82	35	65
9-11	83	36	64
11-13	82	35	65
13-15	81	34	66
15-17	81	35	65

DATE: 24/7/87

DEPTH (cm)	% WATER	% ORGANIC	% MINERAL
0-1	94	36	64
1-2	88	35	65
2-3	86	36	64
3-4	84	44	56
4-5	83	35	65
5-7	85	35	65
7-9	84	35	65
9-11	82	36	64
11-13	81	35	65
13-15	81	35	65
15-17	81	35	65

Appendix D. Concentrations of selected metals in sediments of five lakes.

Beaverskin Lake (metal concentrations in $mg \cdot Kg^{-1}$ dwt).

DEPTH	Al	Ba	Be	Cd	Ca	Cr	Co	Cu	Fe
0-1	18957	97	1	<1	1848	13	3	20	5776
1-2	18072	85	1	<1	1538	12	2	15	5349
2-3	18125	72	2	1	1140	11	2	13	4544
3-4	17066	64	2	<1	995	11	3	12	4291
4-5	18496	70	2	<1	1169	11	3	16	5315
5-7	20640	74	2	<1	1327	13	5	12	7255
7-9	21694	79	2	<1	1407	14	6	13	7887
9-11	21022	75	2	<1	1342	13	6	11	7690
11-14	22721	78	2	<1	1437	14	5	11	7673
14-17	22340	75	2	<1	1411	13	4	10	6976

DEPTH	Pb	Mg	Mn	Ni	P	Sr	Sn	Ti	V	Zn
0-1	82	804	145	8	1272	24	9	633	21	34
1-2	64	752	169	7	1315	20	4	611	21	33
2-3	33	705	133	6	1475	16	6	570	21	66
3-4	13	661	140	5	1498	14	4	528	21	88
4-5	11	722	157	6	1587	15	2	554	21	71
5-7	7	793	183	8	1776	17	2	597	21	64
7-9	6	854	191	8	1853	17	3	646	21	50
9-11	5	812	180	7	1771	17	4	612	21	44
11-14	6	849	188	8	1882	18	4	638	23	52
14-17	5	828	182	7	1824	17	6	632	21	51

CORE B

DEPTH	Al	Ba	Be	Cd	Ca	Cr	Co	Cu	Fe
0-1	18724	95	1	<1	1821	16	3	12	8015
1-2	18716	87	1	<1	1559	13	3	12	6211
2-3	18919	82	1	1	1378	12	3	11	5286
3-4	18649	78	2	<1	1382	12	3	14	4632
4-5	18994	77	2	<1	1425	12	3	14	4837
5-7	20296	81	2	<1	1499	13	3	12	5092
7-9	19640	77	2	<1	1419	12	3	12	5309
9-11	19407	72	2	<1	1375	12	4	10	5419
11-14	19650	71	2	<1	1370	14	7	13	8813
14-17	23081	81	2	<1	1459	14	5	15	7208
17-20	22801	81	2	<1	1373	14	6	12	7625
20-23	23701	85	2	<1	1432	14	7	14	8893
23-26	23018	79	2	<1	1364	13	5	13	6885

Appendix D. cont'd.

Beaverskin Lake cont'd

DEPTH	Pb	Mg	Mn	Ni	P	Sr	Sn	Ti	V	Zn
0-1	84	822	554	8	1351	23	32	664	25	45
1-2	62	752	228	8	1373	21	4	650	24	37
2-3	42	796	212	7	1405	19	5	611	23	71
3-4	24	793	219	7	1492	18	7	616	22	96
4-5	18	809	211	6	1534	19	4	618	20	68
5-7	16	849	220	7	1605	20	4	653	21	50
7-9	11	810	203	6	1595	18	5	617	20	52
9-11	7	795	193	7	1567	17	5	576	19	45
11-14	6	768	211	8	1693	17	5	566	22	54
14-17	9	889	239	8	1939	19	4	679	25	60
17-2	[illegible]	859	213	8	1903	19	6	695	23	60
20-23	7	897	212	9	1906	19	5	719	25	53
23-26	7	847	204	8	1864	18	4	686	23	39

CORE C

DEPTH	Al	Ba	Be	Cd	Ca	Cr	Co	Cu	Fe
0-1									
1-2	16060	81	1	1	1217	15	4	21	6377
2-3	16383	82	1	<1	1249	15	3	21	6529
3-4	16749	79	1	<1	1268	12	3	13	4981
4-5	17379	81	1	<1	1278	13	3	13	5077
5-7	18205	82	1	<1	1344	13	3	10	5141
7-9	16918	69	1	<1	1224	12	3	8	5052
9-11	16807	66	1	<1	1186	11	2	7	5208
11-14	17241	67	2	<1	1212	12	3	8	5340
14-17	17580	72	2	<1	1232	12	3	8	4899

DEPTH	Pb	Mg	Mn	Ni	P	Sr	Sn	Ti	V	Zn
0-1	12	731	345	9	1209	17	4	563	25	37
1-2	12	788	348	8	1228	18	5	568	26	38
2-3	71	789	204	7	1225	17	7	574	21	87
3-4	53	782	258	7	1342	18	6	595	20	76
4-5	30	781	209	7	1401	19	6	603	18	62
5-7	11	714	185	7	1469	16	3	528	18	55
7-9	7	698	191	5	1438	15	3	507	16	43
9-11	7	715	213	6	1510	15	4	523	17	44
11-14	11	722	208	6	1508	16	2	531	17	41

Appendix D. cont'd.

Beaverskin Lake (core B metal concentrations in pct.ign.).

DEPTH	Al	Ti	Ba	Fe	Mn	Ca	Mg	P	SiO_2
0-1	2.67	0.09	0.01	1.15	0.08	0.26	0.12	0.19	95
1-2	2.53	0.09	0.01	0.84	0.03	0.21	0.10	0.19	96
2-3	2.49	0.08	0.01	0.70	0.03	0.18	0.10	0.18	96
3-4	2.42	0.08	0.01	0.60	0.03	0.18	0.10	0.19	96
4-5	2.50	0.08	0.01	0.64	0.03	0.19	0.11	0.20	96
5-7	2.74	0.09	0.01	0.69	0.03	0.20	0.11	0.22	96
7-9	2.65	0.08	0.01	0.72	0.03	0.19	0.11	0.22	96
9-11	2.62	0.08	0.01	0.73	0.03	0.19	0.11	0.21	96
11-14	3.02	0.09	0.01	1.36	0.03	0.21	0.12	0.26	95
14-17	3.55	0.10	0.01	1.11	0.04	0.22	0.14	0.30	95
17-20	3.51	0.11	0.01	1.17	0.03	0.21	0.13	0.29	95
20-23	3.65	0.11	0.01	1.37	0.03	0.22	0.14	0.29	94
23-26	3.54	0.11	0.01	1.06	0.03	0.21	0.13	0.29	95

Beaverskin Lake (core B metal concentrations in ppm ign.).

DEPTH	Cu	Pb	V	Zn	Ni
0-1	17	120	36	64	11
1-2	16	84	32	50	11
2-3	14	55	30	93	9
3-4	18	31	29	125	9
4-5	18	24	26	89	8
5-7	16	22	28	68	9
7-9	16	15	27	70	8
9-11	14	9	26	61	9
11-14	20	9	34	83	12
14-17	23	14	38	92	12
17-20	18	14	35	92	12
20-23	22	11	38	82	14
23-26	20	11	35	60	12

Appendix D. cont'd.

Big Dam East Lake. (metal concentrations in mg·Kg^{-1} dwt).

DEPTH	Al	Ba	Be	Cd	Ca	Cr	Co	Cu	Fe
0-1	20180	80	1	<1	1138	28	6	10	12351
1-2	22806	89	1	<1	1245	29	6	10	12247
2-3	21768	84	1	<1	1227	26	5	10	10481
3-4	22388	88	1	<1	1314	27	5	12	9959
4-5	23187	91	1	<1	1389	28	5	11	10146
5-7	22605	88	1	<1	1325	26	6	10	10353
7-9	23987	93	1	<1	1365	27	7	8	11347
9-11	24739	96	1	<1	1379	27	7	9	11869
11-14	25115	95	1	<1	1366	28	6	9	10944
14-17	26650	96	1	<1	1439	30	7	9	11682
17-20	26126	97	2	<1	1398	29	7	9	11780
20-23	28715	104	2	<1	1506	32	8	10	16160
23-26	29822	116	2	<1	1787	31	9	10	13502

Big Dam East Lake

DEPTH	Pb	Mg	Mn	Ni	P	Sr	Sn	Ti	V	Zn
0-1	59	1032	874	12	975	17	6	673	23	56
1-2	60	1112	513	12	1056	19	2	755	27	55
2-3	59	1057	342	12	1022	19	4	715	23	59
3-4	60	1104	321	11	1043	20	4	732	24	65
4-5	58	1152	324	11	1100	21	5	774	25	69
5-7	34	1087	324	12	1098	20	7	741	23	62
7-9	8	1120	339	11	1170	20	3	745	23	54
9-11	8	1144	347	12	1203	21	2	759	23	54
11-14	7	1135	339	12	1257	20	2	743	24	54
14-17	6	1172	352	12	1390	21	3	771	24	62
17-20	5	1145	352	12	1350	20	4	773	23	55
20-23	6	1340	425	15	1698	22	6	767	27	69
23-26	6	1321	374	15	1431	25	6	833	27	63

Appendix D. cont'd.

Big Dam East Lake (metal concentrations in pct.ign).

DEPTH	Al	Ti	Ba	Fe	Mn	Ca	Mg	P	SiO_2
0-1	2.62	0.09	0.01	1.60	0.11	0.15	0.13	0.13	95
1-2	2.92	0.10	0.01	1.57	0.07	0.16	0.14	0.14	95
2-3	2.79	0.09	0.01	1.34	0.04	0.16	0.14	0.13	95
3-4	2.95	0.10	0.01	1.31	0.04	0.17	0.15	0.14	95
4-5	3.01	0.10	0.01	1.32	0.04	0.18	0.15	0.14	95
5-7	2.90	0.10	0.01	1.33	0.04	0.17	0.14	0.14	95
7-9	3.12	0.10	0.01	1.47	0.04	0.18	0.15	0.15	95
9-11	3.26	0.10	0.01	1.56	0.05	0.18	0.15	0.16	95
11-14	3.30	0.10	0.01	1.44	0.04	0.18	0.15	0.17	95
14-17	3.46	0.10	0.01	1.52	0.05	0.19	0.15	0.18	94
17-20	3.35	0.10	0.01	1.51	0.05	0.18	0.15	0.17	94
20-23	3.68	0.10	0.01	2.07	0.05	0.19	0.17	0.22	93
23-26	3.82	0.11	0.01	1.73	0.05	0.23	0.17	0.18	94

Big Dam East Lake (metal concentrations in ppm. ign).

DEPTH	Cu	Pb	V	Zn	Ni
0-1	13	77	30	73	16
1-2	13	77	35	71	15
2-3	13	76	29	76	15
3-4	16	79	32	86	14
4-5	14	75	32	90	14
5-7	13	44	29	79	15
7-9	10	10	30	70	14
9-11	12	11	30	71	16
11-14	12	9	32	71	16
14-17	12	8	31	81	16
17-20	12	6	30	71	16
20-23	13	8	35	88	19
23-26	13	8	35	81	19

Appendix D. cont'd.

Big Dam West Lake. (metal concentrations in mg·Kg^{-1} dwt).

DEPTH	Al	Ba	Be	Cd	Ca	Cr	Co	Cu	Fe
0-1	21350	135	<1	<1	1407	22	5	15	9373
1-2	21901	141	<1	1	1505	22	5	13	8275
2-3	22854	146	<1	<1	1597	23	5	17	8720
3-4	23007	149	<1	1	1619	22	5	12	8989
4-5	25215	163	<1	<1	1800	24	5	14	9307
5-7	24765	160	<1	<1	1752	22	5	12	8831
7-9	26867	172	<1	<1	1864	24	6	9	9560
9-11	29991	193	<1	1	2045	26	6	10	10481
11-14	30304	192	<1	<1	2101	27	6	10	10589
14-17	29658	185	<1	1	2056	26	7	10	10235
17-20	26423	163	<1	<1	1918	24	6	10	9361
20-22	25761	158	<1	<1	1958	23	5	9	9254

DEPTH	Pb	Mg	Mn	Ni	P	Sr	Sn	Ti	V	Zn
0-1	22	1647	247	9	745	27	3	1185	25	26
1-2	26	1729	257	9	707	28	5	1249	26	26
2-3	27	1818	267	10	713	30	2	1285	26	28
3-4	25	1836	277	10	733	30	5	1302	26	29
4-5	21	2012	312	10	712	33	5	1417	27	36
5-7	17	1983	308	9	644	32	3	1300	28	34
7-9	11	2166	343	9	839	35	3	1527	28	33
9-11	10	2324	390	10	731	39	6	1704	30	32
11-14	10	2287	394	10	820	39	4	1692	30	34
14-17	9	2218	378	10	839	38	1	1637	31	38
17-20	8	1970	340	10	819	33	2	1484	27	34
20-22	7	1945	339	9	822	32	3	1463	26	36

Big Dam West Lake (metal concentrations in pct.ign).

DEPTH	Al	Ti	Ba	Fe	Mn	Ca	Mg	P	SiO_2
0-1	2.81	0.16	0.02	1.23	0.03	0.19	0.22	0.10	95
1-2	2.84	0.16	0.02	1.07	0.03	0.20	0.22	0.09	95
2-3	2.93	0.16	0.02	1.12	0.04	0.20	0.23	0.09	95
3-4	2.95	0.17	0.02	1.15	0.04	0.21	0.24	0.09	95
4-5	3.19	0.18	0.02	1.18	0.04	0.23	0.25	0.09	95
5-7	3.13	0.16	0.02	1.12	0.04	0.22	0.25	0.08	95
7-9	3.49	0.20	0.02	1.24	0.04	0.24	0.28	0.11	94
9-11	3.89	0.22	0.03	1.36	0.05	0.27	0.30	0.09	94
11-14	3.89	0.22	0.02	1.36	0.05	0.27	0.29	0.11	94
14-17	3.80	0.21	0.02	1.31	0.05	0.26	0.28	0.11	94
17-20	3.39	0.19	0.02	1.20	0.04	0.25	0.25	0.11	94
20-22	3.30	0.19	0.02	1.19	0.04	0.25	0.25	0.11	95

Appendix D. cont'd.

Big Dam West (metal concentrations in ppm. ign).

DEPTH	Cu	Pb	V	Zn	Ni
0-1	20	29	33	34	12
1-2	17	34	34	34	12
2-3	22	35	33	36	13
3-4	15	32	33	37	13
4-5	18	27	34	46	13
5-7	15	22	35	43	11
7-9	12	14	36	43	12
9-11	13	13	39	42	13
11-14	13	13	38	44	13
14-17	13	12	40	49	13
17-20	13	10	34	43	13
20-22	12	9	33	46	12

Little Springfield Lake (metal concentrations in mg·Kg^{-1} dwt).

DEPTH	Al	Ba	Be	Cd	Ca	Cr	Co	Cu	Fe
0-1	60231	455	1	<1	1970	58	17	50	54552
1-2	66850	456	1	1	2190	61	23	97	23797
2-3	66215	435	1	<1	2194	58	37	64	26641
3-4	70557	455	2	<1	2070	62	42	63	32339
4-5	67909	422	1	<1	1716	58	42	61	33500
5-7	69498	414	1	<1	1686	56	38	39	34711
7-9	69339	417	1	<1	1701	57	44	52	35036
9-11	43091	238	1	<1	3082	36	13	23	28609
11-14	54460	333	1	<1	3129	45	22	27	35882
14-17	63302	396	1	<1	2630	52	31	33	40075
17-20	66373	396	2	<1	1922	52	44	33	38352

Little Springfield Lake (metal concentrations in pct. ign).

DEPTH	Pb	Mg	Mn	Ni	P	Sr	Sn	Ti	V	Zn
0-1	24	5503	671	32	523	85	13	3861	88	57
1-2	53	6065	852	42	434	95	10	4413	85	99
2-3	64	5990	803	72	669	89	10	4201	85	228
3-4	72	6101	688	85	924	86	11	4078	89	309
4-5	69	5522	540	84	964	75	12	3602	86	362
5-7	52	5264	502	70	953	73	10	3459	82	215
7-9	65	5406	510	85	982	74	12	3546	84	338
9-11	17	2893	374	27	1325	51	9	1703	47	74
11-14	20	4026	456	41	1238	63	8	2400	64	97
14-17	30	4873	504	62	1061	71	8	3011	75	139
17-20	35	4887	438	83	1039	68	7	3088	77	172

Appendix D. cont'd.

Little Springfield Lake cont'd

CORE B

DEPTH	Al	Ba	Be	Cd	Ca	Cr	Co	Cu	Fe
0-1	62402	418	1	1	2549	53	19	78	24702
1-2	56313	352	1	1	2790	46	22	41	19860
2-3	60125	374	1	<1	2764	49	26	43	24131
3-4	63196	388	1	<1	2328	51	30	48	28393
4-5	71086	432	1	<1	2253	56	37	71	33943
5-6	67856	411	1	<1	2189	54	29	44	33412
6-8	60602	367	1	<1	2028	48	24	29	30292
8-10	64626	397	1	<1	2063	51	25	29	34140
10-12	56895	354	1	<1	2040	47	24	28	36896
12-14	45712	274	1	<1	2068	39	19	24	32447
14-16	44712	266	1	<1	2122	37	14	25	28934

DEPTH	Pb	Mg	Mn	Ni	P	Sr	Sn	Ti	V	Zn
0-1	32	5771	1099	32	259	99	8	4870	74	61
1-2	36	5029	1225	39	321	96	5	4746	64	89
2-3	47	5349	1121	51	535	93	12	4564	71	135
3-4	64	5347	868	58	678	85	17	4031	75	194
4-5	65	5844	723	72	831	87	13	3842	84	258
5-6	62	5469	728	57	801	83	10	3989	79	179
6-8	42	4847	672	46	680	76	9	3490	69	138
8-10	41	5128	636	49	788	78	11	3575	75	123
10-12	16	4488	599	48	905	70	9	3086	66	93
12-14	17	3513	511	40	976	60	7	2489	51	73
14-16	16	3305	452	30	1052	56	7	2080	49	62

Little Springfield Lake (metal concentrations in pct.ign).

DEPTH	Al	Ti	Ba	Fe	Mn	Ca	Mg	P	SiO_2
0-1	6.69	0.43	0.05	6.06	0.07	0.22	0.61	0.06	86
1-2	7.27	0.48	0.05	2.59	0.09	0.24	0.66	0.05	89
2-3	7.28	0.46	0.05	2.93	0.09	0.24	0.66	0.07	88
3-4	8.02	0.46	0.05	3.67	0.08	0.24	0.69	0.11	87
4-5	8.38	0.44	0.05	4.14	0.07	0.21	0.68	0.12	86
5-7	8.91	0.44	0.05	4.45	0.06	0.22	0.67	0.12	85
7-9	8.89	0.45	0.05	4.49	0.07	0.22	0.69	0.13	85
9-11	5.90	0.23	0.03	3.92	0.05	0.42	0.40	0.18	89
11-14	7.78	0.34	0.05	5.13	0.07	0.45	0.58	0.18	85
14-17	10.05	0.48	0.06	6.36	0.08	0.42	0.77	0.17	82
17-20	10.54	0.49	0.06	6.09	0.07	0.31	0.78	0.16	82

Appendix D. cont'd.

Little Springfield Lake (metal concentrations in ppm ign).

DEPTH	Cu	Pb	V	Zn	Ni
0-1	56	27	98	63	36
1-2	105	58	92	108	46
2-3	70	70	93	251	79
3-4	72	82	101	351	97
4-5	75	85	106	447	104
5-7	50	67	105	276	90
7-9	67	83	108	433	109
9-11	32	23	64	101	37
11-14	39	29	91	139	59
14-17	52	48	119	221	98
17-20	52	56	122	273	132

Pebbleloggitch Lake (metal concentrations in mg$\cdot$Kg^{-1} dwt).

CORE A

DEPTH	Al	Ba	Be	Cd	Ca	Cr	Co	Cu	Fe
0-1	10564	50	<1	<1	930	9	2	17	5035
1-2	10829	49	<1	<1	945	9	2	16	2597
2-3	11559	52	<1	<1	1021	10	2	17	2752
3-4	10654	50	<1	<1	1008	9	2	18	2096
4-5	11125	52	<1	<1	1082	9	2	21	2047
5-7	11300	55	<1	<1	1057	9	1	15	1971
7-9	12232	59	<1	<1	1268	7	1	15	1848
9-11	13566	67	<1	<1	1466	8	2	13	2071
11-14	14403	70	1	1	1571	9	2	12	2180
14-17	15907	76	1	1	1757	9	2	12	2333
17-20	16008	74	1	1	1730	9	2	10	2498

DEPTH	Pb	Mg	Mn	Ni	P	Sr	Sn	Ti	V	Zn
0-1	39	486	36	5	790	14	3	670	14	16
1-2	40	485	43	5	761	14	2	675	15	14
2-3	41	516	47	6	809	15	4	707	16	16
3-4	45	474	34	5	672	15	4	690	15	12
4-5	44	472	36	5	652	15	2	701	14	13
5-7	35	491	35	5	619	16	1	756	12	12
7-9	17	510	37	4	596	18	2	710	11	11
9-11	10	562	43	4	648	20	<1	789	11	12
11-14	7	602	47	4	687	21	1	849	12	13
14-17	5	659	51	4	706	23	<1	873	12	12
17-20	4	682	52	5	724	22	<1	900	13	13

Appendix D. cont'd.

Pebbleloggitch Lake

CORE B

DEPTH	Al	Ba	Be	Cd	Ca	Cr	Co	Cu	Fe
0-1	9558	47	<1	<1	882	8	2	23	6740
1-2	10050	48	<1	<1	949	8	2	22	2423
2-3	10818	51	<1	<1	1044	9	2	29	2104
3-4	11109	54	<1	<1	1122	8	1	27	1985
4-5	11543	55	<1	1	1169	8	1	21	1965
5-7	12867	65	<1	<1	1373	8	2	12	1964
7-9	13376	67	<1	<1	1466	9	2	12	2044
9-11	14535	72	1	<1	1581	9	2	14	2177
11-14	15012	71	1	<1	1553	9	2	11	2219
14-17	15912	76	1	<1	1739	10	2	10	2412
17-20	15599	72	1	<1	1688	9	2	10	2440

DEPTH	Pb	Mg	Mn	Ni	P	Sr	Sn	Ti	V	Zn
0-1	37	583	29	5	1010	13	1	627	13	22
1-2	47	437	28	5	643	14	5	657	14	15
2-3	47	461	31	4	663	15	4	718	15	17
3-4	48	479	32	4	623	16	1	718	14	15
4-5	39	493	33	5	630	16	3	745	13	13
5-7	14	527	40	4	627	19	2	768	11	11
7-9	13	543	44	4	653	20	3	802	12	12
9-11	7	598	46	4	675	21	2	856	12	13
11-14	7	598	46	4	692	21	2	852	12	12
14-17	5	665	51	5	683	23	2	876	12	13
17-20	4	651	51	4	672	22	1	849	13	13

Pebbleloggitch Lake (metal concentrations in pct. ign).

DEPTH	Al	Ti	Ba	Fe	Mn	Ca	Mg	P	SiO_2
0-1	1.47	0.10	0.01	1.04	0.00	0.14	0.09	0.16	97
1-2	1.57	0.10	0.01	0.38	0.00	0.15	0.07	0.10	98
2-3	1.66	0.11	0.01	0.32	0.00	0.16	0.07	0.10	98
3-4	1.71	0.11	0.01	0.31	0.00	0.17	0.07	0.10	98
4-5	1.78	0.11	0.01	0.30	0.01	0.18	0.08	0.10	97
5-7	1.95	0.12	0.01	0.30	0.01	0.21	0.08	0.10	97
7-9	2.06	0.12	0.01	0.31	0.01	0.23	0.08	0.10	97
9-11	2.27	0.13	0.01	0.34	0.01	0.25	0.09	0.11	97
11-14	2.31	0.13	0.01	0.34	0.01	0.24	0.09	0.11	97
14-17	2.41	0.13	0.01	0.37	0.01	0.26	0.10	0.10	97
17-20	2.40	0.13	0.01	0.38	0.01	0.26	0.10	0.10	97

Appendix D. cont'd.

Pebbleloggitch Lake (metal concentrations in ppm. ign).

DEPTH	Cu	Pb	V	Zn	Ni
0-1	35	57	20	34	8
1-2	34	73	22	23	8
2-3	45	72	23	26	6
3-4	42	74	22	23	6
4-5	32	60	20	20	8
5-7	18	21	17	17	6
7-9	18	20	18	18	6
9-11	22	11	19	20	6
11-14	17	11	18	18	6
14-17	15	8	18	20	8
17-20	15	6	20	20	6

Appendix E. Oxidation reduction potential in the sediments of 5 lakes (expressed as electrode potential in mV).

Beaverskin Lake.

DEPTH	CORE 1	CORE 2	AVGORP
-5			
-4			
-3		220	220
-2	210	220	215
-1	210	200	205
0	200	160	180
1	40	30	35
2	-80	-40	-60
3	-130	-80	-105
4	-140	-130	-135
5	-140	-140	-140
6	-140	-140	-140
7	-140	-140	-140
8	-140	-160	-150
9	-150	-150	-150
10	-160	-160	-160
11	-160	-160	-160
12	-170		-170

Big Dam East Lake.

DEPTH	CORE1	CORE2	AVGORP
-2	110	110	110
-1	130	110	120
0	30	100	65
1	-50	-50	-50
2	-80	-110	-95
3	-90	-120	-105
4	-100	-130	-115
5	-130	-160	-145
6	-140	-160	-150
7	-160	-160	-160
8	-160	-150	-155
9	-170	-170	-170
10	-170	-170	-170
11	-170	-170	-170
12	-170	-170	-170

Appendix E. cont'd.

Big Dam West Lake.

DEPTH	CORE 1	CORE2	AVGORP
-3	270		270
-2	260	220	240
-1	240	250	240
0	200	260	230
1	30	20	25
2	-80	-50	-65
3	-90	-70	-80
4	-100	-80	-90
5	-100	-120	-110
6	-120	-120	-120
7	-120	-120	-120
8	-110	-130	-120
9	-130	-130	-130
10	-130	-110	-130
11	-140	-140	-140
12		-140	-140

Little Springfield Lake.

DEPTH	CORE 1
-1	300
0	250
1	10
2	0
3	-20
4	-30
5	-50
6	-50
7	-70
8	-70
9	-70
10	-70
11	-60
12	-50
13	-50

Appendix E. cont'd.

Pebbleloggitch Lake.

DEPTH	CORE 1	CORE 2	AVGORP
-5	220		220
-4	220		220
-3	200		200
-2	110		110
-1	50		50
0	10		10
1	-40		-40
2	-50	-50	-50
3	-70	-90	-80
4	-90	-100	-95
5	-110	-90	-100
6	-130	-140	-135
7	-140	-140	-140
8	-140	-140	-140
9	-140	-140	-140
10	-140	-140	-140
11	-150	-150	-150
12	-160	-160	-160
13		-160	-160
14		-160	-160
15		-160	-160

Appendix F. Porewater metal concentrations in selected lakes.

Beaverskin Lake.

DEPTH	AL	AL	AL	AVG
-5	0.18	0.15	0.08	0.14
-4	0.14	0.14	0.12	0.13
-3	0.14	0.13	0.19	0.15
-2	0.15	0.12	0.12	0.13
-1	0.15	0.12	0.15	0.14
0	0.15	0.12	0.15	0.14
1	0.25	0.20	0.13	0.19
2	0.17	0.23	0.15	0.18
3	0.21	0.19	0.15	0.18
4	0.19	0.18	0.15	0.17
5	0.31	0.18	0.17	0.22
6	0.20	0.12	0.19	0.17
7	0.18	0.21	0.19	0.19
8	0.22	0.21	0.20	0.21
9	0.17	0.24	0.17	0.19
10	0.23	0.16	0.20	0.20
11	0.31	0.17	0.16	0.21
12	0.12	0.14	0.19	0.15
13	0.28	0.17	0.22	0.22
14	0.36	0.18	0.24	0.26
15	0.31	0.12	0.23	0.22

DEPTH	FE	FE	FE	FE	FE	AVG
-5	0.08	0.00	0.25	0.07	0.21	0.12
-4	0.15	0.00	0.43	0.07	0.33	0.20
-3	0.11	0.00	0.69	0.08		0.22
-2	0.10	0.00	0.98	0.07		0.29
-1	0.10	0.13	1.30			0.51
0	0.10	0.13	1.30			0.51
1	0.10	1.80	1.30	0.06		0.82
2	0.61	1.20	1.70	0.22		0.93
3	2.30	1.30	1.50	0.29	2.20	1.52
4	2.00	1.40	2.10	0.41	1.90	1.56
5	2.00	1.40	1.40	0.65	1.80	1.45
6	2.00	1.50	1.40	0.66	1.60	1.43
7	2.00	1.40	1.40	0.87	1.60	1.45
8	1.80	1.20	1.40	0.98	1.50	1.38
9	1.60	1.10	1.30	1.00	1.40	1.28
10	1.70	1.10	1.30	1.10	1.30	1.30
11	1.60	1.10	1.40	1.00	1.40	1.30
12	1.50	1.20	1.70	0.89	1.30	1.32
13	1.40	1.20	1.30	0.94	1.20	1.21
14	1.40	1.20	1.30	0.90	1.20	1.20
15	1.50	1.20	1.40	0.90	1.30	1.26

Appendix F. cont'd

Beaverskin Lake cont'd

DEPTH	MN	MN	MN	MN	MN	AVG
-5	0.02	0.01	0.03	0.01	0.05	0.02
-4	0.02	0.01	0.11	0.01	0.06	0.04
-3	0.02	0.01	0.16	0.01	0.16	0.07
-2	0.02	0.03	0.19	0.01	0.25	0.10
-1	0.03	0.04	0.28	0.02		0.09
0	0.03	0.04	0.28	0.02		0.09
1	0.13	0.20	0.27	0.07	0.47	0.23
2	0.27	0.29	0.30	0.10	0.38	0.27
3	0.34	0.31	0.28	0.12	0.32	0.27
4	0.36	0.30	0.30	0.18	0.29	0.29
5	0.33	0.30	0.26	0.23	0.28	0.28
6	0.32	0.27	0.26	0.24	0.31	0.28
7	0.30	0.24	0.26	0.25	0.31	0.27
8	0.29	0.22	0.26	0.28	0.29	0.27
9	0.29	0.21	0.25	0.29	0.29	0.27
10	0.30	0.23	0.26	0.28	0.28	0.27
11	0.27	0.23	0.26	0.29	0.27	0.26
12	0.27	0.24	0.32	0.30	0.26	0.28
13	0.26	0.24	0.27		0.26	0.26
14	0.28	0.24	0.27	0.34	0.26	0.28
15	0.29	0.25	0.28	0.36	0.25	0.29

DEPTH	CA	CA	CA	CA	AVG	
-5	0.38	0.38		0.34	0.37	0.01
-4	0.47	0.32		0.34	0.38	0.04
-3	0.34	0.30	0.62	0.49	0.44	0.06
-2	0.36	0.30	0.60	0.52	0.45	0.06
-1	0.39	0.32			0.36	0.02
0	0.39	0.32			0.36	0.02
1	0.34	0.40			0.37	0.02
2	0.50	0.48		0.91	0.63	0.11
3	0.60	0.49		0.80	0.63	0.07
4	0.67	0.63		0.83	0.71	0.05
5	0.69	0.60		0.75	0.68	0.04
6	0.82	0.68	0.79	0.75	0.76	0.03
7	0.79	0.65	0.80	0.75	0.75	0.03
8	1.00	0.63	0.82	0.75	0.80	0.07
9	0.79	0.70		0.72	0.74	0.02
10	1.50	0.63	0.81	0.72	0.92	0.17
11	0.75	0.67		0.69	0.70	0.02
12	0.79	0.69	1.00	0.67	0.79	0.07
13	0.76	0.79			0.78	0.01
14	0.79	0.77			0.78	0.01
15		0.74			0.74	

Appendix F. cont'd

Big Dam East.

DEPTH	AL	AL	AVG
-5			
-4	0.23	0.10	0.17
-3	0.24	0.12	0.18
-2	0.26		0.26
-1	0.18	0.12	0.15
0	0.20	0.11	0.16
1	0.23	0.17	0.20
2	0.27	0.16	0.22
3	0.21	0.14	0.18
4	0.21	0.13	0.17
5			
6	0.21	0.14	0.18
7		0.18	0.18
8	0.13	0.18	0.16
9	0.14	0.20	0.17
10	0.27	0.20	0.24
11	0.13	0.18	0.16
12	0.12	0.19	0.16
13	0.18	0.18	0.18
14	0.33	0.23	0.28
15	0.24	0.18	0.21

DEPTH	FE	FE	FE	FE	FE	AVG
-5	0.20	0.95		0.18	0.05	0.35
-4	0.13	0.60		0.16	0.05	0.24
-3	0.34	1.30	0.14	0.38		0.54
-2	0.44	1.60	0.11	0.16	1.30	0.72
-1	0.36	0.80	0.12	0.21	2.50	0.80
0	0.49	3.60	0.12	1.00	4.00	1.84
1	0.32	3.50	0.57	0.95	2.90	1.65
2	0.45	2.80	4.80	1.10	2.90	2.41
3	0.94	2.60	3.10	1.90	2.70	2.25
4	2.50	3.00	3.60	2.20		2.83
5	2.30	3.40	2.80	1.90	2.70	2.62
6	1.70	2.80	2.80	1.90	2.90	2.42
7	1.60	3.10	2.80	1.80	2.90	2.44
8	1.40	2.90	2.90	2.10	2.70	2.40
9	1.20	3.10	2.90	1.90	2.80	2.38
10	1.10	2.50	2.80	2.00	2.80	2.24
11	1.20	2.40	2.90	2.20	2.60	2.26
12	1.30	2.30	2.80	2.30	2.50	2.24
13	1.10	2.80	2.80	2.30	2.40	2.28
14	1.30	2.50	2.80	2.40	2.60	2.32
15	1.10		2.70			1.90

Appendix F. cont'd.

Big Dam East

DEPTH	MN	MN	MN	MN	MN	AVG
-5	0.02	0.02	0.02	0.03	0.02	0.02
-4	0.02	0.02	0.02	0.04	0.01	0.02
-3	0.02	0.06	0.04	0.04		0.04
-2	0.07	0.12	0.08	0.02	0.06	0.07
-1	0.10	0.14	0.31	0.02	0.28	0.17
0	0.15	0.31	0.38	0.03	0.48	0.27
1	0.14	0.36	0.54	0.08	0.42	0.31
2	0.27	0.40	0.41	0.01	0.42	0.30
3	0.27	0.39	0.38	0.21	0.39	0.33
4	0.28	0.45	0.38	0.31		0.36
5	0.30	0.45	0.39	0.31	0.37	0.36
6	0.29	0.43	0.39	0.28	0.37	0.35
7	0.28	0.42	0.37	0.27	0.37	0.34
8	0.23	0.41	0.39	0.31	0.37	0.34
9	0.25	0.42	0.39	0.29	0.35	0.34
10	0.23	0.40	0.39	0.33	0.36	0.34
11	0.26	0.39	0.38	0.32	0.35	0.34
12	0.22	0.38	0.37	0.32	0.34	0.33
13	0.25	0.38	0.37	0.36	0.32	0.34
14	0.26	0.37	0.35	0.36	0.32	0.33
15	0.25					0.25

DEPTH	CA	CA	CA	AVG
-5				
-4	0.57	0.55		0.56
-3	0.59	0.55		0.57
-2	0.59	0.54	0.77	0.63
-1	0.57	0.55		0.56
0	0.59	0.59	1.30	0.83
1	0.78	1.00		0.89
2	1.10	1.10	1.50	1.23
3	0.96	1.00		0.98
4	0.93	1.20		1.07
5	1.10	1.10	1.50	1.23
6	1.10	1.10	1.60	1.27
7	1.10	1.10	1.50	1.23
8	1.30	1.10	1.60	1.33
9	1.20	1.10	1.50	1.27
10	1.30	1.10	1.50	1.30
11	1.00	1.20	1.60	1.27
12	1.10	1.10	1.50	1.23
13	1.10	1.00	1.05	0.04
14	0.98	1.20	1.50	1.23
15	1.00	1.20		1.10

Appendix F. cont'd.

Big Dam West.

DEPTH	AL	AL	AL	AL	AL	AVG
-5					0.22	0.22
-4				0.37	0.22	0.30
-3				0.38	0.20	0.29
-2	0.50			0.39	0.31	0.40
-1				0.40	0.31	0.36
0	0.50			0.39	0.34	0.41
1	0.90	0.54		0.42	0.50	0.59
2	0.90	0.68	0.52	0.33	0.52	0.59
3	0.90	0.76	0.74	0.37	0.56	0.67
4	0.80	0.65	0.71	0.50	0.60	0.65
5	0.70	0.65	0.74	0.49	0.50	0.62
6	0.80	0.66	0.77	0.53	0.58	0.67
7	0.90		0.70	0.50	0.51	0.65
8	0.90	0.61	0.81	0.52	0.54	0.68
9	0.70	0.55	0.72	0.51		0.62
10	0.90	0.57	0.66	0.48	0.60	0.64
11	0.80	0.64	0.54	0.47		0.61
12	1.10	0.85	0.58	0.48	0.60	0.72
13	1.20	1.31	0.55	0.54	0.61	0.84
14	1.20	1.62	0.56	0.60		1.00
15		2.23	0.52	0.53	0.56	0.96

DEPTH	FE	FE	FE	FE	FE	FE	AVG
-5						0.34	0.34
-4	0.21	0.24	0.48	0.17	0.37	0.29	0.29
-3	0.17	0.28	0.86	0.18	0.31	0.37	0.36
-2	0.17	0.35	0.53	0.21	0.55	0.68	0.42
-1	0.20	0.29	0.66	0.15	0.54	1.60	0.57
0	0.81	0.93	0.86	0.21	0.48	1.50	0.80
1	2.90	2.50	1.80	1.00	1.20	1.50	1.82
2	3.60	2.70	2.40	1.70	1.50	2.90	2.47
3	3.20	2.50	3.30	2.40	1.60	2.70	2.62
4	3.40	2.30	2.80	2.20	1.80	2.70	2.53
5	3.40	2.40	2.60	2.30	1.90	2.00	2.43
6	3.40	2.30	2.50	2.20	2.00	2.50	2.48
7	3.10	2.20	3.10	2.30	1.90	2.60	2.53
8	3.00	2.40	2.10	2.30	1.90	2.50	2.37
9	2.90	2.40	2.70	2.40	2.10		2.50
10	3.50	2.30	2.00	2.30	2.00	2.40	2.42
11	3.20	2.10	2.60	2.20	2.00		2.42
12	3.20	2.50	2.20	2.30	2.10	2.40	2.45
13	3.40	2.60	2.00	2.40	2.50	2.40	2.55
14	2.90	2.50	2.00	2.30	2.10		2.36
15	4.10		2.50	2.30	2.20	3.20	2.86

Appendix F. cont'd

Big Dam West Lake

DEPTH	MN	MN	MN	MN	MN	MN	AVG
-5						0.02	0.02
-4	0.02	0.02	0.01	0.03	0.02	0.02	0.02
-3	0.02	0.02	0.01	0.03	0.02	0.02	0.02
-2	0.02	0.02	0.01	0.03	0.02	0.03	0.02
-1	0.02	0.02	0.01		0.02	0.03	0.02
0	0.03	0.03	0.02	0.02	0.02	0.02	0.02
1	0.05	0.03	0.02	0.03	0.03	0.03	0.03
2	0.05		0.03	0.03	0.04	0.04	0.04
3	0.03	0.05	0.03	0.02	0.03	0.04	0.03
4	0.04	0.05	0.04	0.03	0.04	0.04	0.04
5	0.03	0.05	0.04	0.03	0.04	0.03	0.04
6	0.04	0.04	0.05		0.04	0.04	0.04
7	0.05	0.05	0.05	0.04	0.04	0.04	0.05
8	0.03	0.05	0.04	0.04	0.05	0.04	0.04
9	0.03	0.05	0.05	0.04	0.05		0.04
10	0.04	0.05	0.05	0.05	0.06	0.04	0.05
11	0.03	0.06	0.06	0.05	0.06		0.05
12	0.04	0.05	0.06	0.06	0.06	0.05	0.05
13	0.04	0.05	0.06		0.08	0.06	0.06
14	0.06	0.06	0.07	0.07	0.07		0.07
15	0.05		0.07			0.05	0.06

DEPTH	CA	CA	CA	AVG
-5				
-4	0.57	0.67	0.59	0.61
-3	0.59	0.60	0.60	0.60
-2	0.57	0.62	0.53	0.57
-1	0.57	0.72	0.52	0.60
0	0.59	0.64	0.56	0.60
1	0.77	0.80	0.62	0.73
2	1.00	0.89	0.79	0.89
3	0.97	0.99	0.92	0.96
4	1.10	1.00	1.10	1.07
5	1.00	1.20	1.10	1.10
6	1.10	1.20	1.30	1.20
7	1.10	1.00	1.20	1.10
8	1.10	1.20	1.20	1.17
9	1.00	1.00	1.20	1.07
10	1.20	1.10	1.30	1.20
11	1.00	1.20	1.10	1.10
12	1.00	1.20	1.20	1.13
13	1.10	1.20	1.10	1.13
14	1.10	1.00	1.00	1.03
15	1.10			1.10

Appendix F. cont'd

Little Springfield Lake.

DEPTH	AL	AL	AL	AL	AL	AL	AVG
-4	2.70	2.62	2.28	4.20	2.90	3.30	3.00
-3	2.60	2.59	2.35	4.20	2.80	3.20	2.96
-2	2.40	2.63	2.27	4.30	2.70	3.70	3.00
-1	2.50	2.41	2.34	4.50	2.70	3.60	3.01
0	2.90	2.42	2.73	5.40	2.40	4.10	3.33
1	3.10	2.02	2.75	6.30	2.00	4.50	3.45
2	3.10	2.13	3.33	6.30	1.80	7.20	3.98
3	2.30	2.38	2.74	4.40	1.60	6.80	3.37
4	2.00	2.40	2.84	2.60	1.00	6.40	2.87
5	1.80	2.64	2.54	1.40	0.70	4.80	2.31
6	1.60	2.67	2.54	0.90	0.50	3.90	2.02
7	1.40	2.94	2.53	0.20		3.10	2.03
8	0.70	3.30	2.19	0.20		2.00	1.68
9	0.70	2.92	1.86	0.14	0.09	1.20	1.15
10	0.00	2.74	1.33	0.19	0.10	0.70	0.84
11	0.50	2.50	0.79	0.20	0.10	0.40	0.75
12	0.00	1.98	0.69	0.22	0.08	0.42	0.57
13	0.00	1.19	0.00	0.29	0.09	0.28	0.31
14	0.00	1.02	0.00	0.27	0.09	0.28	0.28
15	0.00	0.64	0.52	0.25	0.09		0.30

DEPTH	FE	FE	FE	FE	FE	FE	FE	AVG
-5	0.92	0.78	1.40	0.65	0.95	0.82		0.92
-4	2.40	1.90	1.40	0.57	0.78	0.68		1.29
-3	6.10	2.10	2.40	0.59	0.88	0.53		2.10
-2	5.90	2.30	3.30	0.66	0.69	0.36	0.75	2.20
-1	4.60	0.41	4.70	0.59	0.58	0.77	0.72	1.94
0	8.00	0.85	7.40	0.66		0.94	0.71	3.09
1	12.00	1.30	5.90	4.20	10.00	1.50	4.80	5.82
2	16.00	3.70	6.50	8.70	12.00	11.70	1.90	9.77
3	19.00	11.30	7.90	6.60	11.00	17.00	2.40	12.13
4	17.00	12.20	8.00	7.70			2.70	11.23
5	15.00	13.70	8.00	7.80	10.20		4.70	10.94
6	12.00	13.50	7.40	7.00	9.30	10.00	4.70	9.81
7	12.00	11.20	6.00	6.60	8.50	13.00	3.20	9.55
8	9.50	10.00	7.90	6.60	8.00	10.90	3.70	8.82
9	9.00	8.90	8.10	6.90	7.80	9.10	3.60	8.30
10	8.30	7.20	6.90	6.60	10.20	8.10		7.88
11	9.10	6.40	8.40	7.00	7.70	6.50	2.70	7.52
12	6.70	5.80	8.00	6.70	6.90	5.40	3.50	6.58
13	6.30	5.20	8.90	6.60	8.60	5.30	5.00	6.82
14	5.10	5.50	7.40	6.10		5.00		5.82

Appendix F. cont'd

Little Springfield Lake.

DEPTH	MN	MN	MN	MN	MN	MN	MN	AVG	
-4	0.36	0.39	0.37	0.35	0.42	0.32		0.37	
-3	0.37	0.55	0.36	0.35	0.41	0.32		0.39	
-2	0.36	0.44	0.36	0.35	0.44	0.32		0.38	
-1	0.35	0.43	0.35	0.36	0.42	0.32	0.32	0.36	
0	0.36	0.37	0.35	0.36	0.41	0.31	0.33	0.36	
1	0.35	0.37	0.34	0.36	0.39	0.32	0.33	0.35	
2	0.35	0.35	0.36	0.35	0.36	0.31	0.34	0.35	
3	0.36	0.31	0.33	0.35	0.35	0.30	0.35	0.34	
4	0.37	0.33	0.34	0.36	0.36	0.31	0.36	0.35	
5	0.40	0.33	0.34	0.36	0.37		0.39	0.37	
6	0.38	0.46	0.34	0.36		0.31	0.41	0.38	
7	0.41	0.38	0.33	0.36	0.39	0.31	0.45	0.38	
8	0.40	0.45	0.35	0.36	0.38	0.32	0.44	0.39	
9	0.41	0.51	0.36	0.36	0.39	0.33	0.46	0.40	
10	0.45	0.44	0.37	0.35	0.39	0.38	0.47	0.41	
11	0.43	0.46	0.38	0.37	0.34	0.41		0.40	
12	0.41	0.55	0.39	0.35	0.24	0.42	0.34	0.39	
13	0.41	0.48	0.42	0.36		0.42	0.49	0.43	
14	0.41	0.49	0.45	0.35	0.39	0.43		0.42	
15	0.37	0.50	0.44	0.35		0.43		0.42	0.44

DEPTH	CA	CA	CA	CA	CA	AVG
-5						
-4	5.70	6.00	6.00	1.40		4.78
-3	5.10	6.00	5.70	1.40		4.55
-2	5.40	6.00	5.70	1.40		4.63
-1	6.00	6.30	5.50	1.40	7.30	5.30
0	6.30	6.00	6.40	6.80	7.50	6.60
1	5.80	6.10	6.00	6.70	7.50	6.42
2	6.00	6.10	6.00	6.40	7.70	6.44
3	5.40	5.80	6.40	5.90	8.10	6.32
4		5.60	5.90	5.90	8.10	6.38
5		6.00	5.50		8.50	6.67
6		6.20	5.40		8.80	6.80
7		6.30	5.60	6.20	9.20	6.83
8	6.60	6.70	5.30	6.50	8.60	6.74
9		6.10	5.00		1.70	4.27
10		6.40	6.30		1.70	4.80
11		6.70	6.30			6.50
12		6.60	4.60	1.40		4.20
13		6.00	4.90	1.40		4.10
14		6.90	4.70	1.40		4.33
15		6.90	4.50	1.40		4.27

Appendix F. cont'd

Pebbleloggitch Lake.

DEPTH	AL	AL	AL	AL		AVG
-5	0.50		0.28	0.53	0.32	0.41
-4	0.50		0.28	0.38	0.32	0.37
-3	0.50		0.35	0.48	0.33	0.42
-2	0.50		0.33	0.40	0.44	0.42
-1	0.50		0.36	0.34	0.49	0.42
1	0.70		0.43	0.28	0.50	0.48
2	0.60	0.58	0.32	0.29	0.46	0.45
3	0.90	0.70	0.32	0.27	0.41	0.52
4	0.90	0.69	0.35	0.37	0.35	0.53
5	0.80	0.68	0.40	0.41	0.33	0.52
6	0.60	0.72	0.39	0.54	0.29	0.51
7	0.50		0.30	0.53	0.35	0.42
8	0.60	0.57	0.34	0.41	0.27	0.44
9	0.50		0.33	0.52	0.29	0.41
10			0.31	0.45	0.28	0.35
11	0.50		0.33	0.47	0.34	0.41
12			0.37	0.43	0.35	0.38
13	0.50		0.44	0.43	0.31	0.42
14	0.50		0.38	0.40	0.31	0.40
15	0.50				0.40	0.45

DEPTH	FE	FE	FE	FE	FE	FE	AVG
-4	0.28	0.22	0.16	0.36	0.36	0.63	0.34
-3	0.22	0.16	0.12	0.40	0.26	0.63	0.30
-2	0.21	0.20	0.17	0.46	0.38	0.71	0.36
-1	0.22	0.14	0.27	0.51	0.46	1.00	0.43
1	0.49	0.20	0.59	0.55	0.77	2.40	0.83
2	0.62	0.78	0.59	0.41	0.93	2.20	0.92
3	1.40	2.10	0.42	0.64	1.10	1.30	1.16
4	1.10	2.20	0.61	0.70	1.30	0.89	1.13
5	1.10	2.20	1.20	0.93	1.40	0.67	1.25
6	0.94	2.00	0.97	0.94	1.20	0.95	1.17
7	0.96	1.60	0.93	1.20	1.20	0.82	1.12
8	0.97	1.30	0.96	1.10	1.30	1.10	1.12
9	1.00	1.00	1.00	1.20	1.20	0.90	1.05
10	0.98	0.99	0.98	1.20	1.20	0.86	1.04
11	1.00	0.93	1.00	1.20	1.20	0.93	1.04
12	0.99	0.98	1.00	1.10	1.40	1.20	1.11
13	0.96	0.99	1.10	1.20	1.30	1.90	1.24
14	1.30	1.00	1.10	1.20	1.00	1.30	1.15
15	1.00	0.97	1.10	1.20	1.10	1.80	1.20

Appendix F. cont'd

Pebbleloggitch Lake

DEPTH	MN	MN	MN	MN	MN	MN	AVG
-5			0.01			0.00	0.01
-4			0.01	0.02	0.01	0.00	0.01
-3			0.01	0.01		0.00	0.01
-2			0.01	0.01		0.00	0.01
-1			0.01	0.01	0.02	0.00	0.01
1				0.01	0.01	0.00	0.01
2					0.01	0.00	0.01
3	0.01	0.01		0.01	0.01	0.00	0.01
4		0.01			0.01	0.00	0.01
5		0.01	0.01		0.01	0.00	0.01
6		0.01	0.01		0.01	0.00	0.01
7	0.01	0.01	0.01		0.01	0.00	0.01
8	0.01	0.01	0.01		0.01	0.00	0.01
9	0.01	0.01	0.01		0.01	0.00	0.01
10	0.01	0.01	0.01		0.01	0.00	0.01
11	0.02	0.01	0.01			0.00	0.01
12	0.01	0.02	0.01		0.01	0.00	0.01
13	0.02	0.01	0.01	0.01	0.01	0.00	0.01
14	0.02	0.02	0.01	0.01	0.01	0.00	0.01
15	0.02		0.01			0.00	0.01

DEPTH	CA	CA	CA	CA	AVG
-5	0.35	0.29	0.26	0.33	0.31
-4	0.40	0.27	0.32	0.33	0.33
-3	0.38	0.27	0.28		0.31
-2	0.33	0.30	0.30		0.31
-1	0.33	0.31	0.40	0.38	0.36
1	0.34	0.34	0.50		0.39
2	0.42	0.44	0.40		0.42
3	0.52	0.49	0.51	0.45	0.49
4	0.57	0.58	0.52	0.42	0.52
5	0.52	0.59	0.60	0.41	0.53
6	0.53	0.59	0.66	0.44	0.56
7	0.47	0.59	0.74	0.48	0.57
8	0.52	0.66	0.71	0.44	0.58
9	0.46	0.80	0.79	0.49	0.64
10	0.52	0.80	0.89	0.52	0.68
11	0.52	0.78	0.89	0.51	0.68
12	0.54	0.66	0.81	0.52	0.63
13	0.73	0.75	0.84	0.52	0.71
14	0.53	0.69	0.89	0.56	0.67
15	0.49	0.64	0.89	0.53	0.64

Appendix G. Enzyme kinetic calculations in sediment and water of 5 lakes.

BEAVERSKIN LAKE (WATER).

	S	V	1/S	1/V	V/S	S/V
1	2.50E-01	5.59E-06	4.00E+00	1.79E+05	2.24E-05	4.47E+04
2	1.25E-01	4.79E-06	8.00E+00	2.09E+05	3.83E-05	2.61E+04
3	6.25E-02	0.00E+00	1.60E+01	0.00E+00	0.00E+00	0.00E+00
4	3.13E-02	0.00E+00	3.19E+01	0.00E+00	0.00E+00	0.00E+00
5	1.60E-02	0.00E+00	6.25E+01	0.00E+00	0.00E+00	0.00E+00
6	8.00E-03	0.00E+00	1.25E+02	0.00E+00	0.00E+00	0.00E+00

BIG DAM EAST (WATER).

	S	V	1/S	1/V	V/S	S/V
1	1.25E-01	3.51E-05	8.00E+00	2.85E+04	2.81E-04	3.56E+03
2	6.25E-02	2.64E-05	1.60E+01	3.79E+04	4.22E-04	2.37E+03
3	3.13E-02	2.48E-05	3.19E+01	4.04E+04	7.91E-04	1.26E+03
4	1.60E-02	2.32E-05	6.25E+01	4.32E+04	1.45E-03	6.91E+02
5	8.00E-03	1.36E-05	1.25E+02	7.36E+04	1.70E-03	5.89E+02

BIG DAM WEST (SEDIMENT).

	S	V	1/S	1/V	V/S	S/V
1	6.71E-02	4.40E-04	1.49E+01	2.27E+03	6.56E-03	1.53E+02
2	1.34E-01	7.10E-04	7.46E+00	1.41E+03	5.30E-03	1.89E+02
3	2.03E-01	9.10E-04	4.93E+00	1.09E+03	4.53E-03	2.21E+02
4	2.70E-01	1.10E-03	3.70E+00	9.09E+02	4.07E-03	2.45E+02

BIG DAM WEST (WATER).

	S	V	1/S	1/V	V/S	S/V
1	2.50E-01	2.00E-05	4.00E+00	5.01E+04	7.99E-05	1.25E+04
2	1.25E-01	1.36E-05	8.00E+00	7.36E+04	1.09E-04	9.21E+03
3	6.25E-02	8.30E-06	1.60E+01	1.20E+05	1.33E-04	7.53E+03
5	1.60E-02	3.20E-06	6.25E+01	3.13E+05	2.00E-04	5.01E+03

LITTLE SPRINGFIELD LAKE (WATER).

	S	V	1/S	1/V	V/S	S/V
1	6.25E-02	3.99E-05	1.60E+01	2.51E+04	6.38E-04	1.57E+03
2	3.13E-02	3.67E-05	3.20E+01	2.72E+04	1.17E-03	8.53E+02
3	1.60E-02	2.90E-05	6.25E+01	3.45E+04	1.81E-03	5.52E+02
4	4.60E-03	1.48E-05	2.50E+02	6.76E+04	3.70E-03	2.70E+02

Appendix G. cont'd.

PEBBLELOGGITCH LAKE (WATER).

	S	V	1/S	1/V	V/S	S/V
1	2.50E-01	6.39E-05	4.00E+00	1.56E+04	2.56E-04	3.91E+03
2	1.25E-01	4.79E-05	8.00E+00	2.09E+04	3.83E-04	2.61E+03
3	6.25E-02	3.04E-05	1.60E+01	3.29E+04	4.86E-04	2.06E+03
4	3.13E-02	1.20E-05	3.19E+01	8.35E+04	3.83E-04	2.61E+03
5	1.60E-02	3.99E-06	6.25E+01	2.50E+05	2.50E-04	4.01E+03

Appendix H. Phosphatase activity and metal concentrations in cores incubated at selected pH's.

BEAVERSKIN LAKE.

pH		AL	FE	MN	CA	SRP	PASE-W	PASE-S
		--------$mg\cdot l^{-1}$---------				$ugP\cdot l^{-1}$	$umoles\cdot l^{-1}\cdot hr^{-1}$	
6.00	1A	0.24	0.13	0.00	0.26	2.0	0.073	
	1B	0.20	0.06	0.00	0.33	2.1	-	
	1C	0.25	0.05	0.04	0.64	3.8	0.054	
	1D	0.22	0.00	0.02	0.60	2.4	0.056	
	1E	0.24	0.06	0.03	0.68	4.2	0.056	
	1F	0.28	0.19	0.29	1.10	2.4	0.053	
	N	6	6	6	6	6	5	
	AVG	0.24	0.08	0.06	0.60	2.8	0.058	
	STDEV	0.02	0.06	0.10	0.27	0.9		
5.20	2A	0.27	0.00	0.07		3.1	0.038	
CONT	2B	0.25	0.27	0.25		3.3	0.058	
	2C	0.22	0.13	0.06	1.60	2.4	0.038	
	2D	0.22	0.00	0.09	0.58	1.8	0.049	
	2E	0.55	0.00	0.04	1.20	1.3	0.068	
	2F	0.21	0.00	0.03	1.40	2.9	0.094	
	N	6	6	6	4	6	6	
	AVG	0.29	0.07	0.09	1.20	2.5	0.058	
	STDEV	0.12	0.10	0.07	0.38	0.73		
4.00	3A	2.60	0.00	0.88	3.60	1.7	0.028	
	3B	2.50	0.09	2.53	6.20	1.0	0.032	
	3C	1.70	0.08	0.71	3.50	3.0	0.013	
	3D	2.60	0.00	1.10	3.70	1.8	0.053	
	3E	1.10	0.07	0.93	4.10	1.4	0.020	
	3F	2.40	0.05	1.13	4.10	1.9	0.012	
	N	6	6	6	6	6	6	
	AVG	2.15	0.05	1.21	4.20	1.8	0.055	
	STDEV	0.56	0.04	0.61	0.92	0.60		
3.00	4A	24.0	4.9	3.0	8.5	1.4	0.100	
	4B	20.0	0.3	1.4	6.6	1.4	0.094	
	4C	24.0	1.1	1.8	7.8	6.1	0.103	
	4D	25.0	0.2	2.0	8.3	4.3	0.104	
	4E	24.0	1.4	1.7	8.4	6.0	0.104	
	4F	29.0	0.1	1.8	9.3	1.5	0.104	
	N	6	6	6	6	6	6	
	AVG	24.3	1.3	1.94	8.2	3.4	0.102	
	STDEV	2.62	1.67	0.52	0.82	2.09		

Appendix H. cont'd.

BIG DAM EAST LAKE.

pH	CORE	AL	FE	MN	CA	SRP	PASE-W	PASE-S
		--------$mg\cdot l^{-1}$			--------	$ugP\cdot l^{-1}$	$umoles\cdot l^{-1}\cdot hr^{-1}$	
6.10	1A	0.29	0.50			4.2	0.184	0.360
CONT	1B	0.21	0.49	0.33		1.8	0.157	0.461
	1C	0.25	0.20	0.84		2.5	0.188	0.444
	1D	0.79	0.10			3.0	0.178	0.438
	1E	0.48	0.46	0.08		5.0	0.145	0.410
	1F	0.18	0.64	0.47		2.5	0.187	0.425
	N	6	6	4	0	6	6	6
	AVG	0.35	0.40	0.43		3.18	0.173	0.423
	STDEV	0.21	0.19	0.27		1.09		
5.00	2A	0.32	0.38	0.59		2.9	0.165	0.339
	2B	0.28	0.47	0.53		2.5	0.140	0.347
	2C	0.24	0.32	0.73		5.3	0.261	0.297
	2D	0.36	0.50	0.73		1.8	0.124	0.310
	2E	0.22	0.45	1.39		2.5	0.204	0.282
	2F	0.38	0.36	0.71		2.3	0.174	0.283
	N	6	6	6	0	6	6	6
	AVG	0.30	0.41	0.78		2.88	0.178	0.310
	STDEV	0.06	0.06	0.28		1.12		
4.00	3A	2.20	2.90	6.76		0.8	0.122	0.161
	3B	3.20	1.10	2.82	5.40	2.3	0.099	0.191
	3C	3.50	0.43	5.07	6.10	3.7	0.161	0.196
	3D	2.40	1.20	2.88	6.40	1.5	0.130	0.254
	3E	2.00	1.20	4.43	5.90	6.2	0.120	0.180
	3F	2.20	0.91	5.29	4.70	2.2	0.095	0.201
	N	6	6	6	5	6	6	6
	AVG	2.58	1.29	4.54	5.70	2.8	0.138	0.197
	STDEV	0.56	0.77	1.38	0.60	1.75		
3.00	4A	32.0	1.00	9.01		6.7	0.201	0.272
	4B	25.0	4.70	4.61		4.6	0.315	0.202
	4C	17.2	1.90	4.21		1.8	0.147	0.260
	4D	21.0	2.10	4.02		7.2	0.221	0.273
	4E	33.0	3.10	6.65		2.3	0.315	0.240
	4F	30.0	1.90	4.47		1.8	0.178	0.228
	N	6	6	6	0	6	6	6
	AVG	26.4	2.45	5.50		4.1	0.230	0.246
	STDEV	5.83	1.18	1.80		2.23		

Appendix H. cont'd

BIG DAM WEST LAKE.

pH		AL	FE	MN	CA	SRP	PASE-W	PASE-S
		--------mg·l^{-1}---------				ugP·l^{-1}	umoles·l^{-1}·hr^{-1}	
6.00	2A	0.40	0.76	0.03		1.1	0.260	0.379
	2B	0.35	0.41	0.02		7.8	0.269	0.334
	2C	0.80	1.20	0.03		1.9	0.182	0.478
	2D	0.39	1.10	0.03		6.9	0.264	0.326
	2E	0.41	0.65	0.02	0.77	8.3	0.221	0.331
	2F	0.62	0.88	0.03		1.0	0.242	0.190
	N	6	6	6	1	6	6	6
	AVG	0.50	0.83	0.03	0.77	4.5	0.240	0.340
	STDEV	0.16	0.27	0.00		3.20		
5.20	1A	0.62	3.60	0.04		2.5	0.182	0.257
CONT	1B	0.42	0.86	0.05		5.8	0.265	0.160
	1C	0.38	1.80	0.05		1.3	0.270	0.263
	1D	0.39	0.51	0.05		5.8	0.217	0.295
	1E	0.45	0.53	0.04		3.9	0.233	0.267
	1F	0.67	1.90			2.7	0.259	0.174
	N	6	6	5	0	6	6	6
	AVG	0.49	1.53	0.05		3.7	0.238	0.236
	STDEV	0.11	1.08	0.00		1.67		
4.00	3A	0.90	0.15	0.13	4.70	1.8	0.139	0.270
	3B	1.00	0.56	0.11	4.10	8.6	0.142	0.248
	3C	0.80	1.20	0.09	2.60	4.0	0.135	0.354
	3D	0.80	0.37	0.16	5.90	3.1	0.129	0.185
	3E	1.10	0.88	0.10	3.80	1.1	0.173	0.254
	3F	-	-	-	-	-	-	-
	N	5	5	5	5	5	5	5
	AVG	0.92	0.63	0.12	4.22	3.7	0.144	0.262
	STDEV	0.12	0.37	0.02	1.08	2.64		
3.00	4A	15.0	0.84	0.43	18.0	1.7	0.363	0.409
	4B	4.8	4.80	0.40	17.0	1.1	0.190	0.421
	4C	9.1	8.90	0.37	14.0	3.1	0.165	0.464
	4D	12.6	0.55	0.31	13.0	3.0	0.221	0.396
	4E	11.5	0.82	0.36	13.0	3.1	0.538	0.393
	4F	-	-	-	-	-	0.533	0.391
	N	5	5	5	5	5	6	6
	AVG	10.6	3.18	0.37	15.0	2.4	0.335	0.412
	STDEV	3.47	3.27	0.04	2.10	0.82		

Appendix H. cont'd.

PEBBLELOGGITCH LAKE.

pH		AL	FE	MN	CA	SRP	PASE-W	PASE-S
		--------mg·l^{-1}---------				ugP·l^{-1}	umoles·l^{-1}·hr^{-1}	
6.00	2A	0.78	2.30	0.04	0.38	9.6	0.125	0.109
	2B	0.45	0.84	0.05		4.7	0.133	0.028
	2C	0.52	2.00			9.8	0.100	0.044
	2D	0.58	1.10	0.04		6.2	0.073	0.048
	2E	0.64	0.76	0.06		6.6	0.068	0.079
	2F	0.51	0.70	0.04		7.1	0.112	0.109
	N	6	6	5	1	6	6	6
	AVG	0.58	1.28	0.05	0.38	7.3	0.097	0.070
	STDEV	0.11	0.63	0.01		1.81		
4.70	1A	0.03	0.60	0.08		3.2	0.222	-
CONT	1B	0.47	0.43	0.05		1.4	0.213	0.217
	1C	0.35	0.52	0.05		6.9	0.217	0.269
	1D	0.41	0.81			3.5	0.218	0.351
	1E	0.30	0.61			4.1	0.218	0.342
	1F	0.38				7.2	0.204	0.536
	N	6	5	3	0	6	6	6
	AVG	0.32	0.59	0.06		4.4	0.215	0.343
	STDEV	0.14	0.13	0.01		2.06		
4.00	3A	3.20		0.09	3.20	1.8	0.202	0.126
	3B	0.62	0.38	0.05		2.6	0.165	0.280
	3C	0.57	3.90	0.04		4.3	0.184	0.191
	3D	0.73	0.08	0.02		1.0	0.136	0.070
	3E	0.61	1.00	0.07		2.2	0.154	0.324
	3F	1.10	2.70	0.08		7.4	0.153	0.204
	N	6	5	6	1	6	6	6
	AVG	1.14	1.61	0.06	3.20	3.2	0.166	0.199
	STDEV	0.94	1.46	0.02	0.00	2.11		
3.00	4A	7.30	29.00	0.12	7.30	1.3	0.155	0.203
	4B	13.00	3.10	0.09	6.90	1.5	0.203	0.114
	4C	8.60	5.00	0.07	4.60	2.6	0.093	0.120
	4D	8.60	2.00	0.12	6.60	3.4	0.261	0.078
	4E	5.60	14.00	0.08		3.7	0.109	0.211
	4F	5.00	23.00	0.09		2.4	0.085	0.156
	N	6	6	6	4	6	6	6
	AVG	8.02	12.68	0.10	6.35	2.5	0.151	0.147
	STDEV	2.61	10.32	0.02	1.04	0.89		

Appendix I. Phosphatase activity in water samples treated with inorganic aluminum.

BL - 1	1	2	3	4	MEAN	STDEV
CONTROL	0.005	0.002	0.008	0.008	0.006	0.003
5.30	0.000	0.000	0.000	0.000	0.000	0.000

BL - 2	1	2	3	4	MEAN	STDEV
CONTROL	0.010	0.006	0.006	0.003	0.006	0.002
5.30	0.000	0.000	0.000	0.000	0.000	0.000

BDE - 1	1	2	3	4	MEAN	STDEV
CONTROL	0.105	0.090	0.076	0.084	0.089	0.011
5.50	0.008	0.001	0.005	0.001	0.004	0.003

BDE - 2	1	2	3	4	MEAN	STDEV
CONTROL	0.107	0.097	0.097	0.084	0.096	0.008
5.50	0.016	0.003	0.006	0.002	0.007	0.005

BDW - 1	1	2	3	4	MEAN	STDEV
CONTROL	0.139	0.121	0.143	0.137	0.135	0.009
5.60	0.000	0.000	0.000	0.000	0.000	0.000

BDW - 2	1	2	3	4	MEAN	STDEV
CONTROL	0.122	0.119	0.121	0.116	0.120	0.002
5.45	0.000	0.001	0.000	0.000	0.000	0.001

PL - 1	1	2	3	4	MEAN	STDEV
CONTROL	0.177	0.179	0.173	0.177	0.175	0.003
4.50	0.066	0.035	0.035	0.043	0.044	0.010

PL - 2	1	2	3	4	MEAN	STDEV
CONTROL	0.186	0.190	0.189	0.190	0.189	0.002
4.60	0.073	0.069	0.061	0.081	0.071	0.006

Appendix J: Changes in dissolved organic carbon concentration in cores following incubation at selected pH levels.

BEAVERSKIN LAKE

	5.40	5.00	4.00	3.00
1	3.9	3.3	3.3	3.3
2	3.9	3.3	3.3	3.3
3	3.3	3.3	3.3	3.3
4	3.9	3.3	3.3	3.3
5	3.3	3.3	3.3	3.3
6	3.9	3.3	3.3	3.3
X	3.7	3.3	3.3	3.3
STDEV	0.3	0	0	0

BIG DAM EAST

	5.90	5.00	4.00	3.00
1	7.3	6.2	3.3	3.3
2	3.9	7.3	3.9	3.3
3	5.0	7.3	3.9	3.3
4	5.0	6.2	3.3	3.3
5	5.0	5.0	3.3	3.3
6	5.0	3.9	3.3	3.3
X	5.2	6.0	3.4	3.3
STDEV	1.1	1.3	0.2	0.0

BIG DAM WEST

	6.00	5.50	4.00	3.00
1	18.0	15.4	9.6	5.0
2	18.8	13.1	9.6	5.0
3	30.3	15.4	9.6	5.0
4	26.9	18.8	8.5	6.2
5	23.4	14.2	8.5	5.0
6	25.7	16.5	10.8	5.0
X	24.0	15.6	9.4	5.2
STDEV	4.6	2.0	0.9	0.5

Appendix J. cont'd

LITTLE SPRINGFIELD LAKE.

	6.00	5.00	3.70	3.00
1	9.6	11.9	3.3	5.0
2	11.9	9.6	3.5	3.3
3	16.5	11.9	3.3	3.3
4	7.3	14.2	3.9	5.0
5	7.3	11.9	3.3	3.3
6	11.9	9.6	3.3	3.3
X	10.8	11.5	3.5	4.4
STDEV	3.5	1.7	0.3	1.2

PEBBLELOGGITCH LAKE.

	6.00	4.70	4.00	3.00
1	30.3	10.8	5.0	5.0
2	28.0	10.8	5.0	3.9
3	28.0	9.6	6.2	5.0
4	30.3	10.8	5.0	5.0
5	30.3	9.6	5.0	5.0
6	28.0	10.8	5.0	5.0
X	29.2	10.4	5.2	4.8
STDEV	1.3	0.6	0.5	0.4

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