

# **Phosphorus Scavenging through Calcite Co-Precipitation: Bringing Clarity to Clear Lake**

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## ABSTRACT

Clear Lake represents an economically significant mesotrophic lake located in southwest Manitoba. In an attempt to describe the biogeochemical factors and mechanisms controlling the cycling of phosphorus in this waterbody various physio-chemical and chemical attributes of the lake water, seston and sediments were measured. Within the water column clear seasonal summer stratification was evident. Hypolimnetic water remained oxic throughout the ice-free period and pH remained neutral to alkaline throughout the entire period of observation. Chemical analysis of the lake indicated the water is enriched in  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ , likely as a result of the calcareous Cretaceous shale in the surrounding watershed. During summer stratification in 2008, large concurrent increases in dissolved oxygen, pH and  $\text{CaCO}_3$  saturation index were observed to occur simultaneously with large reductions in total and dissolved P. This was interpreted as an incidence of biologically-mediated pH shift during an algal bloom leading to a precipitation of  $\text{CaCO}_3$  in association with occluded organic and inorganic P.

Fractional P analysis, conducted on particulate seston and sediment, separated the total P (TP) into Organic P (OP), Non-Apatite Inorganic P (NAIP), and Apatite P (AP). Significant amounts of AP in the seston and sediment provide support for the interpretation that authigenic  $\text{CaCO}_3$  scavenged P from the water column. Within the sediment cores, large and increasing amounts of AP indicate that all co-precipitated P is retained long term within the sediment as refractory AP.

The combination of efficient scavenging during co-precipitation events and long-term storage of P as AP in the sediments suggests that the calcareous nature of the lake is playing an important role in the biogeochemical cycles.

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## **LIST OF ABBREVIATIONS**

P – Phosphorus

TP – Total phosphorus

DP – Dissolved phosphorus

AP – Apatite phosphorus

NAIP – Non-apatite inorganic phosphorus

OP – Organic phosphorus

CSI – Calcite saturation index

DIC – Dissolved Inorganic Carbon

SAR – Sediment Accumulation Rate

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## **DEDICATION**

To my Family, Friends and Colleagues.  
In particular I would like to dedicate this to Morgan  
You are without question the engine driving team 407.

# CHAPTER 1 - SUBJECT INTRODUCTION

## 1.1 Introduction

In response to elevated phosphorus (P) concentrations in Clear Lake Manitoba, managers at Parks Canada decided to undertake a comprehensive study examining the nutrient dynamics within the lake. The fundamental goal of this study was “To understand and confirm the limiting factors for algal growth in Clear Lake” (Hilderman 2005). Previous research has clearly shown that P is the primary limiting nutrient controlling the growth of algae in most aquatic ecosystems (Schindler et al. 1971). For this reason, this study was designed to evaluate and describe the dynamics occurring within the P biogeochemical cycle of Clear Lake. With a comprehensive understanding of the P cycle in Clear Lake, it should be possible to address and describe factors limiting algal growth. At its conclusion, this study will identify the important factors that protect the desirable oligotrophic characteristics of Clear Lake.

In locations all across this country, lakes provide a serene and peaceful escape from the hectic pace of everyday life. However, from the point of view of a P containing molecule, lakes represent a location of dynamic changes. Often these transformations and cycles can be quite complex and as a result, some processes remain poorly understood (Tate 1984). Adding complexity to the P cycle is the specific arrangement of biotic and abiotic factors that exist within every different lake and watershed. The net outcome is a unique aqueous environment, in which the local conditions interact and influence common P transformation pathways.

Prior to the realization that elevated P inputs could negatively impact aquatic ecosystems, many lakes in close proximity to human settlement started showing signs of serious degradation. The most visible sign of this degradation was commonly algal proliferation and a change in the trophic status of the lake. As nutrient levels, particularly P, increased in the surface water, so too were the levels of primary production. In this fashion, natural low-productivity oligotrophic and mesotrophic lakes were transformed into highly-productive, eutrophic lakes. These changes often produced undesirable visible changes and reductions in the recreational value of lakes. This process, called eutrophication has been well documented in the literature. Fortunately, as the dynamics and mechanisms important to P cycling become better understood,

effective management strategies required to prevent and remedy these negative impacts can be developed.

Stated simply, the dynamics of the aquatic P cycle can be examined by A) quantifying the amounts and fluxes of P between the major aquatic sinks and B) determining the important factors influencing those fluxes. Within lakes, there are four main pools in which P may reside. Firstly, P exists as a dissolved inorganic or organic species within the surface water of the lake. This pool is commonly referred to as bioavailable or soluble reactive P and it represents the most important pool that supports biologic production. Secondly, P may be associated with organic biota in the surface water. This pool would include P that has been assimilated into the primary producers, zooplankton and fish. Thirdly, P is found in association with the detrital and authigenic seston settling through the water column to the sediments. This pool includes both organic detritus and inorganic P species from a variety of origins. Lastly, large quantities of P exist within the sediments of a lake. This pool is composed of seston that has recently and historically been deposited on the lakebed. The cycling and interactions among these four P pools provides the nutritional basis that limits primary production in most lakes (Figure 1).

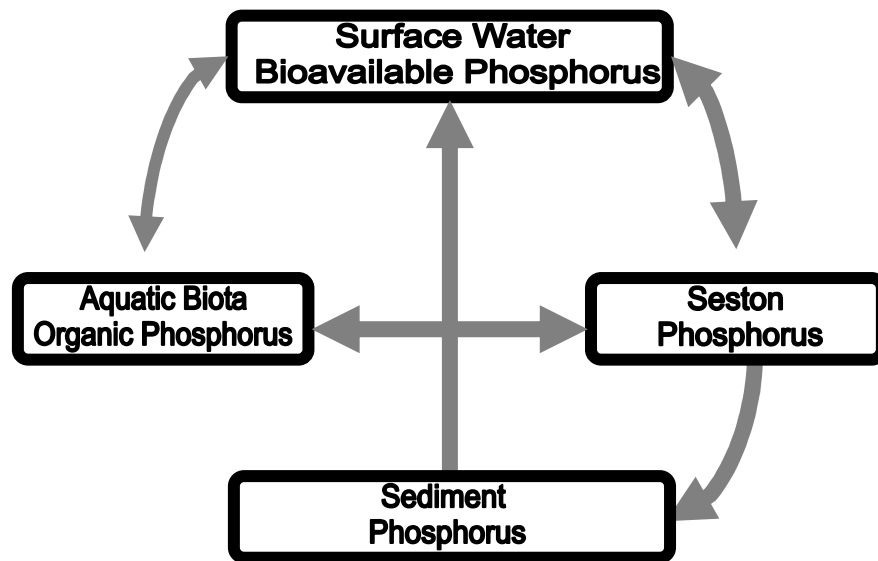


Figure 1. Simplified schematic of the four main phosphorus pools and the pathways of flux among them

Within the four major pools, P may exist in a broad array of organic and inorganic molecules. At the broadest of classifications, this includes P in association with organic molecules, and P in association with inorganic molecules. The inorganic species can be further broken down into P

in association with redox sensitive minerals, including Fe and Mn oxyhydroxides, and P in association with pH sensitive minerals, which includes P bound to Ca. The composition and proportions of these inorganic and organic P species is a vitally important factor that determines the timing, rate and amount of P that will cycle among the pools.

Differences in the composition and proportions of particulate P in the pools are largely the result of the chemistry found in the lake. With respect to P cycling, there are four broad chemical factors that have a strong influence. Firstly, redox potential is very important because it determines the oxidation and reduction state of minerals commonly associated with P. Secondly, anionic effects and competition may be important factors affecting the sorption and release of P. Thirdly, acidity and alkalinity are important factors that influence sorption and organic breakdown. Lastly are the effects of solubility and mineral precipitation, which can influence P scavenging and availability. Depending on the specific conditions present in the lake any one of these factors may prove to be the dominant factor regulating P cycling.

In order to streamline the evaluation process, many authors have developed models that simulate P cycling within lakes (Kirchener and Dillon 1975; Nurnberg 1998; Vollenweider 1969). These models are calibrated against measurements in lakes and provide estimates of surface water P concentrations as well as many other parameters. At the base of these models is a simple mass balance approach, in which P entering the lake must be balanced with P stored in the lake and P leaving the lake. Many researchers have found significant relationships between P levels and morphometric and/or hydrologic characteristics (Dillon 1975; Dillon and Rigler 1974). However, due to the large variability amongst lakes, these empirical models may produce a large prediction error for unique or exceptional lakes. Consequently, prediction accuracy is only certain when quantitative measurements, specific to the lake, are used in forecast or hind cast models.

Over the course of this study, I measured the chemical factors that are influencing the cycling of P amongst the major pools in Clear Lake. I quantified the fluxes of P traveling between the pools. Lastly, I measured the various types of P within the particulate P pools. Together these data show how chemical attributes and the major pools interact to produce the observed P cycle.

## 1.2 History of Eutrophication

Eutrophication is far from a recent phenomenon. It was first defined by Naumann (1931) as “the increase of nutritive substances, notably P and nitrogen (N), in a lake”. An early review prepared by Hasler (1947), details and discusses many of the earliest observations of lake eutrophication observed in both Europe as well as North America. Shortly after this review, impacts and degradation were recognized in many additional waterbodies, and it became evident that eutrophication truly was a global problem.

In North America, the first well-documented study of a culturally eutrophied lake took place in Lake Washington (Edmondson et al. 1956), where a change in the plankton communities from a diverse assemblage of *Anabeana*, diatoms and dinoflagellates to one dominated by blue green algae was observed. This change was accompanied by a sharp increase in hypolimnetic oxygen deficit and hypolimnetic P concentrations. Shortly after this, the same negative impacts observed in Lake Washington appeared on a much larger scale in Lake Erie (Curl 1957; Davis 1962). The evidence of eutrophication observed in Lake Erie, finally provided the governments of North America with the public health concern and financial will to address the growing problem. At this point the body of available literature expanded rapidly.

In response to the growing outcry over changes observed in Canadian lakes, the Fisheries Research Board of Canada developed an innovative and unique proposal that would place Canada at the forefront of limnological research. This strategy involved designating a vast expanse of wilderness in northwestern Ontario as a long-term study area for conducting whole lake limnological experiments. One of the first reports to arise from the Experimental Lakes Area was directed at answering conclusively the question of what single nutrient was responsible for the cultural eutrophication epidemic. These studies showed that P was indeed the limiting nutrient (Schindler et al. 1971). As a result of this report, as well as mounting evidence corroborating the Canadian research, strict limits or out-right bans were placed on phosphates in soaps and detergents in North America.

Once P had been identified as the principal limiting nutrient in freshwater aquatic systems and the ultimate contributor to the cultural eutrophication of lakes, scientific interest shifted to

understanding the underlying processes and P cycling. In the natural environment, P biogeochemical cycling is of vital importance to all primary producers that sustain life on earth (Coleman et al. 1983). These cycles include rapid chemical transformations and translocations between various biotic and abiotic pools, in both terrestrial and aqueous environments. These processes are strongly influenced by a wide variety of climate, watershed and chemical factors. As a result of the complexity associated with the biogeochemical cycles, many processes and influencing factors remain poorly understood (Tate 1984).

### **1.3 Phosphorus in Lakes**

While many authors have acknowledged that P is the limiting nutrient in aquatic systems, to be accurate, it is only that P that is available to the aquatic organisms that will limit a lake's primary productivity (Wetzel 1970; White et al. 1982). Within a lake, P may exist in a number of chemical associations. These chemical associations may be broadly classified into different operational fractions. The nature and chemical behaviour of these fractions largely determines how P is cycled among the major aquatic pools, including the dissolved bio-available pool. The other main pools through which P is internally cycled include organic bound, sestonic and sediment phosphorus. The fluxes that occur between these pools constitute the lake's internal P cycle.

#### **1.3.1 Fractionation**

Various schemes to divide the particulate P fraction in lake sediments into operationally defined groups have existed for some time (Chang and Jackson 1957; Golterman 1996; Hietjjes and Lijklema 1980; Ruttenberg 1992; Williams et al. 1971; Williams et al. 1980). These methods have provided valuable insight into the factors and mechanisms involved with P sedimentation, burial and regeneration from sediments. The basis of these analyses rests upon the behaviour of different operationally defined particulate phosphorus species. Broadly speaking, the methods divide particulate P into four operationally defined groups 1) labile P, which would include P that is loosely adsorbed to clay and organic particles, 2) redox sensitive species, such as would be found in association with particulate Fe, Al and Mn oxyhydrates, 3) organic bound P in association with living or dead organic material, and 4) pH sensitive minerals including apatite bound P and P in association with  $\text{CaCO}_3$ . In addition to these fractions, several authors have

proceeded further and attempted to fractionate out detrital and authigenic apatite ((DeVicente et al. 2006; Jordan et al. 2008; Ruttenberg 1992), and different organic fractions (Oluyedun et al. 1991).

All of the different methods for separating P fractions have advantages and drawbacks. Recently, Pardo et al. (2004) carried out a multi-laboratory comparison of the most highly cited fractionation methods. The results from this comparison showed that the method described by Williams et al. (1976b), provided the greatest level of reproducibility and inter-laboratory comparability. This method has at least two notable drawbacks. Firstly, this method could potentially underestimate the P associated with redox sensitive minerals (Pettersson et al. 1988). This occurs due to the secondary binding of dissolved P onto calcite following liberation from redox sensitive species. Second, it does not provide a measure of the labile P fraction. While it could be useful to observe this value, previous literature has indicated that this fraction is small and insignificant (<1% of Total P) (Kaiserli et al. 2002; Zhang and Shan 2008).

### **1.3.2 Bioavailable Phosphorus**

Bioavailable P represents the fraction of P available to plants to sustain growth and reproduction. It is also the smallest and most dynamic pool of P in the aquatic environment (Rigler 1964). Of this bioavailable component only a fraction exists as orthophosphate ( $\text{H}_2\text{PO}_4$ ) (Hudson et al. 2000). Much of the bioavailable P forms complexes with other inorganic components (Tarapchak et al. 1982). This P partitioning within the water column is an important determinant when evaluating the level of P deficiency in a system. Much of the variability in bioavailable P, observed among lakes is a result of lake morphometry and the algal communities inhabiting the lake (Currie 1990). Due to the vital importance and relative scarcity of reactive P, the rate at which it is assimilated is often extremely rapid (Prepas 1983).

The P uptake rate is partially independent of the concentrations in the water. To get a more accurate measurement of the efficiency with which it is being assimilated, a turnover rate can be calculated. The turnover rate is the ratio of the concentration of bioavailable P relative to the rate at which the aquatic community assimilates it. This ratio is positively related to the concentrations of dissolved P and negatively related to the biomass of the aquatic community

(White et al. 1982). In general, a short turnover time would indicate that the demand for bioavailable P is high in relation to the available supply. Long phosphorus turnover times may indicate that another factor is limiting primary production.

The assimilation of P by plants in the euphotic zone often creates strong spatial and seasonal gradients. As plants grow and reproduce in the spring and summer their demand for bioavailable P increases. As a result, the level of P deficiency in the epilimnion can increase from a low to moderate level in the spring to a high or severe deficiency in the summer (Nedoma et al. 1993). This is clearly illustrated by changes in the P concentrations in the epilimnion, which may decrease by as much as a factor of three to  $<0.005$  mg/L between mid-winter to summer. This same pattern is not as evident in the hypolimnion of the lakes. The hypolimnion of lakes represents the least biologically productive area in a lake. Without the consistent biological assimilation of P in the hypolimnion the levels can increase throughout the year and eventually account for up to 80% of the total phosphorus in the lake (Nurnberg and Peters 1984). The highest levels are generally observed directly above the sediment / water interface, due to the mineralization of organic matter and the lowering of the redox potential. This releases P coprecipitated with Fe and Mn.

### **1.3.3 Organic Bound Phosphorus**

In order to investigate organic bound phosphorus it is important to evaluate the complex interactions between aquatic primary producers, energy (light) and P. In addition to nutrients, primary producers require light energy to drive photosynthesis. Light that is available for utilization by plants is referred to as photosynthetically active radiation (PAR). 100% of the PAR is found at the immediate surface of a lake. As the PAR penetrates through the water column the radiation decreases rapidly, in roughly a logarithmic fashion. In well-circulated lakes photosynthetic organisms experience a variety of depths and receive an average amount of PAR (Diehl 2002). These environments tend to be dominated by diatoms and non-motile algae (Jager et al. 2008). Species diversity and sedimentation rates have been shown to increase in well-mixed environments (Jager et al. 2008).



In poorly circulated lakes some algae would consistently be exposed to high levels of PAR, while others would receive very little (Hulot and Huisman 2004). This lack of circulation provides the ideal situation for vertical niche partitioning to occur. Motile algae dominate the surface region, which receives the majority of the PAR, while deeper regions, with low PAR, become dominated by low light adapted biota. Both niches provide challenges and benefits. In the light rich surface layer, motile algae proliferate rapidly and quickly deplete the biologically available P. Commonly this leads to phosphorus limitation. Conversely, deeper areas with little light may experience increases in dissolved P due to sedimentation from above (Huisman et al. 2006). These areas are more likely to be limited by energy.

This vertical niche partitioning among primary producers, has lead to interesting insights into phosphorus use efficiency. Commonly, the ratio of carbon to P in aquatic algae is approximately 106:1 (Redfield 1958). Algae from a well-mixed lake are often fairly close to this value. However, as light increases and P concentrations decrease, as could be seen in the upper levels of a poorly mixed water column, organisms tend to become enriched in carbon. Conversely, as light decreases and phosphorus increases, as would be seen in the lower layers, organisms transition to being enriched in P (Sternner et al. 1997). In this fashion light tends to encourage the efficient use of P (Sternner et al. 1995).

As we have seen, the biota in a lake play an important role in consuming biologically available P. However, they also play important roles in other aspects of P cycling. Throughout their lifecycle, algae excrete large quantities of P in the form of dissolved organic P. Often, other algae quickly assimilate this P, leading to turnover times as low as 69 minutes (Lean and Nalewajko 1976). In some situations, this dissolved organic P may bind with dissolved and particulate inorganic material and be removed from the water column as seston. Finally, sestonic scavenging of organic detritus from the epilimnion represents a significant flux of phosphorus from the biologically available pool to the sediments.

#### **1.3.4 Seston Phosphorus**

The term seston refers to all of the particulate matter settling from the overlying lake water down towards the lake bottom. It is the primary mode by which P is transported from the

epilimnetic zone of the lake, down to the hypolimnion and lake sediments. The factors affecting seston transport and deposition are dynamic and highly variable amongst lakes. As a result, early attempts at modelling the nutrient fluxes in lakes were forced to make many simplifying assumptions regarding seston deposition (Chapra 1975; Dillon and Rigler 1974).

The composition of settling seston is broadly classified into two large sub-groups; detrital material and authigenic material. The detrital components commonly consist of eroded inorganic material or refractory organic compounds that have been transported to the lake from the surrounding watershed. The authigenic components mainly consist of planktonic debris, bacteria and inorganic compounds. Within both sub-groups, the P content and form may vary widely both on a temporal and spatial scale (Hupfer and Gachter 1995).

In temperate areas, seasonal changes are an important factor influencing seston P concentrations and forms. Generally, winter and spring seston fluxes to sediments are lower than those observed during other times of the year (Garcia-Ruiz et al. 2001; Penn and Auer 1997). Due to low biological activity during winter, seston deposited during this period is primarily composed of detrital minerals and organics from the surrounding watershed. During spring, temperate lakes generally receive their maximum seasonal inputs from the surrounding watershed. This input consists of heavy sediment loads and large fluxes of re-mineralized and mobilized P from material that has decayed (Fabre et al. 1996) or was weathered over the winter (Ruedrich and Siegesmund 2007). Despite the large quantities of P and suspended sediment delivered in the spring, Eckert et al. (2003) observed that the actual P concentrations in the seston were at the lowest concentrations during this season. Likely this was because the heavy sediment loads diluted P concentrations. Overall, the increase of sediment accumulation rates is still great enough to lead to a net increase in seston P accumulation (Oluyedun et al. 1993; Wodka et al. 1985).

Throughout the summer, biological activity in the lake's euphotic zone increases, leading to the consumption and assimilation of large quantities of bioavailable P. In some situations, this may lead to a decrease in total sedimentation and P flux, as measured in seston traps (Oluyedun et al. 1993; Penn and Auer 1997). In other situations biologic activity and increased summer temperatures may indirectly lead to widespread precipitation of calcite ( $\text{CaCO}_3$ ) and increased

total and P sedimentation rates (Dittrich and Koschel 2002; Garcia-Ruiz et al. 2001; Hupfer and Lewandowski 2005; Wodka et al. 1985).

Within temperate regions, the summer period often represents a period of increased precipitation and strong storms. Infrequent large precipitation events have been observed to transport large amounts of sediment and P from the watershed into the lakes (Soranno et al. 1997). This influx of sediment leads to brief periods of sediment accumulation rates of up to 7 kg per m<sup>2</sup>day (Garcia-Ruiz et al. 2001). During the fall, the biological activity within lakes slows and epilimnetic algae gradually die off. This is often reflected in the seston by annual maxima in authigenic organic P (Oluyedun et al. 1993).

In some situations the P concentrations and fractions have been observed to vary spatially around lakes due to lake chemistry (Green et al. 1985) and/or proximity to inflowing streams and rivers (Klump et al. 1997). However, for most lakes the total amount and composition of sediment settling from the epilimnion to the lakebed remains fairly consistent spatially (Douglas and Rippey 2000). For lakes that seasonally stratify, the greatest amount of variability in sestonic P concentration is observed along the depth profile. Depending on the lake, settling seston may either provide a source or a sink for dissolved hypolimnetic P. During productive periods, active P uptake by phytoplankton may cause significant P limitation in epilimnetic algae (Sterner et al. 1997). This is commonly observed in a C:P ratio >106. As this P poor organic seston settles to the lakebed it is capable of assimilating additional dissolved P in the enriched hypolimnion (Gachter and Mares 1985). In addition to organic seston, settling inorganic seston may also play an important role in hypolimnetic P uptake (Brzakova et al. 2003). For extremely deep lakes, re-mineralization of the seston during settling has been shown to reduce the total flux of particulate P to the sediment by up to 94% (Callender and Granina 1997; Maerki et al. 2006).

### **1.3.5 Sediment Phosphorus**

Sediments represent the largest reservoir of P in natural lakes. For this reason, they have been studied extensively. Two main pools of P exist in the sediments 1) P associated with inorganic minerals and 2) P associated with organic material. These broad categories can be sub-divided

based upon their origins, whether they are detrital or authigenic inputs. The inorganic mineral component can be further broken down into P that is loosely adsorbed to clays and organic particles, P associated with redox sensitive minerals and that associated with Ca in apatite minerals. All of these various pools react differently in the sediments and in combination make for a very dynamic system. The rate and efficiency with which the P recycling occurs is influenced by a number of different factors. Broadly speaking the important factors include the chemical conditions within the sediment, the physiochemical behaviour of the P species and the physical characteristics of the sediment and lake. Once mobilized, the recycled P can act as a significant source of P to the surface water and bears consideration in the overall P budget of the lake (Nurnberg and Peters 1984).

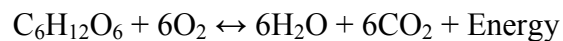
The dissolved oxygen content and pH are the primary factors that influence P cycling in the sediments. During spring overturn in dimictic lakes, the dissolved oxygen content within the hypolimnion is restored to near saturation levels. This provides a concentration gradient that favours the slow diffusion of dissolved oxygen back into the sediments of the lake. Once in the sediments it becomes available to sediment bacteria and microbes that rapidly consume it to power their metabolic pathways. The slow rate of diffusion coupled with the fact that constant microbial metabolism is occurring, restricts oxygen to the top few centimeters of sediment (Wetzel 2001). In situations where dissolved oxygen is abundant, aerobic microbes can quickly oxidize organic material. A portion of the P that is re-mineralized during this process becomes assimilated by the microbes to facilitate growth and reproduction (Eckert et al. 1997; Oluyedun et al. 1993). The remainder is released, as dissolved P, into the sediment porewater. In situations where high rates of microbial oxidation are occurring, dissolved oxygen in the sediments and hypolimnion can be rapidly depleted (Labounty and Burns 2007). This is especially common in highly productive lakes and can result in anoxic conditions throughout the stratified period. In lakes with anoxic hypolimnia microbial metabolism in the sediments proceeds through alternate metabolic pathways that are less favoured energetically. This can result in significantly slower P turnover rates (McIntyre and Reddy 1998). Overall, the oxic surface layer of sediments has the greatest abundance of microbial activity (Drabkova 1983).

Despite, the fact that microbial diagenesis occurs most efficiently under oxic conditions, these periods do not correspond to high levels of internal P loading from sediments (Hupfer et al.

1995; Penn et al. 2000; Rydin 2000). The reason for this lies in the physiochemical behaviour of redox sensitive elements including iron (Fe) and manganese (Mn) in the sediment. Under oxic conditions Fe and Mn in the sediment is commonly found in association with oxygen as oxide/hydroxides. In this form, they are insoluble and readily adsorb dissolved P from the sediment porewater and surface water (Patrick and Khalid 1974). This strong adsorption reaction binds up much of the dissolved P in the sediment, preventing its release into the overlying water. Sediment with dissolved oxygen concentrations greater than 1 mg/L have been observed to prevent the internal cycling of virtually all dissolved sediment P (Mortimer 1971).

In contrast, under anoxic conditions, Fe and Mn are rapidly reduced into soluble species. When this occurs, P that had been previously been adsorbed onto insoluble minerals is released to solution (Smolders and Roelofs 1993). This can lead to rapid fluxes of dissolved P into the overlying surface water (Christophoridis and Fytianos 2006; Mortimer 1971; Nurnberg and Peters 1984; Penn et al. 2000). In many situations this release of redox sensitive P can be further intensified by a concurrent release of bioavailable P from microbial decomposition as aerobic species are replaced by anaerobic species (Eckert et al. 1997).

During aerobic metabolism, microbes oxidize organics in the presence of oxygen. The result of this reaction is water molecules, carbon dioxide molecules and energy for the microbe.



A portion of the carbon dioxide formed during the process will then react with a water molecule forming carbonic acid.



The addition of carbonic acid into the water decreases pH. In this fashion the hypolimnion of lakes are both depleted of dissolved oxygen and enriched in protons. The pH of the water influences the P cycling within the lake in four important ways.

Firstly, acidic conditions have been found to inhibit the growth of certain fungi and microbes responsible for organic P remineralization (Kok et al. 1992; Lee and Bukaveckas 2002). This is especially noticeable in highly acidic bogs and wetlands, which preserve organics for extended periods.

Secondly, the reduction reactions of Fe and Mn compounds are pH dependent. As pH increases the redox potential required to reduce the oxidized particulate species increases, from  $-50\text{mv}$  at pH 7 to  $-150\text{mv}$  at pH 9 (Gomez et al. 1999). This has important implications for the release of P adsorbed onto oxy/hydroxides.

Thirdly, changes in the water pH affects the pH sensitive P pool that is bound to Ca species including apatite and calcite. At pH values below 6.0 dissolution of these species can occur, releasing any P that had previously been bound into Ca minerals. (Gomez et al. 1999). Below a pH of 5.0 approximately 90% of this P fraction had been recycled back into the overlying surface water in wastewater treatment ponds (Peng et al. 2007).

Lastly, changes in pH can bring about competition for anionic binding sites in the sediments. This occurs when acid anions ( $\text{HCO}_3^-$ ,  $\text{SO}_4^{2-}$ ) provide anionic competition to  $\text{HPO}_4^-$  for limited binding sites (Curtis 1989; Reddy et al. 1999). In this fashion this addition of acids increases the availability of bioavailable P by reducing the number of chemical binding sites onto which P can adsorb.

In most lakes, the combination of sedimentary processes causes a logarithmic decrease of total P with increasing depth in sediments (Livingstone and Boykin 1962; Penn et al. 1995). This has been attributed to a number of different factors, including recent changes in loading (Shapiro et al. 1971; Zhang and Shan 2008), P re-mineralization and diffusion (Ulen 1979), and sediment P diagenesis (Rydin 2000). In reality, it is likely a combination of all three mechanisms. At the surface, total concentrations of sediment P will commonly range between 0.2 and 4.0 mg/L, and occasionally reach concentrations greater than 6.0 mg/g (Sondergaard et al. 1996). This value includes a portion of the sediment P that will eventually be recycled back into the surface water (labile) and a portion that will be permanently buried (refractory). Comparisons between the settling seston and recently deposited sediment suggest that in some lakes P recycling can occur rapidly from the newly deposited sediment (Dillon and Evans 1993; Hupfer and Lewandowski 2005; Hupfer et al. 1995). However, others report that comparable results are found between the two measures (Penn et al. 1995).

Sediments that are high in redox-sensitive species often exhibit the fastest cycling of bioavailable P back into the overlying surface water (Nurnberg 1988). This is often seen during periods of hypolimnetic anoxia and low redox potentials (Eckert et al. 1997; Mortimer 1971). For this reason, calculated recycling coefficients may consider the redox sensitive pool separately when developing loss rate models (Penn et al. 1995). Overall, the role of redox sensitive P in the sediment is so great that it was found to positively influence the trophic status of a lake (Maassen et al. 2005).

P in association with organics also exhibits significant rates of recycling in the top 10 cm of sediment (Hupfer and Lewandowski 2005; Rydin 2000). This recycling primarily occurs during oxic periods in the hypolimnion and sediments (Drabkova 1983), where any re-mineralized P may be assimilated in microbial biomass (Oluyedun et al. 1993) and/or adsorbed to redox sensitive oxides and hydroxides (Patrick and Khalid 1974). Upon the depletion of oxygen from the upper sediments during periods of stratification, the assimilated and adsorbed P is recycled back to the surface water (Eckert et al. 1997).

At pH values  $>6.0$ , the calcium bound fraction remains fairly stable throughout the sediment profile (Williams et al. 1976a). Where present, this fraction is the dominant long-term burial species, comprising  $>50\%$  of the permanently buried P (Hupfer et al. 1995; Kaiserli et al. 2002; Mayer et al. 2006). Sometimes this fraction is attributed to detrital material transported from the surrounding watershed (Borgnino et al. 2006; Mayer et al. 2006; Williams et al. 1976b). However, in many situations this Ca bound fraction represents authigenic calcite that has formed in the lake and co-precipitated out both inorganic and organic P (DeVicente et al. 2006). Regardless of the source, the Ca bound fraction appears to recycle very little of the P associated with it. In culturally eutrophic lakes this fact has been exploited by managers seeking to permanently remove bioavailable P from the water column (Berg et al. 2004; Dittrich and Koschel 2002).

## 1.4 In Lake Chemical Processes and Factors

### 1.4.1 Redox Potential

At the base of most organic and inorganic geochemical cycles are microbes. These organisms derive energy by mediating the transfer of electrons from one molecule to another. Part of the energy released during these reactions can then provide metabolic energy back to the microbe. In aquatic systems, metabolism follows a progression from highest to lowest oxidizing potentials through a predictable series of agents. In well oxygenated water, oxygen always provides the highest redox potential. As oxygen is depleted, Mn (II),  $\text{NO}_3^-$ , Fe(II), and  $\text{SO}_4^{2-}$  all provide decreasing levels of redox potential (Buffle and De Vitre 1994). In aquatic systems with abundant dissolved oxygen, microbial oxidation of organics can result in high P turnover rates, between 2 minutes and 36 hours (Prepas 1983). In deeper, anaerobic environments, the oxidation of organics must occur through lower potential pathways, resulting in significant reductions in P turnover rates (McIntyre and Reddy 1998). As microbial decomposition is carried out in stratified waterbodies, oxygen may become depleted in the hypolimnion. This results in decreasing redox potential within the water.

Reducing environments are nearly always present in the sediments of a lake. Any oxygen present in the sediments must diffuse from the overlying water. Due to slow rates of diffusion, abundance of organic detritus and strong reducing conditions, dissolved oxygen is confined to the top few centimeters in the sediment (Wetzel 2001). Below this point the alternate electron acceptors rapidly become reduced. As a result, organic decomposition and P turnover will occur very slowly in the deep sediments. As the alternate electron acceptors become reduced, certain aspects of their chemical behaviour change. Of particular importance to the P cycle is iron (Fe). P commonly adsorbs to insoluble iron(hydr)oxides (Patrick and Khalid 1974). In oxidizing situations, with high levels of iron(hydr)oxides this adsorption can be very strong and lead to significant reductions in bio-available P (Froelich 1988). Under reducing conditions, reduced Fe (ferrous iron) is highly soluble and has a reduced anionic adsorption capacity as compared with the oxidized iron (ferric iron). In anaerobic situations, as are common in lake sediments, this can lead to significant increases of dissolved P and Fe (Smolders and Roelofs 1993). These dissolved species will diffuse up through the sediments, where they will encounter oxidizing conditions. Fe(II) will be oxidized to insoluble Fe(III), leading to the



adsorption of dissolved P. This series of events will occur countless times, with Fe transforming back and forth between insoluble and dissolved forms, and P will adsorb and desorb repeatedly.

### 1.4.2 Anionic Effects

Anions, specifically sulphate ( $\text{SO}_4^{2-}$ ) and nitrate ( $\text{NO}_3^-$ ) can have pronounced effects on the cycling of P in the aquatic environment. Lake sediments offer limited anionic binding sites, some of which are occupied by dissolved P species such as  $\text{HPO}_4^-$ .  $\text{HS}^-$  and  $\text{SO}_4^{2-}$  offer competitive exclusion from some of these binding sites resulting in higher concentrations of dissolved P in the water column (Caraco et al. 1989; Curtis 1989). Over the long-term, exposure of anoxic sediments to  $\text{SO}_4^{2-}$  has been shown to cause significant semi-permanent changes to the  $\text{HPO}_4^-$  adsorption capacity of lake sediments. The main reason for this is because a large portion of the sediment Fe may become bound as insoluble FeS (Smolders et al. 2006). While  $\text{SO}_4^{2-}$  occurs naturally in the environment, its concentration has been significantly increased due to anthropogenic activities (Likens et al. 1972).

Previously, it was shown that intensive fertilization in agricultural areas has brought about increased dissolved  $\text{SO}_4^{2-}$  levels. Pauwels et al. (1998) describes a process by which dissolved nitrate ( $\text{NO}_3^-$ ) percolates down from a fertilized field and enters pyrite ( $\text{FeS}_2$ ) containing aquifers. Since  $\text{NO}_3^-$  has a higher reduction potential than both Fe and sulphur (S), denitrifying bacteria are able to reduce the  $\text{NO}_3^-$  and oxidize the  $\text{FeS}_2$  to Fe(III) and dissolved  $\text{SO}_4^{2-}$ . Interestingly, this relationship has also been shown to have antagonistic effects on the release of additional P. This occurs due to an increase of P adsorbed to the Fe(III) in the water and a decrease of anionic binding sites resulting from anionic competition with  $\text{SO}_4^{2-}$  (Lucassen et al. 2004). When  $\text{NO}_3^-$  enters a lake directly, from runoff or shallow interflow, it provides an indirect increase in the adsorption capacity of the sediment. By providing an alternate electron acceptor to anaerobic microbes,  $\text{NO}_3^-$  can limit the amount of Fe that is reduced (Buffle and De Vitre 1994). In this sense  $\text{NO}_3^-$  can operate as a redox buffer, similar to alkalinity.

### 1.4.3 Acidity and Alkalinity

Acids play an important role in the rate of turnover and cycling of P within a lacustrine environment. Acidity is produced in the natural environment through a number of different mechanisms. It may be produced by terrestrial plants as a tool to extract and hydrolyse adsorbed nutrients, including P (Koo et al. 2006). It is produced as a result of the decomposition of organic matter (Ugolini et al. 1977) and some acidity is produced naturally with the dissolution of CO<sub>2</sub> from the atmosphere. As acidity levels rise fungal and bacterial growth is inhibited, thus causing an associated decrease in the rate of organic P mineralization (Kok et al. 1992; Lee and Bukaveckas 2002). This can become an important factor in wetlands and shallow lakes as they contain large quantities of decaying organic material, which may produce organic acids. For this reason acidic wetlands exhibit slower rates of decomposition and subsequently longer P turnover rates. Conversely, organic acids can form soluble complexes with Fe, indirectly preventing dissolved P from adsorbing to them and thereby enhancing the concentrations of dissolved P in the water (Ugolini et al. 1977).

Alkalinity is the capacity of water to neutralize acid and buffer pH. Alkalinity is derived from the weathering of alumino-silicates as well as carbonates (Markewitz et al. 2006; Szramek et al. 2007). In many groundwater situations CaCO<sub>3</sub> becomes supersaturated in the groundwater, with respect to surface water (Szramek et al. 2007). Upon discharge, precipitation of CaCO<sub>3</sub> can occur. Buffering can increase the rate of organic decomposition and subsequent phosphorus turnover by preventing the inhibition of fungal and microbial activities observed in acidic waters (Kok et al. 1992). Within the normal range of surface water pH values the primary species contributing to alkalinity is bicarbonate (HCO<sub>3</sub><sup>-</sup>). This species has been shown to provide competitive exclusion to HPO<sub>4</sub><sup>-</sup> from anionic binding sites similar to those observed with SO<sub>4</sub><sup>2-</sup> (Reddy et al. 1999; Smolders et al. 2006). The overall effect of increased alkalinity appears to be an increase in P turnover rate and a decrease in adsorption capacity of the sediments.

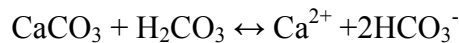
### 1.4.4 Solubility and Mineral Precipitation

P coprecipitation with CaCO<sub>3</sub> is an important P removal mechanism for many hard water lakes (Otsuki and Wetzel 1972). It has been estimated that in some lakes it can account for up to 97% of the total P removed from the epilimnion (House 1990). The solubility of CaCO<sub>3</sub> is governed

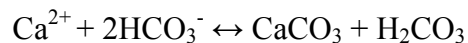
by a number of different factors; these include the dissolved inorganic carbon (DIC) concentrations and speciation, the pH of the water, the temperature of the water, the availability and size of nucleation sites, and the concentrations of various inhibiting species. Providing that conditions are favourable for the precipitation of  $\text{CaCO}_3$ , P co-precipitation might occur as direct co-precipitation of the inorganic P or indirectly as organics occluded in the mineral matrix.

The concentrations of DIC in the water and the pH of the water are, to a large extent, dependent on one another. Initially, all DIC dissolves into the water as atmospheric  $\text{CO}_2$  or from carbonate minerals. Once dissolved it will speciate according to the pH of the water. The potential species include carbonic acid ( $\text{H}_2\text{CO}_3$ ), bicarbonate ( $\text{HCO}_3^-$ ) and carbonate ( $\text{CO}_3^{2-}$ ). The proportions of each species are determined by the pH of the water. Within the range of pH values commonly observed in natural waters, the dominant species is  $\text{HCO}_3^-$ . As pH values increase, the amount of DIC speciated into  $\text{CO}_3^{2-}$  increases continuously from pH 4.5 upward. This is important because  $\text{CO}_3^{2-}$  is active in the formation of  $\text{CaCO}_3$  precipitate (e.g.,  $\text{Ca}^{2+} + \text{CO}_3^{2-} \leftrightarrow \text{CaCO}_3$ ). Additionally, as the pH of water increases above 6.3 the total amount of DIC that the water may dissolve also increases.

The pH of water will also play a role in determining the  $\text{Ca}^{2+}$  concentration in water. Carbonation weathering is the most common mode by which  $\text{Ca}^{2+}$  becomes dissolved in water. Calcium bearing carbonate minerals undergo carbonation type weathering via the following pathway:



During carbonation weathering, carbon dioxide is dissolved into water producing carbonic acid ( $\text{H}_2\text{CO}_3$ ), which subsequently enhances the dissolution of rocks and minerals. The carbonation weathering reaction is reversible and precipitates  $\text{CaCO}_3$  back out of solution via the reverse reaction.



During the precipitation of  $\text{CaCO}_3$ ,  $\text{CO}_2$  is released back into solution where it may dissolve and form carbonic acid and decrease pH (Hartley et al. 1997). Alternatively it may simply degas to the atmosphere across the water-air interface. In this fashion, pH is the master variable that

controls both the concentration of inorganic carbon ( $\text{CO}_3^{2-}$ ) and the  $\text{Ca}^{2+}$  required in the  $\text{CaCO}_3$  precipitation reaction.

The solubility of  $\text{CaCO}_3$  is related inversely to temperature, consequently more  $\text{CaCO}_3$  will dissolve in solution. This has important implications because groundwater is commonly colder than the surface water it enters. When calcite-saturated groundwater is discharged and heated in a warmer lake, precipitation will occur until the  $\text{CaCO}_3$  level re-equilibrates with the higher temperature (Brunskill 1969; Jager and Rohrs 1990). Within deeper lakes temperature may also play an indirect role in  $\text{CaCO}_3$  precipitation. Throughout the stratification period, high concentrations of  $\text{H}_2\text{CO}_3$  and  $\text{Ca}^{2+}$  will build up in the hypolimnion of a lake. With the additional pressure from the overlying water, the dissolved  $\text{CO}_2$  will remain in solution. However, upon the breakdown of the thermal stratification in the autumn, this water is circulated to the surface of the lake, where the pressure is reduced. At this point,  $\text{CO}_2$  will degas from the lake surface, the pH will rapidly increase and a  $\text{CaCO}_3$  precipitation event may be triggered (Jager and Rohrs 1990).

In the event waters become supersaturated with  $\text{CaCO}_3$  the availability (Dove and Hochella 1993; Kuchler-Krischun and Kleiner 1990; Stabel 1986; Zhang and Dawe 2000) and size of nucleation sites will play a role in determining the rate of precipitation (Berg et al. 2004; Kleiner 1988). In situations where no nucleation sites are available, spontaneous  $\text{CaCO}_3$  precipitation may not occur until the water reaches levels up to 100 times over saturation (Stabel 1986). Alternatively, in solutions with abundant small nucleation sites, as might be provided by clay particles or small organic particles, precipitation may occur at saturation levels as low as 1 (Dove and Hochella 1993). In addition to fostering precipitation, small nucleation sites increase the rate that  $\text{CaCO}_3$  crystals will grow and the P binding capacity of the forming crystals (Berg et al. 2004; Kleiner 1988). Generally, larger nucleation sites exhibit slower  $\text{CaCO}_3$  crystal growth rates and faster sediment settling velocities (Kuchler-Krischun and Kleiner 1990). This would allow for reduced opportunity for P co-precipitation and lower total amounts of calcite precipitation.

In ideal solutions containing nothing but saturated levels of  $\text{Ca}^{2+}$  and  $\text{CO}_3^{2-}$  precipitation should occur at the exact point saturation is reached. However, many matrix effects have been

observed that impact and retard the precipitation of  $\text{CaCO}_3$ . Natural waters enriched in  $\text{Ca}^{2+}$  are commonly also enriched in other divalent cations including  $\text{Mg}^{2+}$ . During  $\text{CaCO}_3$  precipitation reactions,  $\text{Mg}^{2+}$  can become included into the mineral matrix through simple ionic substitution. This causes slight imperfections in the crystal lattice and will prevent further crystal growth at that location (Hakanson et al. 2005; Meyer 1984; Zhang and Dawe 2000). When this occurs the developing  $\text{CaCO}_3$  crystal will exhibit jagged or amorphous facies and growth will be slowed (Dove and Hochella 1993; Teranes et al. 1999). It is for this reason that the formation of  $\text{CaCO}_3$  in the ocean is a slow and incomplete process (Gomez et al. 1999). In a similar fashion, high concentrations of dissolved P have been shown to inhibit the growth of  $\text{CaCO}_3$  (Meyer 1984; Reddy 1977). For example, Meyer (1984) observed a 20% reduction in  $\text{CaCO}_3$  at only 95  $\mu\text{g/L}$ , while Reddy (1977) observed a 50% reduction at 189  $\mu\text{g/L}$ . In a natural system the actual degree of inhibition would be a factor of complex matrix effects. However, it has been noted that the inhibition of  $\text{CaCO}_3$  becomes more efficient as pH levels decrease (Lin and Singer 2006).

Direct co-precipitation of  $\text{CaCO}_3$  and P involves intimate interaction between the dissolved P and the growing  $\text{CaCO}_3$  crystal. House (1990) estimates that approximately 35% of the total P removed by co-precipitation may be removed in this fashion. Otsuki and Wetzel (1972) noted that this process would be aided by increased turbulent mixing caused by wind. Often the initial P species precipitated is only an intermediate step and over time may transform into a very insoluble hydroxyl apatite mineral ( $\text{Ca}_5(\text{PO}_4)_3\text{OH}$ ) (Berg et al. 2004).

In contrast, indirect co-precipitation involves the inclusion of particulate P and/or dissolved organics into the  $\text{CaCO}_3$  crystal. This can occur in situations where an algal cell or suspended particle becomes a nucleating site (Koschel et al. 1983). This is commonly the dominant mechanism in situations where precipitation is biotically driven (De Vincente et al. 2006; Hartley et al. 1997; Kuchler-Krischun and Kleiner 1990; Stabel 1986). In biotically driven precipitation, photosynthesizing algae consume large quantities of dissolved  $\text{CO}_2$  from the water. In turn, this lowers the amount of carbonic acid dissolved in solution, which increases the pH of the water. This change in pH causes a shift in DIC speciation that favours the production of additional  $\text{CO}_3^{2-}$  and enhances the precipitation reaction. By increasing pH the

algae cause the water to become supersaturated with respect to  $\text{CaCO}_3$ , increasing the likelihood of a precipitation event (Murphy et al. 1983).

## **1.5 Previous Work at Clear Lake**

Studies at Clear Lake began prior to its inclusion within the newly formed Riding Mountain National Park in 1931. Early limnological studies were conducted to improve the sport fishery of the lake. A comprehensive account of these activities is presented by Kooyman and Hutchison (1979). Early limnological highlights include reports prepared by Bajkov (1932). This series of reports provides the first account of some of the basic physical, chemical, and biological conditions existing at Clear Lake. Rawson (1935) completed and presented a more detailed and complete limnological account of the conditions at Clear Lake. Both of these studies were conducted in order to determine the lake's suitability for the stocking of a new species of game fish. Foskett (1958) examined the winter oxygen conditions in Clear Lake. Specifically he was concerned with whether or not a significant oxygen deficit existed beneath the ice, which could hamper efforts to establish a lake trout population in Clear Lake. It was determined that while oxygen content was reduced annually under the ice, sufficient oxygen existed for the benthic dwelling lake trout.

Starting in the early 1960s studies of Clear Lake shifted focus away from fisheries improvement to inventorying the resources of the lake and park. In 1960 the Water Survey of Canada set up a water level monitoring station at the Wasagaming Pier. This station was monitored during the ice-free periods until 1978 (McGinn et al. 1998). In the 1970s a comprehensive inventory of the aquatic resources in Riding Mountain National Park was completed. The results of this inventory are summarized by Kooyman and Hutchison (1979). Beginning in 1978 Dr. K. Patalas and A. Salki began collecting baseline chemical and zooplankton data at Clear Lake and other waterbodies in the park (Salki 18/08/2007). This sampling continued until 1988 and provides a valuable source of baseline data.

The primary focus of recent projects has been developing management strategies and direction to prevent degradation of the water quality and recreational value of Clear Lake. Two areas in particular have been studied. Firstly, Delcan (1982) developed a management strategy to deal

with deterioration of beach conditions adjacent to the Wasagaming pier. The second area of concern that has received significant attention is the potential negative impact caused by anthropogenic nutrient enrichment, with primary focus on the Wasagaming wastewater treatment plant. In 1978, potential impacts of seepage into the groundwater from the sewage lagoons were assessed (Mclaren 1978). Further investigation was made on the lagoons by Bergman (1987), who determined the overall effectiveness for removing nutrients. Both reports conclude that overall the system does function effectively, however, both acknowledge that nutrients do seep from the site and could pose a risk to ground and surface water supplies. In order to assess the impacts that any additional nutrients were having on Clear Lake a detailed assessment of the algal productivity of the lake was conducted by Hawryliuk (2000). As a component of this report, a statistical analysis was conducted to determine what factors are responsible for regulating the lake's productivity. Unfortunately, no specific factor or combination of factors could be identified. In response to the uncertainty surrounding the nature and magnitude of the impacts occurring at Clear Lake, a management plan was drafted by Hilderman (2005). As a component of this report Hilderman recommended that a comprehensive investigation be made into nutrient dynamics and biogeochemical cycling of P in Clear Lake.

# **CHAPTER 2: FACTORS REGULATING PHOSPHORUS CYCLING: A CASE STUDY FROM CLEAR LAKE, MANITOBA**

## **2.1 Introduction**

In response to elevated phosphorus (P) concentrations in Clear Lake, Manitoba, Parks Canada decided to undertake a comprehensive study examining the nutrient dynamics and biogeochemical cycling within the lake. The fundamental goal of this study was “To understand and confirm the limiting factors for algal growth in Clear Lake” (Hilderman 2005 p. 6).

Previous studies have shown that, in most circumstances, P is the primary nutrient limiting the growth of algae in aquatic ecosystems (Schindler et al. 1971). For this reason, this study was designed to evaluate and describe the dynamics occurring within the P biogeochemical cycle of Clear Lake.

Typically, the biogeochemical cycling of P within lakes involves dynamic P transformations and translocations among four main pools. The four P pools include bioavailable P, organic P, sestonic P and lastly, particulate P in the lake’s sediments. For the purpose of this study, bioavailable P is defined as P that may be efficiently assimilated by the lake’s primary producers. It may be in association with carbon as dissolved organic molecules or in dissolved inorganic forms. Organic P is defined as P in association with living biota. Sestonic P represents both the inorganic and organic P in association with the detrital material settling through the water column towards the sediments. Finally, the sedimentary P pool is composed of the total inorganic and organic P within the lake sediments.

The dynamics occurring within these individual P pools have been extensively studied and documented. However, it is rare to see a study that effectively investigates all of the important P pools in a holistic fashion and synthesizes the results into a complete mechanistic picture of the important factors operating within the P biogeochemical cycle of a lake (Hakanson et al. 2005).

Bioavailable P in lake water represents a vital and often limiting nutrient to aquatic primary producers, which in turn support the aquatic food web in lakes. Broadly speaking this P may



arrive in a lake in the form of runoff from the surrounding watershed or as atmospheric deposition directly on the lake's surface. Due to the biologic importance and relatively scarcity in the terrestrial environment, the bioavailable P pool often represents the smallest of the four main lacustrine P pools in temperate settings (Rigler 1964). When bioavailable P is present, it will often be assimilated by aquatic biota extremely rapidly (Prepas 1983). The rate and quantity of organic assimilation may be greatly influenced by chemical and morphometric conditions (Jager et al. 2008; Tarapchak et al. 1982). Once assimilated by living organisms, the organic P may become incorporated into higher trophic levels of the food chain or be rapidly cycled among primary producers in the form of dissolved organic exudates (Lean and Nalewajko 1976).

Regardless of the trophic level, all biota will eventually die. At this point any P in association with suspended organic detritus will enter the sestonic pool. The fate of sestonic P depends on environmental conditions. In some situations seston will act as a source for re-mineralized inorganic P into the bioavailable pool (Callender and Granina 1997; Maerki et al. 2006). In other situations it will act to secondarily adsorb dissolved P and scavenge resources from living aquatic biota (Brzakova et al. 2003; Gachter and Mares 1985).

As seston settles to the profundal sediments, P enters the sedimentary P pool. The sediments represent the largest reservoir for P in temperate lakes (Rigler 1964). As the largest potential source for P, the biogeochemical cycling that occurs in the sediments may greatly impact the trophic status of lakes (Nurnberg and Peters 1984).

Most freshwater systems are ionically dominated by  $\text{Ca}^{2+}$  and  $\text{HCO}_3^-$ . This is especially true for temperate calcareous lakes. In calcareous lakes, elevated concentrations of  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  and  $\text{CO}_3^{2-}$  may influence the biogeochemical cycling of P in two important ways. Firstly, in situations where  $\text{Ca}^{2+}$  and  $\text{CO}_3^{2-}$  concentrations exceed the solubility product of calcite ( $\text{CaCO}_3$ ), precipitation of  $\text{CaCO}_3$  may occur (Brunskill 1969; Strong and Eadie 1976). During this precipitation process, crystalline  $\text{CaCO}_3$  may adsorb and scavenge inorganic and organic P from the surface waters (Murphy et al. 1983; Otsuki and Wetzel 1972). This mechanism has been shown to account for the removal of up to 97% of the total epilimnetic P in some lakes (House 1990).

In an ideal solution  $\text{Ca}^{2+}$  and  $\text{CO}_3^{2-}$  mineral precipitation will take place when the solution exceeds the solubility product of  $\text{CaCO}_3$ , provided that nucleation sites are present to foster the growing crystals (Kleiner 1988). However, in situations where elevated  $\text{Mg}^{2+}$  and  $\text{HPO}_4^{3-}$  are also present in solution, competition for ionic binding sites may affect and inhibit the precipitation process (Meyer 1984; Zhang and Dawe 2000). As a result, dissolved  $\text{Ca}^{2+}$  and  $\text{CO}_3^{2-}$  in the water may build up to levels that far exceed the theoretical  $\text{CaCO}_3$  solubility product.

The second important way that  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  and  $\text{CO}_3^{2-}$  may affect the biogeochemical cycling of P has to do with the important role they may play in influencing the rate and efficiency of sediment P recycling. High levels of  $\text{Ca}^{2+}$  and  $\text{CaCO}_3$  in the sediment promote the incorporation of P into highly recalcitrant apatite minerals (Berg et al. 2004). Additionally, the alkaline pH conditions and increased  $\text{CaCO}_3$  saturation levels, common in calcareous lakes, favour the stability of P adsorbed to  $\text{CaCO}_3$  and apatite minerals. Commonly, the net result in undisturbed calcareous lakes is reduced levels of primary productivity, relative to lakes that do not exhibit calcareous characteristics (Wetzel 1970).

The objective of this study was to examine the cycling of P in Clear Lake by A) quantifying the fluxes of P between the major pools and B) determining the important factors influencing the observed fluxes. To quantify P fluxes, measurements of the four main P pools were gathered and analysed. Total and dissolved phosphorus were measured directly from the surface waters of the lake. While this is an overestimation of bioavailable P (Fisher and Lean 1992), it provides an important indication of the potential bioavailable pool. The sestonic P pool was measured in submerged seston traps deployed over the ice-free periods of 2007 and 2008. The sedimentary P pool was examined directly from 2 dated sediment cores gathered during the ice-covered period of 2008. The organic P pool was not directly measured. Instead chemical fractionation of the particulate P found in the seston and sediments provided insight into short-term seasonal changes and longer-term annual changes to organic P fluxes.

The important factors and mechanisms influencing cycling of P within Clear Lake were assessed by examining a comprehensive suite of lake water physiochemical characteristics

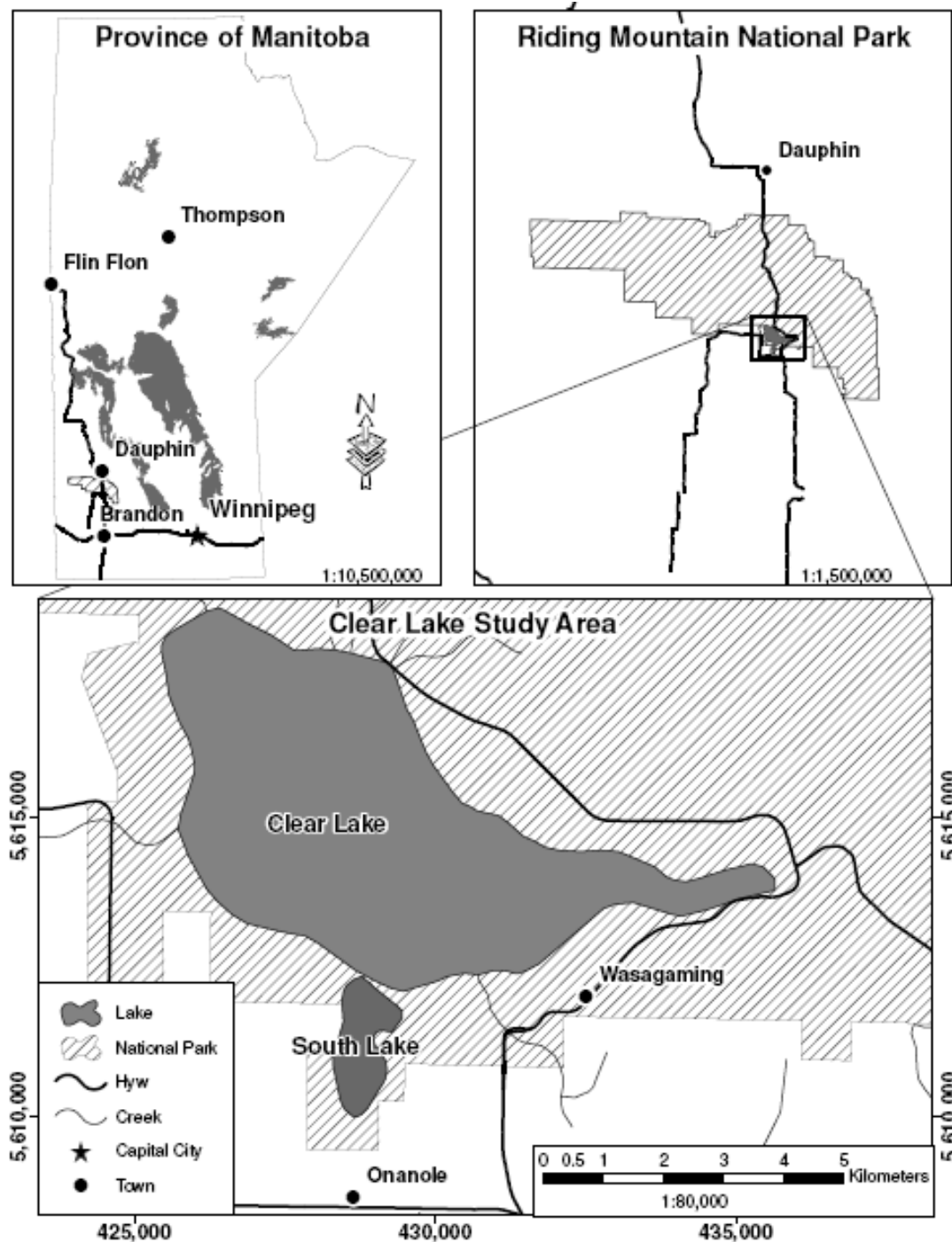
gathered during the ice-free periods of 2007 and 2008. With these data, annual patterns and important limnological characteristics affecting P cycling were noted and placed into context with the measured fluxes. Based upon these measurements and observations I constructed a comprehensive picture of the magnitudes and important factors operating in the P biogeochemical cycle of Clear Lake. Finally, I extrapolated across the entire basin of Clear Lake to place a total value on the P fluxes annually entering and leaving the lake basin.

## **2.2 Site Description**

Riding Mountain National Park (RMNP) (Figure 2) represents an oasis of pre-European forest cover surrounded by a sea of intensely cultivated agricultural land. It extends over a distance of almost 100 km from west to east and covers a total area of 2973 km<sup>2</sup> (Hawryliuk 2000).

Located wholly within the boundaries of RMNP, Clear Lake represents the primary destination for a large majority of park visitors. The southern shore of the lake provides the setting for the seasonally occupied town site of Wasagaming, Manitoba. The footprint of the lake covers an area of 2626 ha, or approximately 23% of the 11648 ha watershed area. At its deepest point, the lake measures 34.2 metres deep (Delcan 1982), while the mean depth is roughly 8 metres. In total the lake contains approximately  $3.08 \times 10^8$  m<sup>3</sup> of water.

RMNP is situated on an escarpment, at the boundary of the Manitoba Lowlands and the Saskatchewan Plain. The escarpment is primarily composed of Cretaceous period shale ranging in age between 90-100 million years old (Lang 1974). The surficial geology of the area was shaped during the last glacial period, during the Pleistocene epoch. Retreating glaciers deposited a blanket of sediment consisting of clay, gravel, cobble and boulder sized particles across the entire area of RMNP. These deposits were subsequently sorted and redistributed on the landscape by glacial meltwater, resulting in the knob and kettle topography seen today (Lang 1974).



**Figure 2. Location of Clear Lake and Riding Mountain National Park in relation to the Province of Manitoba**

RMNP experiences a continental climate with four distinct seasons. Specifically, it may be characterized by long cold winters and short warm summers. The park itself is situated within a microclimate influenced by the elevation difference between the surrounding agricultural

prairies and the escarpment. At its highest point RMNP rises 475m above the surrounding plains. The result of this elevation difference is a decrease in mean annual temperature by 2 to 4° C, as compared to the surrounding plains (Keck 1975). Surprisingly, these highlands do not appear to receive additional precipitation due to orographic uplift. Instead, Keck (1975) observed lower precipitation values for the park as compared with the surrounding area.

The town of Wasagaming, Manitoba, on the shores of Clear Lake, represents the destination for the majority of the visitors to RMNP. As a result of the lake's seasonal popularity and resulting increase in anthropogenic P, the lake faces the prospect of possible nutrient degradation and eutrophication. Previous studies investigating the sewage treatment system and inputs of nutrients into the lake confirmed that the treatment systems in place were indeed functioning properly and efficiently (Bergman 1987; McLaren 1978). Despite this, recent studies have suggested that the surface water, in this naturally mesotrophic lake, were indeed exhibiting P concentrations more commonly associated with eutrophic systems (Hawryliuk 2000).

## **2.3 Methods**

### **2.3.1 Water Chemistry**

During the ice-free periods of 2007 and 2008, water samples were collected from Clear Lake. These included representative samples from across the depth profile. During unstratified periods samples were collected from 1m, 5m, 10m, 15m, 20m and 28m depths. Upon the onset of stratification slight adjustments were made to the 15m sample to include a sample representative of the metalimnion. Water samples were collected using an acrylic Kemmerer bottle and stored in 500 ml polyethylene bottles for transport to the laboratory. At the time of sampling, a suite of water quality measurements were gathered at 1 m intervals along the depth profile. These included measurements of dissolved oxygen, conductivity, temperature and pH. The measurements were taken using a YSI 600R water quality sampling sonde and a 650MDS multi-display meter.

Chemical variables were analyzed at the Okanagan Region Chemical Analysis Centre. The analysed variables included; total P (TP), dissolved P (DP), major cations and anions, and finally alkalinity. P samples were prepared using a digestion technique (Menzel and Corwin

1965), followed by the single solution spectrophotometric method originally described by Murphy and Riley (1962). P Measurements were made on a Varian CARY 50 UV-Visible Spectrophotometer. Dissolved anion ( $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{NO}_2^-$ , and  $\text{SO}_4^{2-}$ ), and cation ( $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Fe}^{2+}$ ,  $\text{Mn}^{2+}$ ) samples were first filtered through 0.45  $\mu\text{m}$  glass fibre filters, that had previously been muffled at 450°C for 60 minutes. Anions were measured in a Varian Prostar liquid chromatograph, equipped with a 410 autosampler, CD25 conductivity detector and Ultra II suppressor column. Cation analysis was carried out on a Thermo Electron Corporation iCAP 6000 series, Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES). Alkalinity measurements were made using a QC titrate auto-titrator and values determined using Gran method calculations.

### **2.3.2 Seston Analysis**

Sediment traps were deployed throughout the spring and summer periods of 2007 and 2008. Sediment traps were constructed of PVC pipe, with an inside diameter of 5.1 cm and a length of 30 cm, as is recommended by Bloesch and Burns (1980). Sediment traps were anchored in the hypolimnion of Clear Lake, at a depth of 25 metres below the surface. A subsurface float was used to mark the traps and proved effective at minimizing any turbulence from wind and wave action. The traps were emptied at intervals between 1 – 2 weeks, to limit the potential of re-mineralization of the seston in traps. Collected samples were emptied into individual polyethylene bags and frozen prior to analysis.

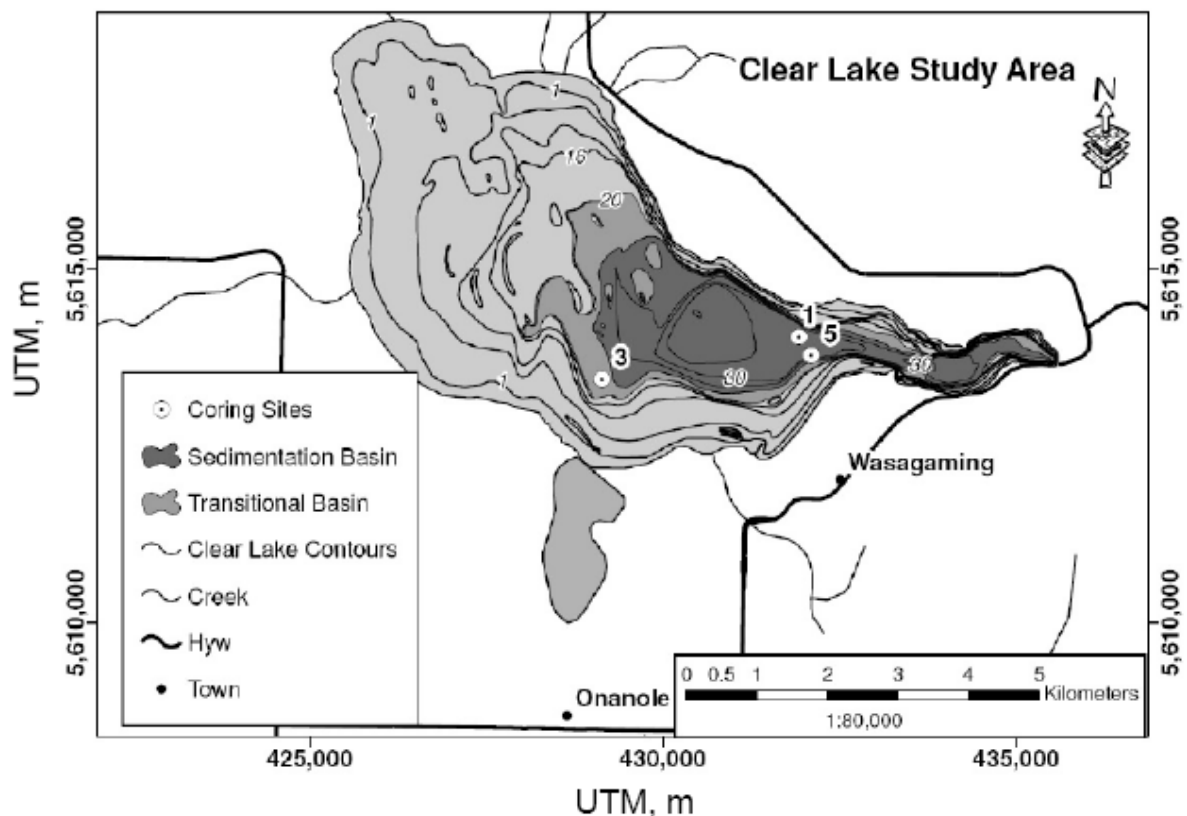
Frozen samples were transferred to individual 50ml polyethylene centrifuge tubes. The tubes were freeze-dried and weighed to determine the total dry mass of the seston. All samples were homogenized in preparation for the P fractionation. The P fractionation was carried out using the method described by Pardo et al. (2004). For consistency, all P measurements were made using the same methods described for the water samples and sediment samples.

In total, 27 seston samples were taken in 2007 and 2008. Each sample was a composite of two seston collection chambers on each trap. With the exception of the samples from between June 5<sup>th</sup> and July 11<sup>th</sup> 2007 all of the samples were done in duplicate and averaged. Sediment dry weight flux ( $\text{g DW} / \text{m}^2 \text{ day}$ ) falling to the sediments was calculated for each trap deployment

period by dividing the total collected dry mass by the number of days and the area of the trap opening

### 2.3.3 Sediment Cores

Sediment samples were collected through the ice at three locations around the sedimentary basin of Clear Lake in February 2008 (Figure 3). Cores were gathered using a polycarbonate HTH gravity corer, with an inside diameter of 70 mm. Upon the initial extraction, the sediment cores were extruded into 1cm sections that were packaged individually in polyethylene bags prior to freezing and transport.



**Figure 3.** Clear Lake bathymetry, sampling sites indicated with small black dots. Lightest shades of gray indicate areas of estimated sediment resuspension (<20m), intermediate gray tones indicate areas of potential sediment accumulation (20 – 24m) and darkest gray tones indicate estimated boundary of the sediment depositional boundary (>24m)

In the lab, samples were weighed, freeze-dried and reweighed to establish a dry weight (DW). Dried samples were chemically treated to extract total P (TP), organic P (OP), non-apatite inorganic P (NAIP) and apatite P (AP) (Pardo et al. 2004; Williams et al. 1980). As with all P

fractionation methods, advantages and disadvantages have been outlined. The primary advantage to this method is its straightforward and expedient procedure, as compared with the other described methods (i.e., Chang and Jackson 1957; Golterman 1996; Hieltjes and Lijklema 1980; Ruttenberg 1992; Williams et al. 1971). The principal drawback to the P fractionation method is that some P readsorption can occur onto carbonates in the sediments (Pettersson et al. 1988). While this was a concern for the calcareous sediments of Clear Lake, Ruban et al. (1999, 2001) confirmed that this method provided accurate results on a variety of different lake sediments and standard reference materials, including those from calcareous lakes.

Chemical extractions were carried out in boro-silicate centrifuge vials, complete with caps lined with unreactive Teflon<sup>™</sup>. All of the extracted samples were centrifuged at 1800 RPM for 15 minutes, prior to the removal of the extractant for P analysis. Once P had been extracted from the sediment, samples were prepared and analysed using the same method as that used for the surface water samples. Selected sub-samples from the cores were sent to MYCORE Laboratories for Pb-210 dating. Based upon these dates and the measured sediment dry weights, a sediment accumulation rate (SAR) for the sediment layers was calculated using the constant rate of supply model (Appleby and Oldfield, 1978).

### **2.3.4 Calcite Saturation Index (CSI)**

The calcite saturation index estimates the degree of calcite saturation in water. In order to calculate the CSI of Clear Lake water it was necessary to measure and calculate the concentrations of  $\text{Ca}^{2+}$  and  $\text{CO}_3^{2-}$ .  $\text{Ca}^{2+}$  concentrations were measured using ICP-OES, along with several other elements (previously described).  $\text{CO}_3^{2-}$  concentrations were calculated using field-measured pH and air equilibrated alkalinity measurements (previously described).

The simplified definition of alkalinity is shown in equation 1.

$$\text{Alkalinity (meq/L)} = (\text{OH}^-) + (\text{HCO}_3^-) + 2(\text{CO}_3^{2-}) - (\text{H}^+) \quad (1)$$

For my samples, pH values ranged between 7.76 and 9.00, at these values the concentration of  $(\text{H}^+)$  was assumed to be negligible in relation to the  $(\text{OH}^-)$  and therefore was treated as zero. The measured alkalinity and pH was then used to calculate the total inorganic carbon using the equation 2.



$$\text{TOT CO}_3 = \frac{\text{Alkalinity(meq/L)}}{\frac{(\text{H}^+)\text{K}_{\alpha 1}}{X} + \frac{2 \text{K}_{\alpha 1}\text{K}_{\alpha 2}}{X}} \quad (2)$$

Where,

$$\text{K}_{\alpha 1} = 10^{-6.35} \quad (3)$$

$$\text{K}_{\alpha 2} = 10^{-10.33} \quad (4)$$

$$X = (\text{H}^+)^2 + (\text{H}^+)\text{K}_{\alpha 1} + \text{K}_{\alpha 1}\text{K}_{\alpha 2} \quad (5)$$

With the  $\text{TOT CO}_3$ , as well as  $\text{K}_{\alpha 1}$  and  $\text{K}_{\alpha 2}$ , the concentrations of all three of the inorganic carbon species were calculated.

Once the concentrations of both the dissolved  $\text{Ca}^{2+}$  and  $\text{CO}_3^{2-}$  were known, the ion activity product (IAP) of  $\text{CaCO}_3$  within the water was calculated (equation 6). This value is then compared against the temperature dependent solubility constant ( $\text{K}_c$ ) of  $\text{CaCO}_3$  (equation 7), presented here for a solution at  $25^\circ\text{C}$ . The result is a saturation index (SI) for calcite in the sampled waters (equation 8 and 9). If this number is positive it confirms that the sampled waters are supersaturated with respect to  $\text{CaCO}_3$ . If the number is negative, the water is below the saturation point and may dissolve additional  $\text{Ca}^{2+}$  and  $\text{CO}_3^{2-}$ . As the scale is logarithmic, a sample with a CSI value of 1.0 is 10 times over the theoretical SI.

$$\text{IAP} = \alpha\text{Ca}^{2+} + \alpha\text{CO}_3^{2-} \quad (6)$$

$$\text{K}_c = \alpha\text{Ca}^{2+} + \alpha\text{CO}_3^{2-} = 3.36 \times 10^{-9} \quad (7)$$

$$\text{SI} = 10^{\left(\frac{\text{IAP}}{\text{K}_c}\right)} \quad (8)$$

$$\log(\text{SI}) = \frac{\text{IAP}}{\text{K}_c} \quad (9)$$

For this project, the CSI was calculated using a chemical equilibrium-modelling program (PHREEQC). This program provided the saturation indices for many common minerals based upon the aqueous concentrations of major and minor ions ( $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{PO}_4^{3-}$ ), as well as  $\text{HCO}_3^-$  alkalinity, pH and water temperature. To compensate for the lack of vertical mixing within the lake during stratification the epi/metalimnion and hypolimnion were treated separately. Samples taken in the epilimnion and metalimnion were treated as systems

open to the atmosphere, while the hypolimnion was treated as a closed system, with a fixed amount of dissolved inorganic carbon.

## **2.3.5 Nutrient Flux Calculation**

### **2.3.5.1 Basin Delineation**

The annual P flux to and from the sediments of Clear Lake was estimated from the gathered seston samples and sediment cores. In order to do this, it was necessary to make a couple of simplifying assumptions regarding the depositional basin of the lake. Firstly, I assumed that the seston samples and sediment cores were representative of the entire depositional basin. While variability around any basin is inevitable, the relatively small size of Clear Lake, would likely reduce the likelihood of significant variability that has been observed in larger lakes (Loizeau et al. 1997; Thomas et al. 1972). Secondly, it was necessary to delineate the boundaries of the depositional basin. Hakanson (1977) showed that sediment of different sizes was secondarily sorted and redistributed, as a result of wind and wave action within a lake basin prior to permanent burial. Finer sediments were preferentially resuspended by the turbulence and focused into the deepest areas. In theory, the depositional basin, or “mud deposition boundary depth” (Rowan et al. 1992), represents the minimum depth at which the fine (<medium silt) is permanently deposited. The fine sediments are important to the calculation of P fluxes because it is the small organic and inorganic colloids, clay and silt sized  $\text{CaCO}_3$  particles that present the greatest rates of P adsorption/assimilation and release (Berg et al. 2004; Drabkova 1983; Hupfer and Gachter 1995; Hupfer et al. 1995)

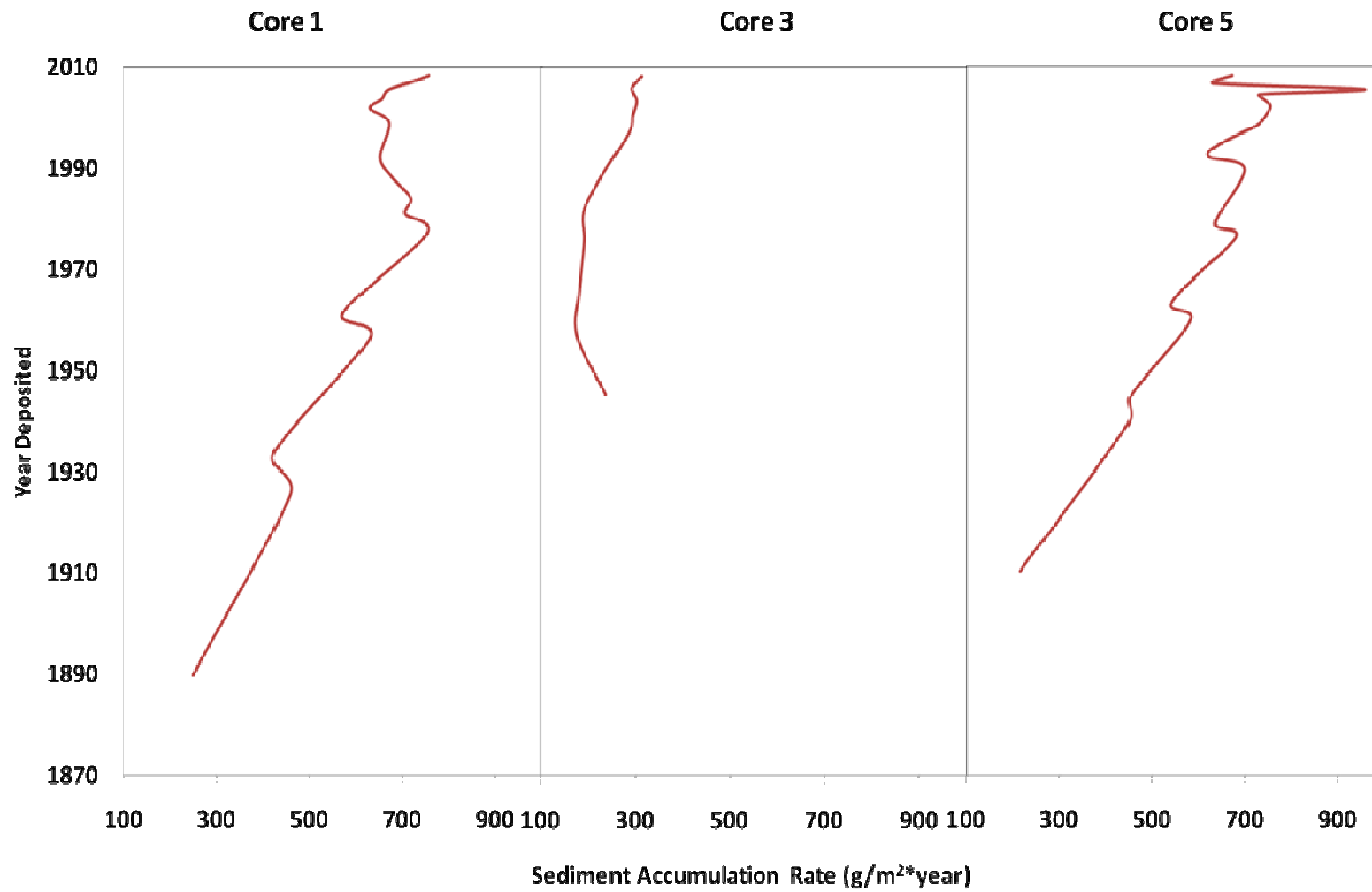


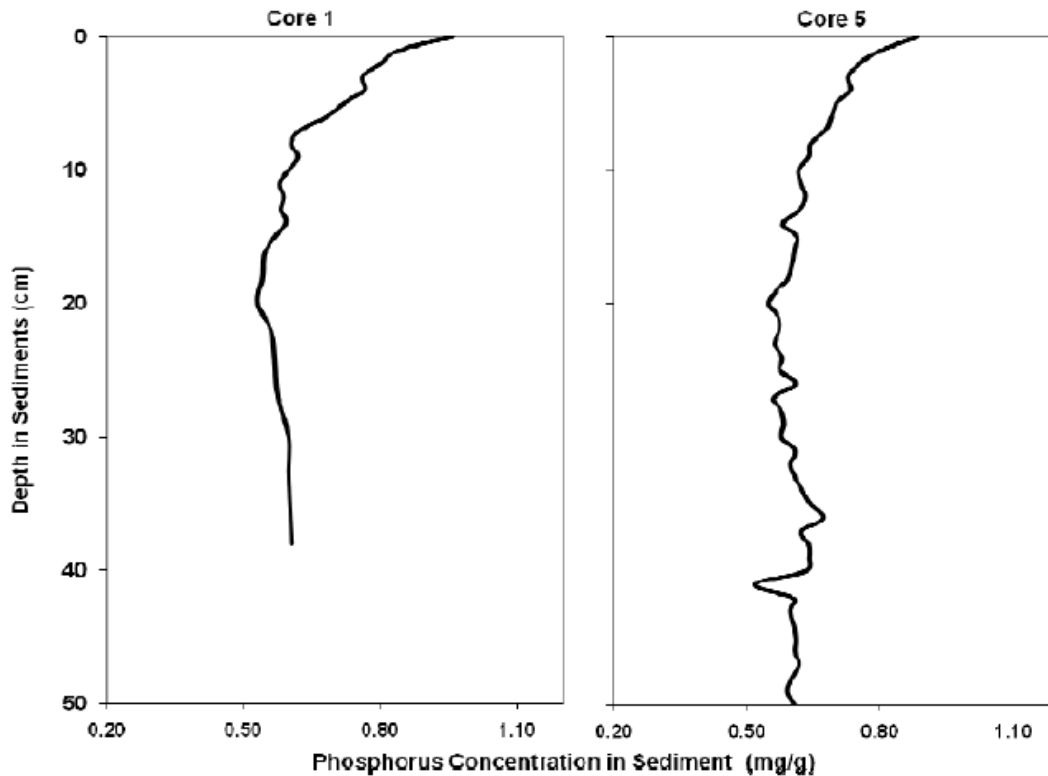
Figure 4. Sediment accumulation rates measured in Clear Lake sediment cores 1, 3 and 5

The sediment accumulation rate (SAR) was calculated for three Clear Lake cores. Cores 1 and 5 were gathered from approximately 30 metres depth and exhibited SAR values of 758 and 671 g/m<sup>2</sup> year respectively. Within core 3, which was gathered from 22 m depth and was meant to represent the shallow hypolimnion, the calculated SAR was 313 g/m<sup>2</sup> year. This suggests that the boundary of the depositional basin occurs below 22m. In addition to internal wave action focusing sediment, slope has been shown to influence sediment deposition and storage (Håkanson 1997; Rowan et al. 1992). While the bathymetry of the coring location does not suggest that the area has a significant slope (Figure 3), it is not out of the question that the sample was gathered from an isolated inconsistency. For this reason, I estimated the boundary of the depositional basin to occur between 20 and 24m, corresponding to depositional basins of 5.98 and 4.03 km<sup>2</sup>, respectively

#### **2.3.5.2 Sediment Phosphorus Recycling**

Previous studies have attempted to use the operationally defined sedimentary P fractions to evaluate the refractory and labile P components in the sediments. Commonly, these studies observe that a combination of a large fraction of the NAIP (Bostrom 1984) and OP (Drabkova 1983) contribute to the labile P fraction. Other authors have pointed to the AP fraction as a potential source (Eckert et al. 1997; Kamp-Nielsen 1974; Penn et al. 1995), however, this is not the case in many lakes, where AP concentrations represent stable or increasing proportions as sediment depth increases (Rydin 2000; Williams et al. 1976a). The separation of labile and refractory P components based upon operationally defined fractions can become even more difficult when sediment cores are examined over millennia instead of centuries. In older sediment cores, anomalous changes in TP and apparently labile P fractions have been observed in sediments > 1000 years old (Mayer et al. 2006; Selig and Fischer 2005).

For this project, the rate and extent of P recycling from the sediments was calculated by comparing the initial P concentrations, measured in the seston, with the concentrations of P remaining at various depths in the sediment, as was done by Penn et al. (1995). The potentially labile P fraction was determined by visually examining the TP profile in Cores 1 and 5 (Figure 5). Both cores exhibit maximum TP concentrations in the shallowest sediments. These initial concentrations rapidly decrease as the sediment depth increases. This decrease is most



**Figure 5. Total phosphorus concentrations in sediment cores 1 and 5**

pronounced within the top 10cm of sediment, however, it appears to continue at a reduced rate over the next few years. Once the sediment reaches approximately 20 centimetres of depth the TP concentrations appear to stabilize and asymptote for the remainder of the analyzed core depth.

Previously, Jorgenson et al. (1975), found good agreement between the labile P component in the sediment and the integral bounded by the initial sediment TP and the relatively stable concentration in the older sediments. To be conservative I used the concentration of TP remaining in sediments at the base of the sediment core to represent the refractory component. While some error in dating is associated with these sediments, the sediments at the base of the dated portions of the cores were both approximately 100 years old. This same methodology was extended to examine the behaviour of the various measured P fractions.

For this comparison it is necessary to assume that the initial composition of the sediment has remained stable at 2007 and 2008 values throughout the period represented in the sediment core.

Specifically, this would assume that both the total P concentration and the fractional percentages of P have remained stable over the period of observation. While this assumption is likely not explicitly true, previous studies suggest that slow shifts in sediment deposition resulting from land use changes are less important than annual and seasonal variability (Eckert et al. 1997; Penn and Auer 1997).

With the initial P concentrations, measured in the seston traps and the labile and refractory components that were observed in the sediment profile, a sediment P recycling rate was calculated. This recycling rate was considered to occur at a rate that may be represented by a first rate loss coefficient (equation 10) (Jorgenson et al. 1975; Lung et al. 1976).

$$- \text{Ln} \frac{P_{L-i}}{P_{L-0}} = kt \quad (10)$$

Where  $P_{L-i}$  and  $P_{L-0}$  are the labile P concentrations at time  $i$  and  $0$ ,  $k$  represents the first-rate loss coefficient and  $t$  represents the time in years since the initial deposition. In this study the age of the various sediment layers was determined by  $^{210}\text{Pb}$  dating.

While we are assuming that the composition of the sediment has remained stable over the 100-year period of observation, Figure 4 demonstrates that the total sediment accumulation rate has not remained stable. Increases in sediment accumulation rate could lead to burial of material prior to the completion of aerobic decomposition. However, Moosman et al.(2006) observed that the recycling efficiency of P from the sediments was independent of dissolved oxygen concentration in sediments. This confirms results presented by Hammond et al. (1999) and Klump et al. (1997) who observed P recycling efficiency to remain stable over wide distributions of sediment accumulation rates. In summary, the quantities of P recycled are proportional to the SAR, however, the efficiency with which it is recycled is independent. Instead the efficiency appears to be related to the sediment composition (Nurnberg 1998) and hypolimnetic conditions (Christophoridis and Fytianos 2006). In this project recycled flux was calculated based on current SAR values.

## 2.4 Results

### 2.4.1 General Conditions

During the years of observation, Clear Lake began to thermally stratify in May; however, in both years this process was delayed or reset by prolonged strong wind events. By early July, the lake had become fully stratified, at depths between 10 and 15 m (Figure 6a). When stratified, the percentage of the lake volume within the epilimnion ranged between 60 and 75 %. Surface water temperatures peaked in mid August at approximately 22° C. After this time temperatures declined, leading to a breakdown in the stratification mid to late October.

### 2.4.2 Water Chemistry

#### 2.4.2.1 pH

Prior to the ice melt in spring, pH values in the surface water were slightly greater than 8.00. Through the spring and summer, pH values were observed to increase slightly, up to a value of 8.38 on July 14<sup>th</sup>. Between July 14<sup>th</sup> and July 18<sup>th</sup>, the pH in the epilimnion of Clear Lake rapidly increased up to a value of 8.77.

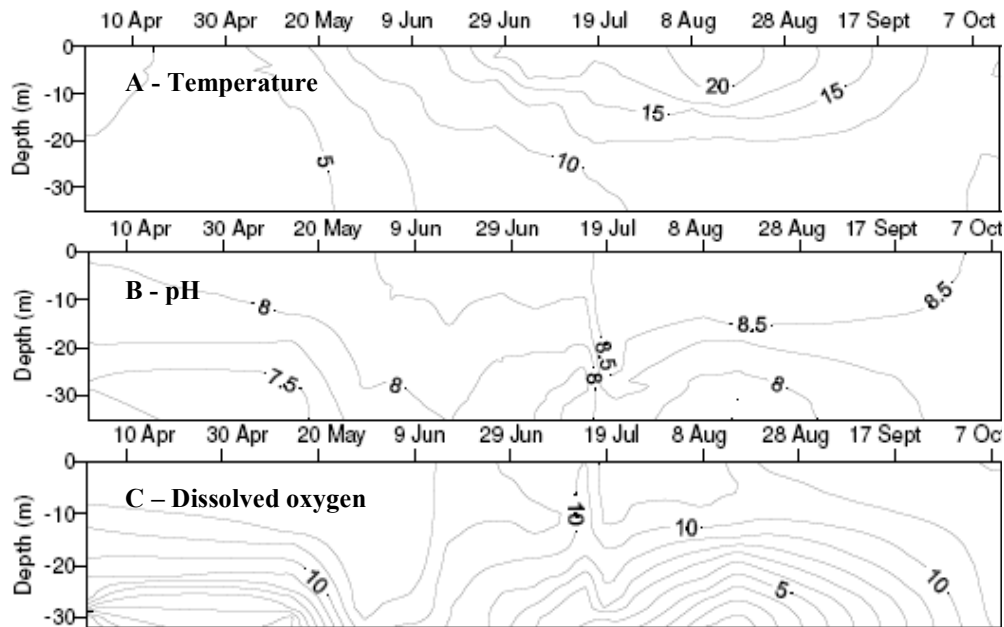


Figure 6. Time depth plots for Clear Lake during the 2008 sampling season. A) Isotherms (°C) B) pH isopleths, C) dissolved oxygen isopleths (mg/L)

Following this sudden increase, the pH values in the epilimnion remained at or slightly above 8.77 for the remainder of July and August. As surface waters cooled in the fall, the pH began slowly decreasing towards the values observed during winter sampling (Figure 5B).

This pattern is typical for lakes where biologic uptake of CO<sub>2</sub> is responsible for changes in pH (Schindler et al. 1971). Within the hypolimnion, pH values remained slightly alkaline year round, reaching a minimum of 7.02 under the ice in 2008.

#### **2.4.2.2 Dissolved Oxygen**

Throughout much of the stratification period, the hypolimnion remained oxic (>1 mg/L). The one exception, was a period between mid August and mid September 2007 when water deeper than 30m became anoxic (Figure 6C). During the winter of 2007/2008, the deepest waters in Clear Lake became anoxic towards the end of the ice-covered period. Within the epilimnion, dissolved oxygen levels remained fairly stable at the saturation point throughout the ice covered and spring period. However, commencing on July 14<sup>th</sup> 2008, the dissolved oxygen concentration exhibited a pronounced and rapid increase. This increase resulted in the epilimnion becoming supersaturated with respect to dissolved oxygen (>11 mg/L). Dissolved oxygen concentrations remained at or above saturation levels for the remainder of the summer. As the surface water began to cool in the late summer and fall, dissolved oxygen concentrations throughout the entire water column increased, coinciding with the increased saturation levels.

#### **2.4.2.3 Calcite Saturation Index**

The CSI levels within Clear Lake followed an annual pattern (Figure 7A). The lowest annual values were observed in the hypolimnion during the stratification period, while the highest were observed in the epilimnion during mid to late summer. Important abiotic factors influencing CSI are temperature and pH. Both of these factors are positively correlated with CSI at Clear Lake (Figures 8 and 9). Interestingly, the CSI displays a pronounced increase in July 2008 coincident with spikes in pH and dissolved oxygen.

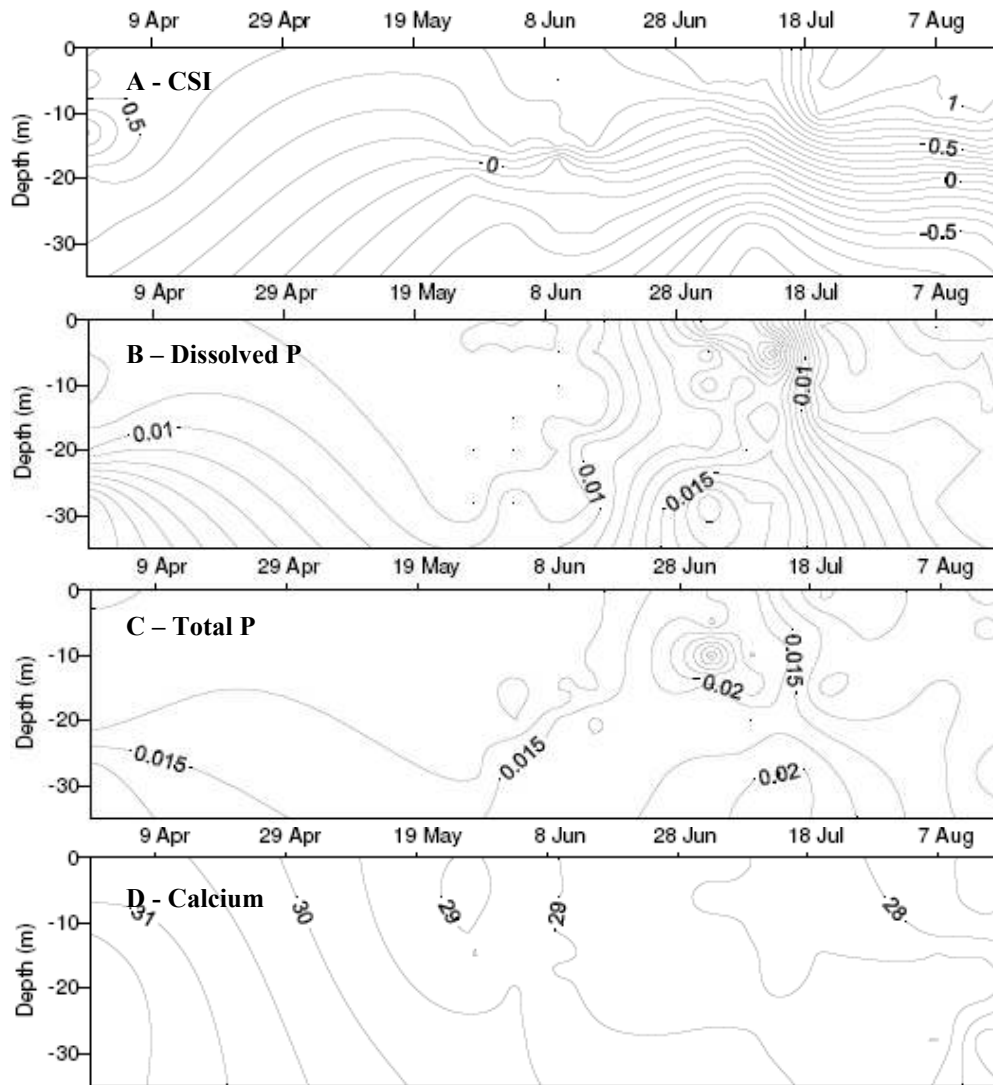
#### **2.4.2.4 Dissolved and Total Phosphorus**

Over the period of observation, total P concentrations in the surface water ranged between 0.007 mg/L to 0.033 mg/L. Aside from slight increases in total P concentrations observed in the



hypolimnion during periods of stratification, concentrations remained fairly uniform across the water column profile. Based upon the observed ranges of total P and average secchi transparency depths (4.56m), this lake may be classified as mesotrophic (Vollenweider 1979).

In 2008, P concentrations were observed to fluctuate seasonally (Figure 6B and 6C). Towards the end of the ice-covered period total and dissolved P in the surface waters were fairly stable at 0.012 and 0.008 mg/L respectively.



**Figure 7. Time depth plots for Clear Lake during the 2008 sampling season. A) calcite saturation index, B) dissolved P(mg/L), C) total P(mg/L), D) total calcium (mg/L)**

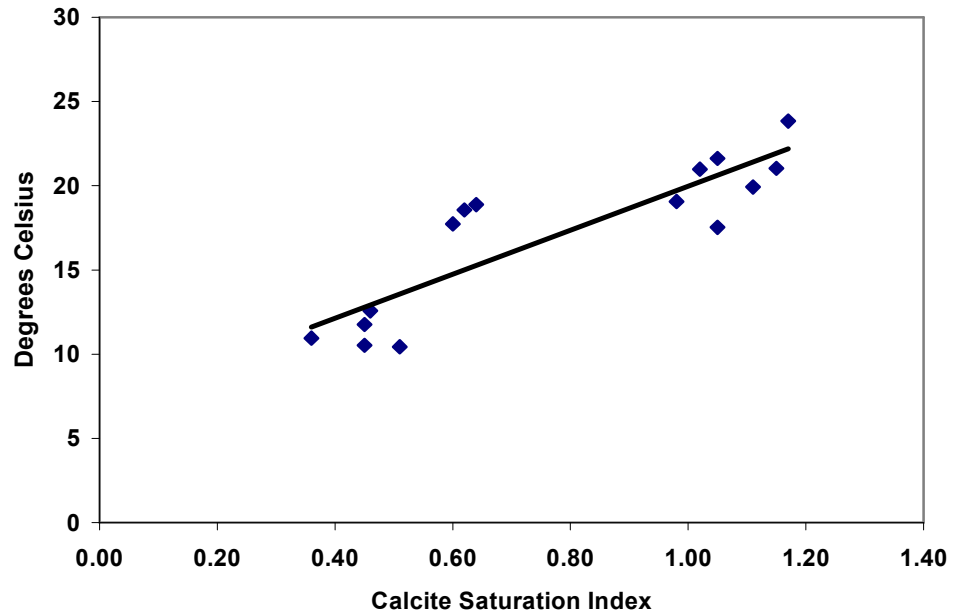


Figure 8. Calculated calcite saturation index as a function of water temperature. Best fit linear trend line (equation  $13.07x + 6.90$ ,  $R^2 = 0.76$ ) ( $p < 0.0001$ )

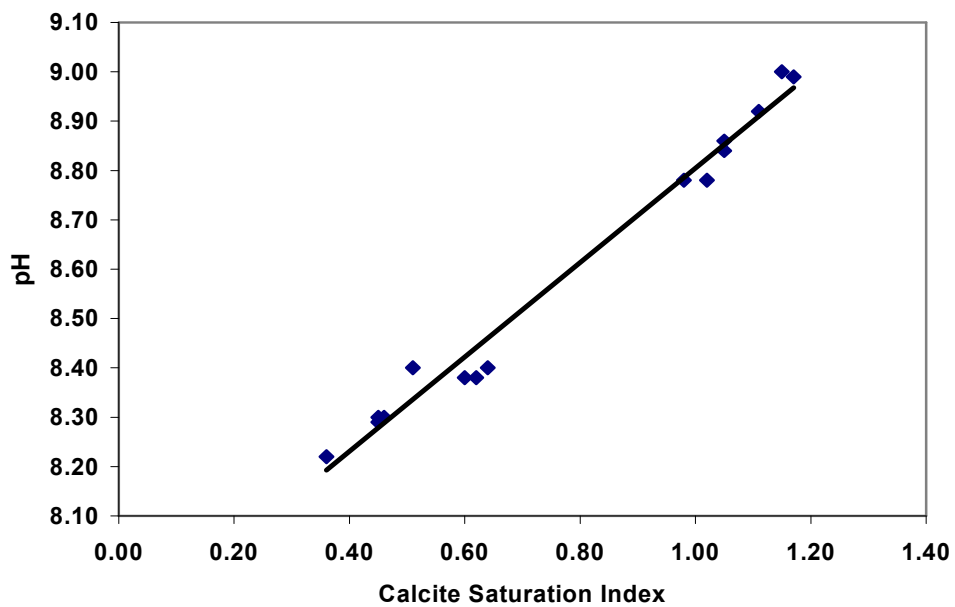


Figure 9. Calculated calcite saturation index as a function of water pH. Best fit linear trend line (equation  $0.96x + 7.84$ ,  $R^2 = 0.98$ ) ( $p < 0.0001$ )

Following this, concentrations of both decreased slightly by approximately 0.001mg/L as the ice came off and the spring progressed. This decline may have come as a result of dilution effects caused by meltwater entering the lake (Canfield et al. 1983). Throughout the late spring and early summer total and dissolved P concentrations in the epilimnion increased. Concentrations continued to increase until approximately July 14<sup>th</sup>. At this point the total and dissolved P concentrations rapidly decreased back to the seasonal low values observed in early spring.

The rapid and pronounced decrease of dissolved P from the epilimnion of the lake (<16 m deep) between July 14<sup>th</sup> and July 21<sup>st</sup> 2008 represented an overall reduction of 0.009 mg/L, or 60%, of the initial DP concentration. During this same period TP in the epilimnion decreased by a value of 0.007 mg/L, representing a 40% decrease from the initial value. This implies that there was a slight increase in particulate P (0.002 mg/L) during this period. When this value is extrapolated across the entire volume of Clear Lake between the surface and 16m ( $2.39 \times 10^{11}$  litres), this represents a loss of total P from the epilimnion of 1673 kg between July 14<sup>th</sup> and July 21<sup>st</sup>

#### **2.4.2.5 Calcium and Magnesium**

The average annual  $\text{Ca}^{2+}$  concentration in the lake was slightly less than 30 mg/L. Higher concentrations were observed during ice covered periods (Figure 7D). During the open water season the  $\text{Ca}^{2+}$  concentrations steadily decreased throughout the entire water column. An increase in concentrations was evident in the hypolimnion during stratified periods, however this change was small (<2 mg/L). Towards the end of summer it appeared that  $\text{Ca}^{2+}$  concentrations began to increase as water temperatures decreased. The average  $\text{Mg}^{2+}$  concentrations observed in Clear Lake remained fairly stable throughout the observation period at concentrations slightly greater than 30 mg/L.

#### **2.4.2.6 Calcite Saturation Index and Phosphorus**

The observations made in July 2008 are all consistent with a large algal bloom that caused a pronounced biologically mediated shift in pH and subsequent increase in CSI. The growing algae appear to have assimilated a large quantity (60%) of the dissolved P in the epilimnion. In response to the elevated CSI,  $\text{CaCO}_3$  began to precipitate around the growing algae. This

resulted in a large portion of the algae being scavenged from the epilimnion, towards the lake bottom. The net result of the process was a slight increase in particulate P but an overall loss of 40%, or 1673 Kg, of P from the epilimnion of Clear Lake. Regression analysis confirms that both TP and DP are significantly ( $p < 0.05$ ), inversely correlated to CSI in Clear Lake (Figure 10A and 10B). Interestingly, the calcium and particulate P concentrations were not significantly impacted by changes to the CSI of Clear Lake (Figure 15C and 15D).

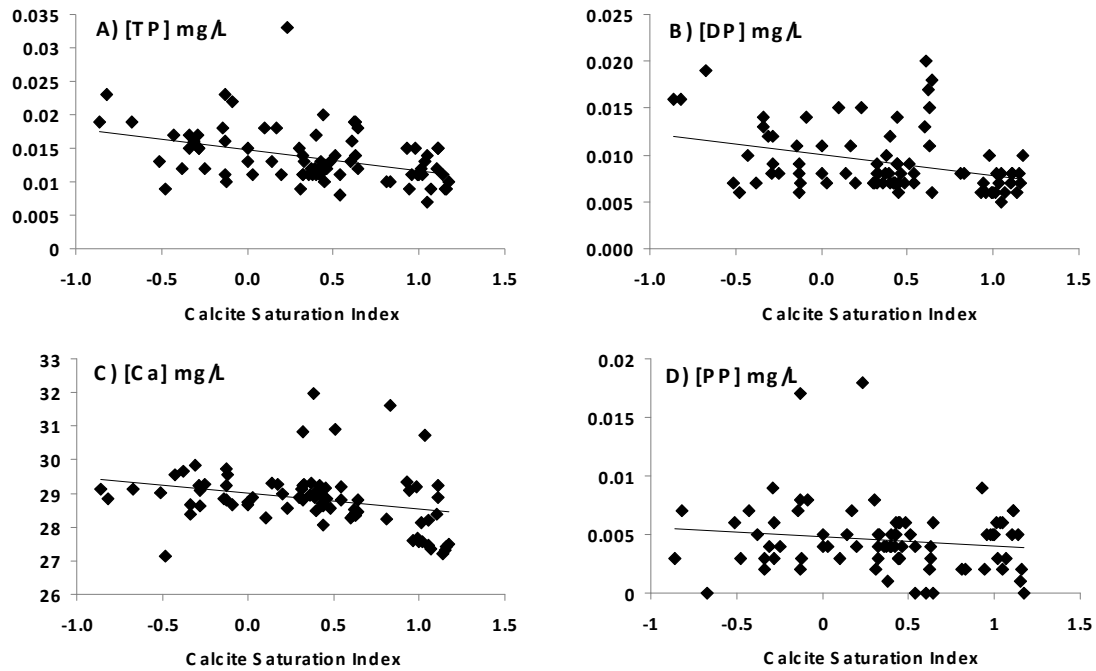


Figure 10. The relationship between calcite saturation index and A) total P concentrations ( $y = -0.003x + 0.014$ ,  $R^2 = 0.165$ ,  $p < 0.05$ ,  $n = 83$ ), B) dissolved P concentrations ( $y = -0.002x + 0.010$ ,  $R^2 = 0.123$ ,  $p < 0.05$ ,  $n = 83$ ), C) total calcium ( $y = -0.47x + 29.01$ ,  $R^2 = 0.08$ ,  $p > 0.05$ ,  $n = 83$  – not significant), and D) Particulate P concentrations ( $y = -0.001x + 0.005$ ,  $R^2 = 0.0120$ ,  $p > 0.05$ ,  $n = 83$  – not significant)

### 2.4.3 Sediment Trap Analysis

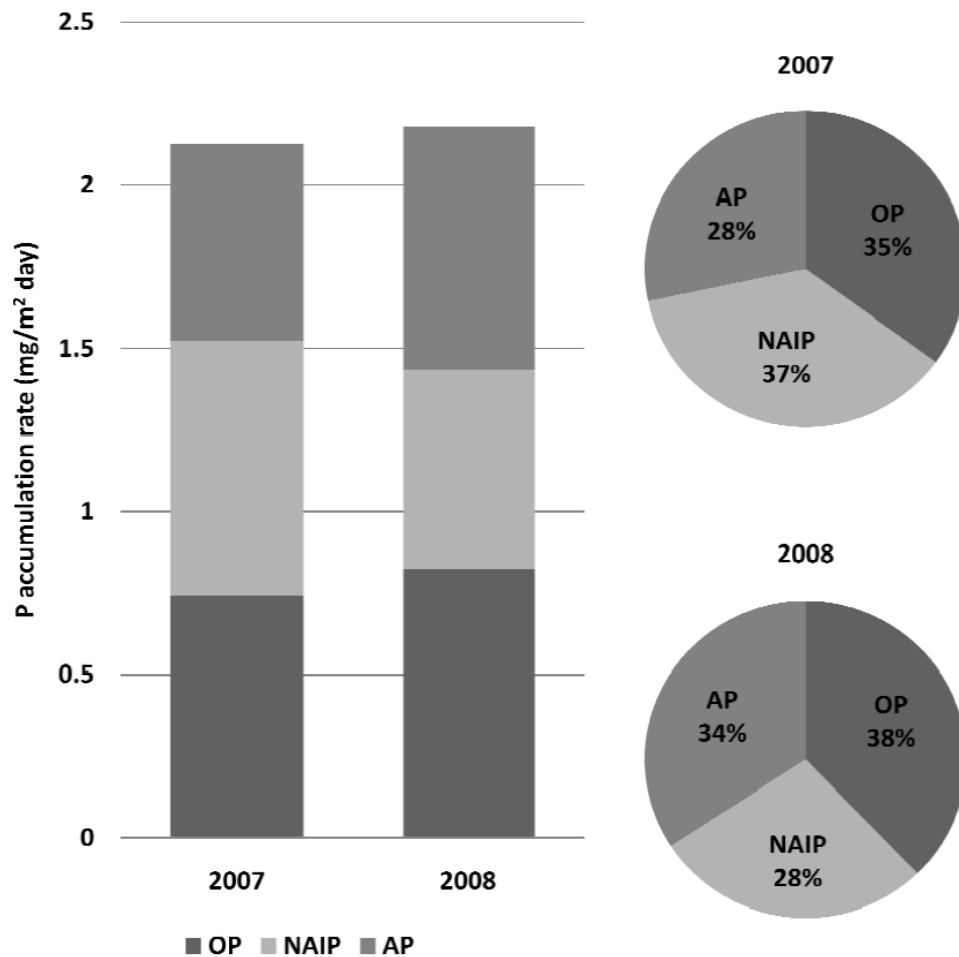
Total P sedimentation rates ( $\text{mg/m}^2 \text{ day}$ ) over the study period closely followed the dry bulk sediment accumulation rate ( $\text{g/m}^2 \text{ day}$ ). The greatest P accumulation rates occurred during the late spring and early summer, after which accumulation rates declined until a smaller peak was observed in July. The P accumulation continued declining after the brief July increase, to their lowest annual values. Overall, the average dry sediment accumulation rate in Clear Lake during the observed periods was  $2.56 \text{ g/m}^2 \text{ day}$ . Within this seston the average downward flux of P to

the sediment was 2.15 mg/m<sup>2</sup> day. The average total P concentration measured in the seston was 0.83 mg/g.

**Table 1. Annual P concentrations found in the sediment traps. Total P represents the average P concentration in (mg/g), while the various fractions are represented as a percentage of the total**

Sediment Traps	TP (mg/g)	OP (%)	NAIP (%)	AP (%)
2007	0.81	35	37	28
2008	0.84	38	28	34
Average	0.83	36.5	32.5	31

All three particulate fractions were observed in approximately equal proportions (Table 1). On average, the organic, non-apatite inorganic, and apatite P represented 36.5, 32.5 and 31 percent of the total sediment P accumulation, respectively (Figure 11).



**Figure 11. Annual averages of total and fractional P measured in the seston of Clear Lake in 2007 and 2008**

These values provide a useful estimate of the initial sediment composition, prior to any diagenetic processes acting upon it. Some temporal variation in the distribution among fractions was observed over the sampling period, however no distinct patterns were evident (Figure 12).

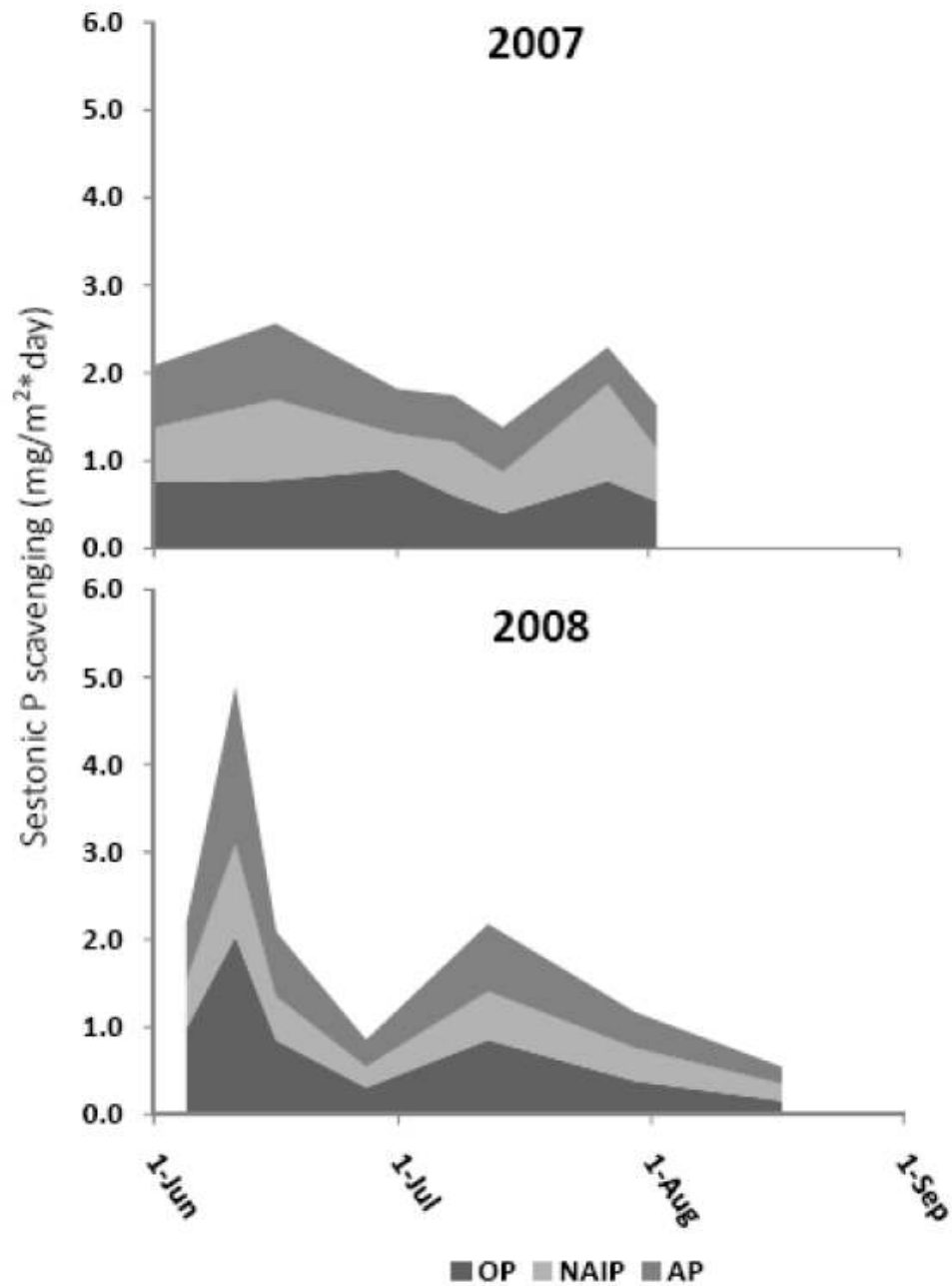


Figure 12. Temporal variation in the total and fractional composition of sestonic P observed in Clear Lake during 2007 and 2008

## **2.4.4 Sediment Cores**

### **2.4.4.1 Sediment Accumulation Rates**

Initially, three sediment cores were gathered from Clear Lake for chemical analysis and  $^{210}\text{Pb}$  dating. Two of the cores (no. 1 and 5) were obtained from the deepest part of the lake sedimentary basin (>30m). The third core (identified as no. 3) was gathered from a depth of 22 m and was meant to represent the shallow hypolimnetic depositional environment. Calculated sediment accumulation rates at the sediment-water interface in sediment cores 1 and 5 were 758 and 671 g/m<sup>2</sup> year respectively. Alternatively, the calculated sediment accumulation rate at the sediment-water interface in core 3 was only 313 g/m<sup>2</sup> year and exhibited a unconformity in the profile consistent with a rapid removal of sediment, as may occur in a turbidite flow (Figure 4). Based upon these differences, it was decided that core 3 did not accurately reflect the depositional environment in Clear Lake and it was not considered in further analysis.

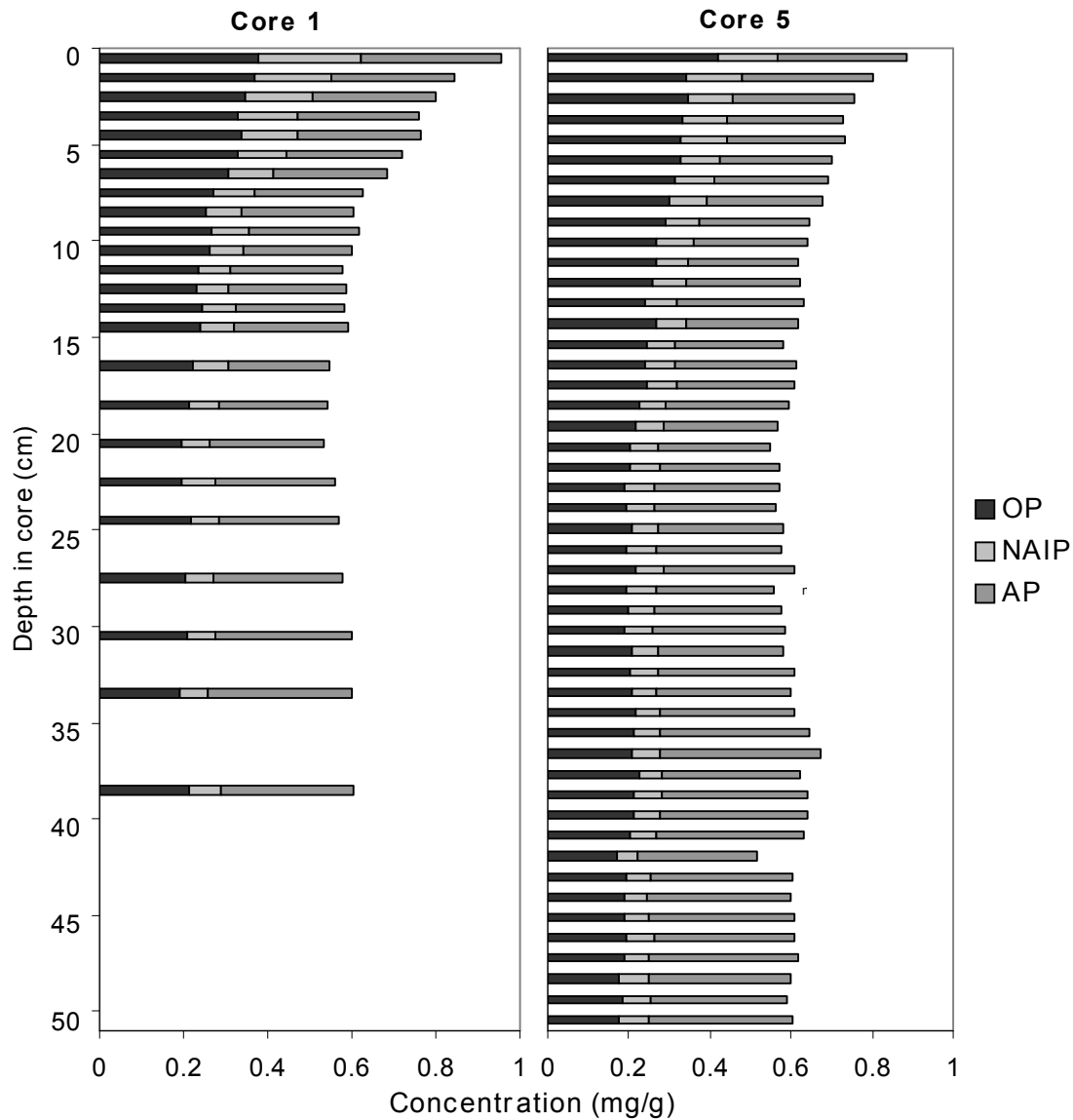
Bulk sediment accumulation rates calculated from the two considered sediment cores indicated that the sediment accumulation rates in Clear Lake have increased by roughly 300% over the last century.

### **2.4.4.2 Sediment Phosphorus Profiles**

At the sediment surface, the mean total P concentrations were 0.92 mg/g (Table 4). Below the surface, P concentrations rapidly declined to between 0.55 and 0.60 mg/g at a depth of approximately 15cm (Figure 5). Below 20cm, the total P concentration in the sediment appears to stabilize and remain relatively uniform for the remainder of the core length.

P fractionation analysis of the sediment cores provided valuable insight into the fractions responsible for the observed decrease in sedimentary TP (Figure 13). At the sediment surface OP concentrations constituted 43% of the total sediment P. The AP fraction represented the second most abundant fraction, constituting 36% of sediment P, while NAIP represented 21% of the total (Table 4). Below the sediment surface, both the OP and NAIP concentrations decreased rapidly in the top 10cm of lake sediment. This represented a 31% and 50% decrease from surface values, respectively. Mean AP concentrations decreased to a lesser extent over the same interval (17%). Below a depth of 10cm, OP and NAIP concentrations continued to

decrease at a slower rate and approached steady state below 20 cm. Conversely, the AP fraction was observed to increase in the anoxic sediments, approaching and surpassing concentrations initially observed in the surface sediment. Within both cores AP constituted the dominant P fraction beneath a depth of approximately 10cm. This change was primarily due to a disproportionate reduction in the OP fraction accompanied by a slight increase in AP concentrations (Figure 13).



**Figure 13. Proportional composition of P fractions in Cores 1 and 5**

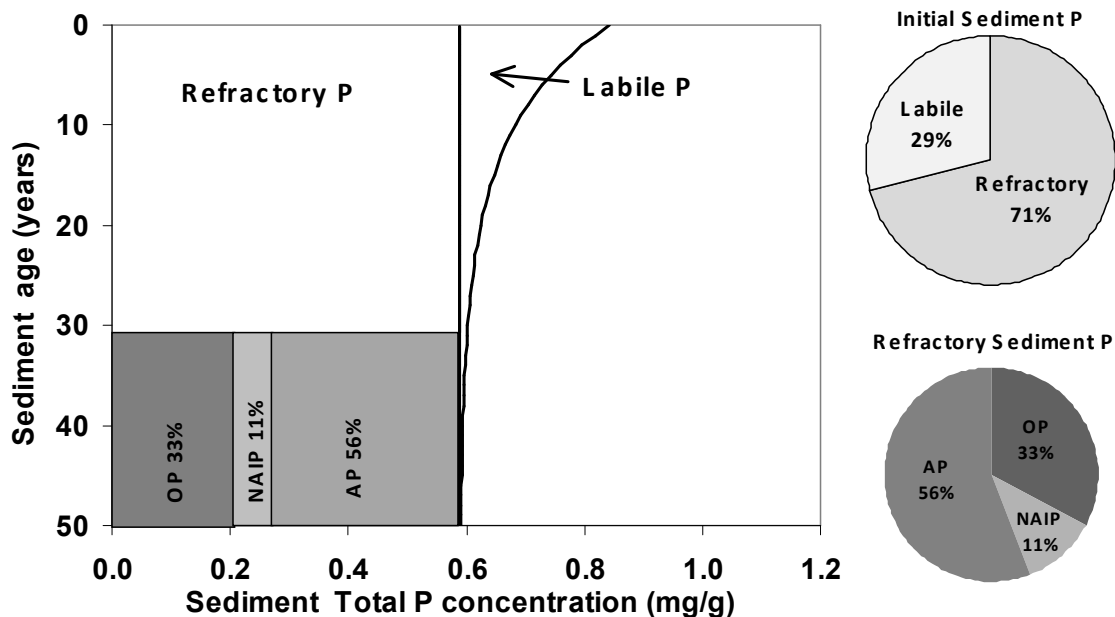


### 2.4.4.3 Labile and Refractory Sediment Phosphorus

Initially the settling seston in the lake exhibited a TP concentration of 0.830 mg/g (Table 2). After approximately 100 years, the observed TP concentration in the sediments had been reduced by 29% to 0.590 mg/g (Figure 5). Accounting for this 29% decrease in TP was a 40% reduction in OP and a 78% decrease in NAIP. Partially offsetting these losses, was an 11% increase in the AP concentration at the base of the cores, compared with the surface. The refractory component of the sediment P constitutes 71% of the initial sediment load. It is composed largely (56%) of P within the AP fraction (Figure 14).

**Table 2. Recycling efficiency of the TP and P fractions in Clear Lake sediments. Values represent the percentages of the various P fractions that remained 100 years following deposition and thus are refractory within the sediments**

	TP (%)	OP (%)	NAIP (%)	AP (%)
Core 1	69	60	22	105
Core 5	73	60	23	116
Refractory	71	60	22	111
Recycled	29	40	78	(11)

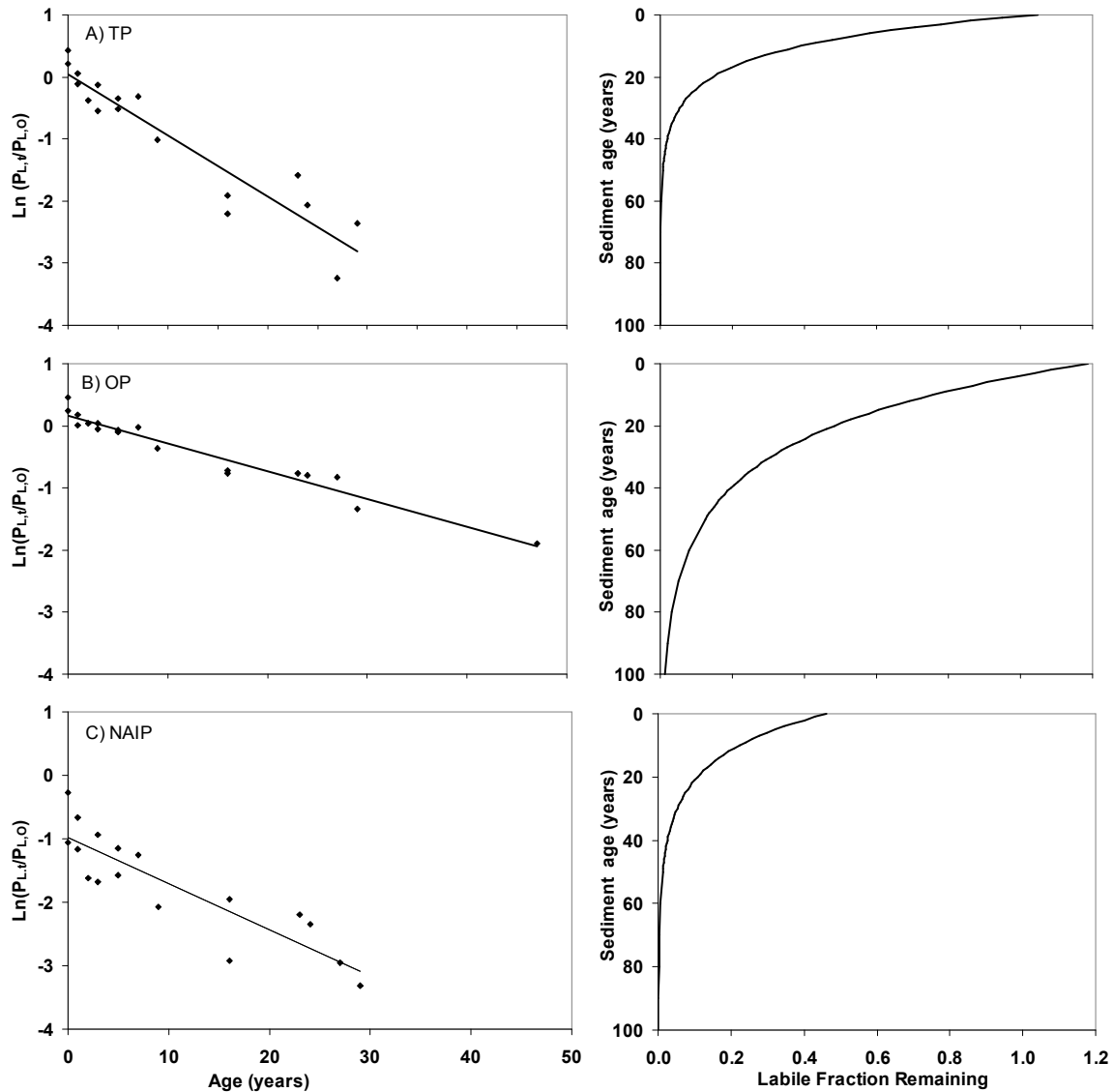


**Figure 14. Graph representing the labile and the refractory P components within the sediment. Chart representative of the initially labile and refractory percentages and the fractional composition of the refractory sedimentary P**

The remainder of the refractory component is comprised of OP (33%) and NAIP (11%) (Figure 14). In terms of P concentration, the sediment appears to reach a steady state of 0.59 mg/g after approximately 50 years.

#### 2.4.4.4 Phosphorus Recycling Rate

Assuming the P concentrations and composition remained stable at 2007/2008 values. P recycling rates were calculated for TP, NAIP, and OP using equation 4 (Figure 15).



**Figure 15. Recycling rates of A) Total P (Best fit trend line equation  $y = 0.0985x + 0.463$ ), B) Organic P (Best fit trend line equation  $y = 0.045x + 0.1717$ ), and C) Non-Apatite Inorganic P (Best fit trend line equation  $y = -0.0727x - 0.9389$ )**

A recycling rate could not be calculated for the AP fraction because overall this fraction exhibited a net increase in P concentrations over the analyzed sample period (11%).

TP in the sediments is recycled at a rate constant of 0.0985. This essentially means that 9.85% of the remaining labile P is recycled on an annual basis. At this rate 14% of the potentially labile P will remain in the sediments 20 years after deposition and less than 2% will remain after 50 years. In regards to the fractional recycling rate, the NAIP fraction exhibited the greatest loss coefficient at 0.073 while the OP fraction was recycled at a loss coefficient of 0.045 per year (Figure 14).

## **2.5 Discussion**

### **2.5.1 Water Chemistry**

#### **2.5.1.1 Dissolved Oxygen and pH**

Between July 14<sup>th</sup> and July 21<sup>st</sup> 2008, rapid and pronounced changes were observed in several important limnological characteristics. Firstly, dissolved oxygen concentrations in the epilimnion jumped from a saturated level of 9.97 mg/L on July 15<sup>th</sup> up to supersaturated levels exceeding 11.45 mg/L on July 18<sup>th</sup>. During this same period, the pH levels in the epilimnion increased from background levels (between 8.21 and 8.39), up to levels of between 8.77 and 8.90. These concurrent changes are consistent with photosynthesis by an extensive bloom of algae within the epilimnion.

This can occur when blooming algae uptake inorganic carbon in the form of carbonic acid ( $\text{H}_2\text{CO}_3$ ) at the initiation of photosynthesis. As a result of the reduction in acidic species, the pH of the water will temporarily shift towards alkaline conditions. Following the photosynthetic reaction, the algae release oxygen into the water as a by-product, which in turn increases the dissolved oxygen concentration. The net result of the algal bloom is water with elevated pH and dissolved oxygen. Due to the late start to the field season, the same pattern was not observed in 2007.

In addition to nutrients, many climatic factors influence the algal population dynamics within lakes (Bouterfas et al. 2002; Dauta et al. 1990). Research carried out by Hawryliuk (2000) at Clear Lake, indicated that temperature, light intensity and wind intensity were important factors regulating algal growth. It is difficult to say what combination of conditions lead to the rapid proliferation of algae in July of 2008. However, no rapid increase in lake surface temperature coincided with the bloom (Figure 5A). Climate data, recorded at Wasagaming during July (not shown), does not suggest that any extreme temperature, irradiance or wind speed observations coincided with the timing of this bloom. Likely, it was the culmination of many factors and as such may bear further research.

#### **2.5.1.2 Calcite Saturation Index**

Regardless of the factors leading up to the apparent algal bloom, the limnological changes had important implications for the seasonal pattern of calcite saturation in the lake. While ice-covered, the CSI of the entire lake volume remained positive. This occurred despite the fact that water temperatures during this period were at their seasonal minimum and subsequently would have had their highest  $\text{CaCO}_3$  equilibrium concentrations. Jager and Rohrs (1990) have previously attributed this pattern to decomposition and re-mineralization of  $\text{Ca}^{2+}$  and alkalinity during anoxic periods under the ice. Observations of winter anoxia in the hypolimnion and seasonal maximums of dissolved calcium during this period in Clear Lake are consistent with this suggestion (Figure 5C and 6D). During the spring and summer at Clear Lake the CSI in the epilimnion remained above saturation. Conversely, CSI values in the hypolimnion fell below saturation levels shortly after ice out in mid April, where it remained throughout the ice-free period.

In July 2008, during the period of the apparent algal bloom, the CSI in the epilimnion rapidly increased from 0.61 on July 14<sup>th</sup> to 1.09 on July 21<sup>st</sup>. For the most part this increase was confined to the photic region of the water column of the lake, providing further confirmation that these changes were indeed the result of photosynthesizing algae. In addition to the abundant circumstantial evidence supporting a large algal bloom, earlier authors have also implicated algal photosynthesis as the primary factor influencing calcite saturation in many hard water lakes (Green et al. 1985; Ohlendorf and Sturm 2001). Subsequent to the large fluctuations

observed in July 2008, the CSI value in the epilimnion of Clear Lake remained fairly stable at the elevated levels through the end of July and into early August.

The CSI values measured at Clear Lake are relatively high compared to other lakes. With the exception of a couple of European lakes presented by Ohlendorf and Sturm (2001), Clear Lake represents one of the highest CSI values recorded. The extremely high European values are believed to have been caused by severe orthophosphate inhibition during  $\text{CaCO}_3$  crystal growth. In these situations orthophosphate inhibited the formation of mineral calcite from supersaturated waters, resulting in extreme supersaturation.

The net result of the apparent algal bloom in July 2008 appears to have been a pronounced increase in dissolved oxygen and pH levels within the epilimnion of Clear Lake. As a consequence of this rapid pH change, the CSI value increased to some of the highest values ever observed within natural lakes. At similar and lower CSI values all of the lakes summarized in Table 3 have been shown to authigenically precipitate mineral  $\text{CaCO}_3$ .

**Table 3. CSI values for lakes reported within the literature**

<b>Lake</b>	<b>Minimum CSI</b>	<b>Maximum CSI</b>	<b>Reference</b>
Green Lake, Fayetteville	0.3	0.95	Brunskill (1969)
Green Lake, Jamesville	-0.5	0.84	Effler et al. (1981)
Cazenovia Lake	-0.6	0.78	Effler et al. (1982)
Lake Huron, Saginaw Bay	<0	1.30	Effler (1984)
Onodaga Lake	0.08	1.11	Effler and Driscoll (1985)
Acton Lake	-0.4	1.15	Green et al. (1985)
Lake Manitoba	0.3	1.04	Last (1982)
Hagelseewii	-1.5	0.93	Ohlendorf and Sturm (2001)
Zurich	-0.46	1.04	Ohlendorf and Sturm (2001)
Baldegger See	-0.74	1.69	Ohlendorf and Sturm (2001)
Greifensee	-0.11	1.61	Ohlendorf and Sturm (2001)
Lucerne	-0.82	1.0	Ohlendorf and Sturm (2001)
Lake Garda	0	0.95	Salmaso and Decet (1998)
Lake Constance	<0	0.95	Stabel (1986)
Lake Michigan	-0.30	0.60	Strong and Eadie (1976)
Lake Erie	-0.30	0.74	Strong and Eadie (1976)
Lake Ontario	-0.30	0.90	Strong and Eadie (1976)
Clear Lake	-0.89	1.17	This study

Calculation of the CSI values in the epilimnion of Clear Lake confirms that  $\text{CaCO}_3$  may be precipitating throughout the year. The likelihood of this occurring increases substantially in

conjunction with an apparent algal bloom in July 2008. Beyond influencing the calcium and inorganic carbon cycles in a lake,  $\text{CaCO}_3$  precipitation may also have important implications for other dissolved elements including organics, P (Otsuki and Wetzel 1972) and magnesium (Degroot and Duyvis 1966).

### **2.5.1.3 Phosphorus**

Biologically mediated shifts in epilimnetic pH have been linked to many examples of calcareous lakes known to precipitate  $\text{CaCO}_3$  and subsequently co-precipitate P (Dittrich and Obst 2004; Green et al. 1985; Hamilton et al. 2009; Hartley et al. 1997; Kuchler-Krischun and Kleiner 1990; Murphy et al. 1983; Obst et al. 2009; Ohlendorf and Sturm 2001; Otsuki and Wetzel 1972; Stabel 1986; Thompson and Ferris 1990; Thompson et al. 1997). In Clear Lake, the rapid decline in epilimnetic Total P and dissolved P concentrations (Figure 6B and 6C) coincides with the pronounced changes in pH and dissolved oxygen, as previously discussed, suggesting that these events are related.

The relationship between aquatic P and precipitating calcite includes both positive and negative feedbacks. On one hand, aquatic P has been found to inhibit the formation of calcite crystals (Lin and Singer 2006). Meyer (1984), found that the rate of calcite crystal growth was reduced by as much as 20% in solutions with an orthophosphate concentration as low as  $9.5\mu\text{g/L}$ . This inhibition may only increase in solutions with other phosphorus containing species and higher orthophosphate concentrations. Based upon this, the inhibition of  $\text{CaCO}_3$  precipitation occurring in Clear Lake during the period of maximum epilimnetic P concentrations may have been greater than 20%. On the other hand, the primary driver of authigenic calcite precipitation, aquatic algae and plankton, require biologically available P to grow and reproduce. As a result, lakes require some P to establish sufficient algal colonies to shift pH. Once an algal bloom has been initiated, the expanding population will consume bioavailable P from the surface water and thereby reduce the level of  $\text{CaCO}_3$  inhibition resulting from orthophosphate.

In 2008, the surface waters of Clear Lake exhibited steadily increasing TP, through the spring and early summer. By July 14<sup>th</sup> the average TP and DP concentrations in the epilimnion were 0.017 and 0.016 mg/L respectively. However, over the course of the next seven days, the

concentrations of both the TP and DP were reduced by factors of 40 and 60% respectively. This change was coincident with the other rapid increases in CSI, dissolved oxygen and pH, suggesting that all of the observed changes were the result of an algal bloom. This algal bloom would have acted to scavenge P from the water in two important ways. Firstly, biologically available P was certainly reduced as a result of biological assimilation by the growing algal population. Secondly, it is highly likely that some P was scavenged from the water column as a result of direct co-precipitation with growing  $\text{CaCO}_3$  crystals (House 1990; Otsuki and Wetzel 1972). In reality, these two processes are not mutually exclusive and function quite efficiently together in a process called indirect co-precipitation (Koschel et al. 1983).

During the indirect co-precipitation process, algal cells function in two important ways to accelerate P co-precipitation. Initially, the photosynthesizing algal cell consumes  $\text{CO}_2$  from the water immediately surrounding the cell. This leads to a corresponding increase in water pH and a shift in speciation of the dissolved inorganic carbon. Both of these factors directly influence the CSI value and the likelihood of calcite precipitation in a narrow envelope immediately surrounding the cell. In situations where the CSI increases to super saturated levels, the photosynthesizing cell may then provide a suitable nucleation site for calcite crystal formation. With the additional mass of precipitated mineral  $\text{CaCO}_3$ , the settling velocity of the algal cell is greatly accelerated resulting in the rapid scavenging of both the  $\text{CaCO}_3$  and algae to the lake bottom (Stabel 1986). In this fashion, biologically driven  $\text{CaCO}_3$  precipitation has been observed to efficiently settle organic P, in the form of occluded algal cells, out from the epilimnion of lakes (De Vincente et al. 2006; Hartley et al. 1997; Kuchler-Krischun and Kleiner 1990; Stabel 1986)

Alternatively, in the event that waters reach positive CSI values, direct coprecipitation may also operate to scavenge P from the surface water. Direct coprecipitation involves the intimate interaction between dissolved phosphate ions and the growing  $\text{CaCO}_3$  crystal (Otsuki and Wetzel 1972). During crystal precipitation, P may become included into the  $\text{CaCO}_3$  crystal matrix through simple ionic substitution. This causes slight imperfections in the crystal lattice and prevents further growth from that site (Hakanson et al. 2005; Meyer 1984; Zhang and Dawe 2000). As the  $\text{CaCO}_3$  crystal continues to grow, P may occupy additional sites until the crystal settles out of water with a positive CSI values and the crystal stops growing. In situations where

the epilimnion is well mixed due to wind turbulence,  $\text{CaCO}_3$  crystals may remain in the positive CSI areas for longer periods and may, as a result, co-precipitate additional P (Otsuki and Wetzel 1972). Laboratory studies have estimated that direct coprecipitation may be responsible for the removal of approximately 35% of the dissolved P from surface water (House 1990; Kleiner 1998). Interestingly, the  $\text{CaCO}_3$  with occluded P may only represent an intermediate step and over time may transform into insoluble hydroxyl apatite minerals after they have settled to the lake bottom (Berg et al. 2004).

#### **2.5.1.4 Calcium and Magnesium**

In general, lakes with  $\text{Ca}^{2+}$  concentrations between 10 and 30 mg/L are considered hard water systems (Hakanson et al. 2005). At concentrations of  $\text{Ca}^{2+}$  greater than 30 mg/L, lakes will usually precipitate out calcite when the water reaches a positive CSI (Koschel et al. 1983). Below this level, the precipitation of calcite may be significantly influenced by other factors including ionic competition and the availability of nucleation sites (Hakanson et al. 2005).

In Clear Lake, the average dissolved  $\text{Ca}^{2+}$  concentrations in the water were slightly less than 30 mg/L. However, as CSI calculations showed, they were great enough to be supersaturated with respect to  $\text{CaCO}_3$ . The average concentrations of  $\text{Mg}^{2+}$  in Clear Lake were slightly greater than 30 mg/L. The average  $\text{Mg}^{2+}/\text{Ca}^{2+}$  ratio over the period of observation was 1.16. At these ratios, in the event that Clear Lake was to precipitate out  $\text{CaCO}_3$ , it would likely be precipitating out pure calcite as opposed to high magnesian  $\text{CaCO}_3$  or dolomite (Muller et al. 1972). Seasonally, this ratio was lowest in the spring and steadily increased throughout the summer.

The high  $\text{Mg}^{2+}/\text{Ca}^{2+}$  ratio observed throughout the water column was substantially greater than any of the inflowing surface and groundwater sources (Neumann and Curtis In press). This discrepancy likely resulted from preferential scavenging of the  $\text{Ca}^{2+}$  ion during calcite precipitation. The seasonal values observed in the  $\text{Mg}^{2+}/\text{Ca}^{2+}$  relationship suggest that this scavenging occurs to a greater extent during the summer periods; at a reduced rate during the winter. This is consistent with temperature controlled chemical equilibria of  $\text{CaCO}_3$ .

In regards to ionic competition from  $\text{Mg}^{2+}$ , the reported ranges of  $\text{CaCO}_3$  growth inhibition range between 20% at concentrations  $\gg 1.22$  mg/L (Meyer 1984) to a 50% reduction at



concentrations of as little as 2.4 mg/L (Reddy and Wang 1980). In natural systems however, the dynamics behind this and other inhibitions are likely far more complex and involve factors such as  $\text{Mg}^{2+}/\text{Ca}^{2+}$  (De Choudens-Sanchez and Gonzalez 2009) and pH (Lin and Singer 2006). Regardless of the dynamics at work, the  $\text{Mg}^{2+}$  concentrations observed in Clear Lake are unquestionably high enough to be interfering and inhibiting the precipitation of calcite (Meyer 1984; Reddy and Wang 1980).

By inhibiting the precipitation of  $\text{CaCO}_3$  from the surface water of Clear Lake, the  $\text{Mg}^{2+}$  may be playing an important role in artificially maintaining positive CSI values. In turn, these positive CSI values would prevent the dissolution of any authigenically precipitated  $\text{CaCO}_3$  that was formed and maintain any coprecipitated P in the mineral matrix. In this way the elevated concentrations of  $\text{Mg}^{2+}$  in the waters of Clear Lake could have important implications for the biogeochemical P cycle.

### 2.5.2 Sediment Traps

Overall, the average dry sediment accumulation rate in Clear Lake during the observed periods was 2.56 g/m<sup>2</sup> day. This sediment flux value is similar to others that have been reported for lakes that exhibit positive CSI values and calcite precipitation events (Table 4).

**Table 4. Flux of sediment and P for similar lakes with positive CSI values**

Lake	Sediment Flux (g DW/m <sup>2</sup> day)	P Flux (mg/m <sup>2</sup> day)	Sampling Period	Reference
Onodaga Lake	~9	22.9	July – Nov 1984	Penn and Auer (1997)
Lake Constance	2.76	4.46	Jan. 1985 – Dec. 1987	Kleiner and Stabel (1989)
Green Lake (Fayetteville)	0.82	0.4	Mar. – Nov 1967	Brunskill (1969)
Lake Michigan	0.70	0.80	Apr. – Nov. 1981	Eadie et al. (1984)
Lake Ontario	1.60	3.0	Mar. – Nov. 1981	Rosa (1985)
Clear Lake	2.56	2.15	May – Aug 2007, 2008	This study

For the most part TP fluxes closely followed the total sedimentation fluxes measured in the sediment traps. Seasonally the total P flux value was greatest in the spring, coinciding with the freshet and the largest contributions of surface water (Neumann and Curtis, in press). During the summer, the flux value decreased, likely reflecting a reduction in surface water discharge and a shift from detrital to authigenic seston sources (Oluyedon et al. 1993; Penn and Auer

1997). Interestingly, increases in P flux were observed in July during both 2007 and 2008 (Figure 12). In calcareous lakes, increased temperature and biologic activity, as was evident in Clear Lake during summer, have been shown to indirectly lead to increased  $\text{CaCO}_3$  precipitation and an associated increase in total seston and P flux to the sediments (Dittrich and Koschel 2002; Garcia-Ruiz et al. 2001; Hupfer and Lewandowski 2005; Wodka et al. 1985). It is possible that the increased P flux observed in July was the result of authigenic  $\text{CaCO}_3$  precipitation combined with indirectly and directly coprecipitated P.

P fractionation of the seston confirmed that calcium bound phosphorus was indeed present in the open water throughout the year. The ultimate source of this material is a matter of some debate and likely varies depending on the waterbody. In other lakes, AP in the sediment has been shown to originate from terrestrial sources (Eckert et al. 2003; Williams et al. 1976b). In sestonic studies, resuspension of this detrital material has been shown to be a major contributor to AP fluxes (Douglas and Rippey 2000). However, as previously mentioned, AP in the seston may also have its origin from authigenically precipitated material

Over the study period the ratios of the three P fractions remain fairly stable, regardless of total P flux (Figure 12). The fact that they represent fairly equal percentages is interesting because other similar studies have observed a much greater importance of OP at the expense of AP and NAIP (Ulen 1979; Wodka et al. 1985). Eckert et al. (2003) observed similar proportions to those observed in Clear Lake only as a result of reduced inflow and increased resuspension due to a decrease in depth.

### **2.5.3 Sediment Phosphorus Profiles**

In general, there was good agreement between the analyzed seston and the surface sediments in Clear Lake. Of the observed variability, the most apparent is within the NAIP pool. In this situation, the decreased NAIP concentration between the seston and sediment may reflect the rapid diagenesis and remobilization of P associated with reductively soluble minerals (e.g., Fe and Mn) under anoxic situations (Mortimer 1971; Nurnberg and Peters 1984). The OP fraction exhibited the opposite pattern, whereby the seston contained lower concentrations as compared with the surface sediments. This likely reflects an abundance of microbial life, actively metabolizing the seston in the surface sediment (Drabkova 1983). The AP concentration

exhibited very little change between these two pools, confirming that this fraction is relatively stable over the short term. When deeper sediments are examined it becomes apparent that the AP stability is maintained throughout the duration of time represented in the sediment cores (>100 years). Overall, the sediment surface exhibited slightly greater concentrations of Particulate P than the settling seston.

**Table 5. Comparison between the seston TP concentrations and the corresponding sediment core values**

<b>Sediment Core Surface</b>	<b>TP (mg/g)</b>	<b>OP (%)</b>	<b>NAIP (%)</b>	<b>AP (%)</b>
<b>Core 1</b>	<b>0.95</b>	<b>47.0</b>	<b>17.0</b>	<b>36.0</b>
<b>Core 5</b>	<b>0.88</b>	<b>40.0</b>	<b>25.0</b>	<b>35.0</b>
<b>Sediment Core Average</b>	<b>0.92</b>	<b>43.5</b>	<b>21.0</b>	<b>35.5</b>
<b>Sediment Trap Average</b>	<b>0.83</b>	<b>37.0</b>	<b>31.5</b>	<b>31.5</b>
<b>Standard Deviation</b>	<b>0.06</b>	<b>4.6</b>	<b>7.4</b>	<b>2.8</b>

Dating of the Clear Lake cores indicate that the initial 30 cm of the sediment profile roughly reflects the previous 100 years of sestonic deposition. Over this period, the TP concentrations in the sediment steadily declined as the sediment aged. In total 71% of the initially deposited P remained in the sediments for the 100 years recorded in the core (Figure 4). Of the observed 29% decrease, 98.5% occurred in the 50 years following deposition.

Many previous P distribution studies have observed similar P distributions patterns to those observed in the sediments of Clear Lake (Shapiro et al. 1971; Williams et al. 1971). This pattern is likely the result of two factors. Firstly, sedimentary P is recycled back into the overlying waters, contributing in some cases large quantities to the overall water budget (Nurnberg and Peters 1984; Premazzi and Provini 1985). The rate and efficiency with which this occurs is largely a function of pH (Boers 1991; Eckert et al. 1997), redox condition (Mortimer 1971; Nurnberg 1988) and the initial fractional composition of P species (Drabkova 1983; Sondergaard et al. 1996). Secondly, in situations where potentially labile P is buried due to slow diagenesis kinetics or rapid sedimentation, the remineralized P may become dissolved in anoxic sediments and redistributed to the upper oxic layers of the core (Carignan and Flett 1981).

In Clear Lake, the surface sediments contain on average 0.09 mg/g more particulate P than the seston. This difference represents the effects of P remobilization and redistribution in the sediment profile. Previously the effects of secondary remobilization and redistribution have

lead to misinterpretation of sedimentary P profiles. Additionally, it may complicate matters, when attempting to calculate P recycling rates. During this study, recycling rates were calculated using the initial P concentrations in the seston as opposed to those in the surface sediment.

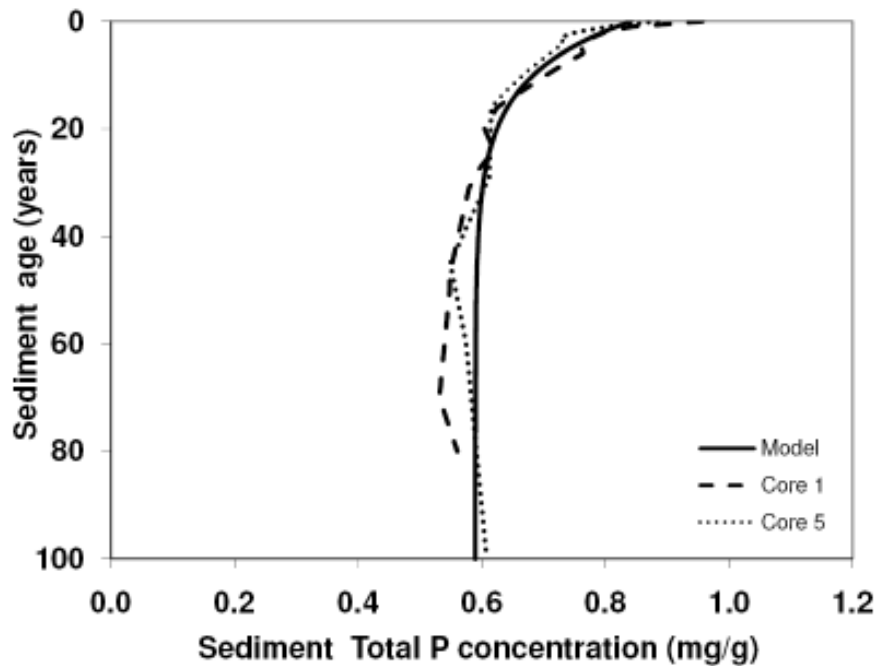
Assuming that the initial P concentration of seston has remained fairly stable over the period of observation, the decrease in sediment P from the initial sestonic levels represents the P that has been recycled back into the overlying waters. Seston and sediment P fractionation indicated that NAIP and OP were responsible for all of the 29% reduction observed in the sedimentary P concentration. Alternatively, the percentage composition and total amount of AP increased over the sediment profile to account for 56% of the 0.59 mg/g of refractory P that is stored in the sediments.

This increase in the AP concentrations in the sediment may represent secondary binding of remobilized sediment P. Once adsorbed onto the  $\text{CaCO}_3$  crystal, the meta-stable calcium phosphate complex represents an intermediate chemical species. It may become re-dissolved in acidic situations or in waters that are under saturated with respect to  $\text{CaCO}_3$ . Or alternatively it may transform into highly stable hydroxyapatite minerals (Freeman and Rowell 1981; Steefel and Vancappellen 1990). In Clear Lake, the hypolimnion was never observed to decrease to pH values beneath 7.0 and any carbonate mineral would therefore not be subject to large-scale dissolution due to acidity. The CSI levels did decrease below saturation, however levels of AP bound P were not observed to decrease. Instead, it appears that the calcium phosphate complex is remaining in the sediment long enough to undergo the slow kinetic transformation into a highly stable hydroxyapatite mineral.

#### **2.5.4 Sediment Recycling Rate and Efficiency**

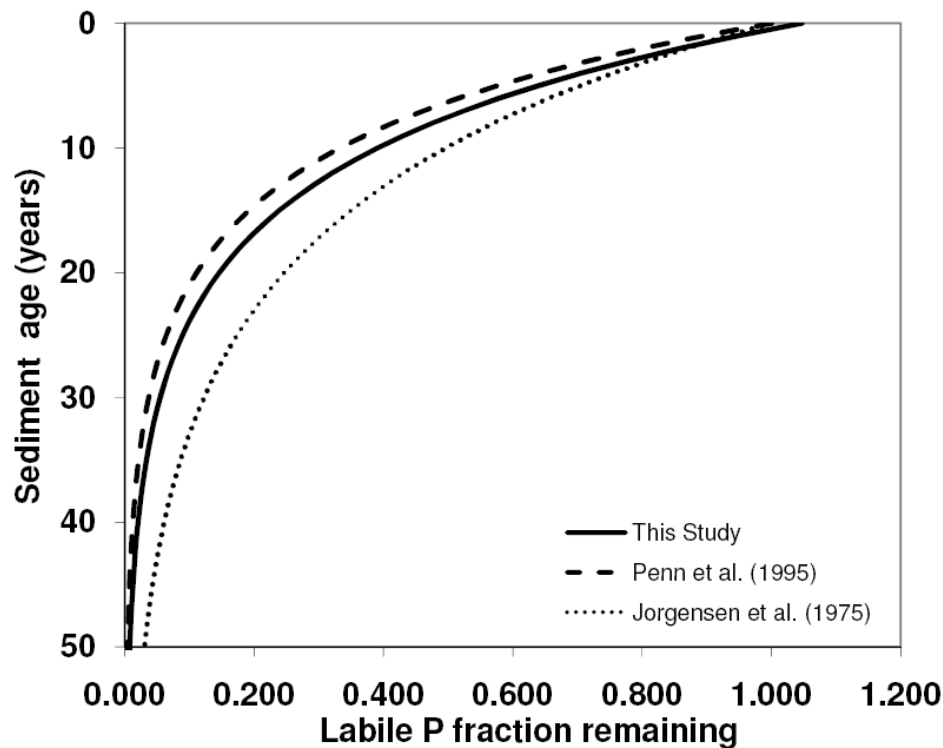
The sediment profiles and recycling rates were observed to closely follow the first order loss coefficient previously described (Jorgenson et al. 1975; Lung et al. 1976). The calculated loss coefficient for P in the sediments was 0.0985, meaning on an annual basis, slightly less than 10% of the remaining labile P is recycled back to the surface waters. Overall, the model was in good agreement with the observed P profiles (Figure 16). These rates of P regeneration from the sediment are similar to those observed in previous studies (Figure 17). While these values

are not exceptional within the context of other published literature, it effectively illustrates why lakes exhibit slow recovery rates subsequent to P enrichment and eutrophication. In the case of Clear Lake it would take roughly 50 years to recycle all of the labile P from the sediment. The resulting large flux of phosphorus would represent a significant source of P to the surface water and would occur independent of any changes that have been made to the external loading. Essentially, the labile sediment P represents a long lasting legacy for the future and any attempt to utilize sediments as an effective tool for P storage should be viewed at best as a short-term solution – with long-term consequences.



**Figure 16. Sediment recycling rate (first order loss coefficient  $-0.0985$ ) in comparison to observed sediment P profiles**

The sediments of Clear Lake retain 71% of the initially deposited particulate P for a period of at least 100 years. This is greater than the majority of examined lakes in which retention is near or below 50% for the 100 year sediment record (Hobbs et al. 2005; Jorgenson et al. 1975; Livingstone and Boykin 1962; Sondergaard et al. 1996; Williams et al. 1976b; Zhang and Shan 2008).



**Figure 17. Sediment recycling rates (first rate loss coefficients) calculated during this study in comparison to those calculated in previous studies**

The one exception to this is Penn et al. (1995), who observed a large spike in sediment P approximately 30cm down the sediment profile. In this situation, the spike was attributed to a large reduction in areal P loading resulting from a ban of P in detergents (Devan and Effler 1984). Sediment P fractionation indicates that the increased rate of sediment P retention in Clear Lake is largely due to the AP fraction. All indications, including the CSI and the seston measurement indicate that  $\text{CaCO}_3$  is precipitating, and that algal blooms are contributing to this process. Once in the sediment, the neutral to alkaline pH of the hypolimnion favours preservation and allows for the transformation into stable hydroxyapatite (Berg et al. 2004).

While sediment accumulation rates have increased in Clear Lake, no concentration or dilution of sedimentary P is readily apparent. Previous investigators have observed that increasing trophic status has lead to increases of seston flux to the sediments (De Vincente et al. 2008). This is commonly due to an increase in authigenic organic production and subsequent sedimentation. However, in many situations this authigenic organic component represents only a portion of the total accumulated sediment. For this reason, large increases in SAR as a result of increased

trophic status are usually observed in relatively closed systems that receive little detrital material. In addition, the authigenic organic component represents a highly labile source, which to a large extent is remineralized (Sturner et al. 2008).

While it is impossible to say for sure what has caused the increased SAR in Clear Lake, the distribution of sediment within the core can provide a couple of important insights. Firstly, the sediments of Clear Lake are comprised of many components including detrital and authigenic inorganic and organic material. If the trophic state of the lake had changed as a result of increased P, this has not translated into a larger OP fraction in the core. If the observed increased SAR occurred as a result of increased detrital matter (organic or otherwise) no observed changes in P fractionation are evident within the core. From the analyzed core it would appear that the fractional composition of P bearing species in the sediment have remained stable despite the apparent increase in SAR. Secondly, the fact that no dilution or concentration of P within the sediments was observed in the sediments despite the increase in SAR confirms that the sediments are annually retaining proportionally more P.

Regardless of the overall SAR, it is likely that the efficiency with which P is recycled from the sediments has remained the same in the sediments of Clear Lake. Hammond et al. (1999) and Klump et al. (1997), showed that P recycling efficiency remained constant over a wide range of SARs in both marine and fresh water. Moosmann et al. (2006) confirmed this to be true for lakes below a threshold P concentration of 36 mg/L and under variable dissolved oxygen concentrations. Within Clear Lake this suggests that the lake is not only retaining more P, it is also recycling more P. The P fluxes calculated for Clear Lake are based on 2007/2008 seston values.

### **2.5.5 Nutrient Fluxes**

Currently, the average SAR in Clear Lake is 714 g/m<sup>2</sup> (Figure 11). Of this annually accumulating sediment, sediment trap measurements confirm that the average P concentration of the recently deposited sediments is 0.83 mg/g (Table 4). At this rate 592.6 mg/m<sup>2</sup> of particulate P are settling to the sediment on an annual basis. When this is extrapolated across the entire depositional basin of the lake it accounts for between 3544 and 2390 Kg of P annually

settling to the lake's sediments (Table 6). It is important to remember at this point that a total of 1673 kg was lost from the epilimnion over a one-week stretch in July 2008.

**Table 6. Estimated annual sedimentary P fluxes, based upon a depth of deposition zone between 20-24 metres and a recycling efficiency of 29%**

<b>Annual Sedimentary P fluxes</b>	<b>Lower Estimate (Kg)</b>	<b>High Estimate (Kg)</b>
Scavenged to sediments	2390	3544
Recycled from sediments	693	1027
Permanently buried	1697	2516

Bear in mind that sediment core analysis revealed that on average 29% of the initial sediment P was eventually recycled over approximately 50 years. This means that the estimated internal load from Clear Lake sediments on an annual basis is between 693 and 1027 kg. By difference, between 1697 and 2516 kg of P will be permanently buried annually. Of this permanently buried P, between 950 and 1409 kg is buried as refractory AP species.

## 2.6 Conclusion

As a result of an apparent algal bloom in July 2008, Clear Lake exhibited rapid and pronounced changes to the dissolved oxygen and pH values in the epilimnion. These changes in turn caused the CSI value in the epilimnion to increase to some of the highest levels reported for natural lakes. Prior to this event, aqueous P concentrations in the surface waters had been consistently increasing throughout the ice-free period. Upon initiation of the algal bloom and inferred calcite precipitation event, Total and dissolved P concentrations rapidly decreased. When extrapolated across the entire epilimnetic lake volume this decrease represents a total loss of 40% (1673 kg) of the TP between July 14<sup>th</sup> and July 21<sup>st</sup>.

The fractionation of the sestonic and sedimentary P pool confirmed that a large percentage of the particulate P exists as AP. The CSI value in the lake water confirms that the conditions are in place for the precipitation of CaCO<sub>3</sub>. The high concentrations of AP within the sediment support the theory that CaCO<sub>3</sub> may have co-precipitated with dissolved and/or organic P. Observations made in the older sections of the sediment core indicate that AP concentrations increase with depth in the core. From this we may suggest that the sediments are secondarily binding dissolved P from the sediment pore water. Perhaps this is occurring during a chemical



transformation between a meta-stable  $\text{CaCO}_3$ -P species and a highly stable hydroxyapatite species.

Sediment P profiles indicate that approximately 71% of the initially deposited P is refractory and permanently buried. Of the labile P, roughly 82% is released to the lake water within the first 20 years following deposition. Fractionation tells us that this amount consists of roughly 40% of the initial OP fraction and 78% of the NAIP fraction. Fractionation of the refractory component indicates that the sediments retain and permanently bury more AP than is initially deposited. In total, AP accounts for 59% of the permanently retained P in the sediment and as such provides a valuable scavenging and storage mechanism operating in the biogeochemical cycle.

Estimates of the total magnitude of sedimentary P fluxes suggests that roughly 3000 kg of P is annually deposited into the sedimentary basin of Clear Lake. Of this roughly 860 kg is released back into the lake as internal P load, while approximately 2100 kg is currently permanently stored on an annual basis.

## CHAPTER 3: CONCLUSIONS, MANAGEMENT OPTIONS AND FUTURE DIRECTIONS

### 3.1 Conclusions

In response to elevated phosphorus (P) concentrations in Clear Lake, Manitoba, a comprehensive study was initiated to describe and quantify the factors, mechanisms and fluxes operating in the P biogeochemical cycle. Physiochemical measurements of the lake's water chemistry confirmed that the epilimnetic waters remain supersaturated with calcite ( $\text{CaCO}_3$ ) throughout the year. As a result of an inferred algal bloom in July 2008 the calcite saturation index (CSI) increased in the epilimnion up to 1.17, one of the highest levels previously observed in natural lakes. During this same period a significant decrease in total and dissolved P (40% and 60% respectively) was observed in the hypolimnion of the lake.

These concurrent events have been interpreted as an authigenically produced  $\text{CaCO}_3$  co-precipitation scavenging event. Regression analysis confirms that the CSI of the lake water and the total and dissolved P are inversely correlated ( $p < 0.05$ ). Due to the inferred presence of large quantities of algal producers and growing  $\text{CaCO}_3$  crystals, it is reasonable to conclude that a portion of the P scavenging occurred as indirect precipitation of the algal organisms.

Collection and measurements carried out on the settling seston of the lake confirm that P bound to calcium, in the form of AP, is present in the lake throughout the year. In terms of seasonal distribution, the total P flux to sediments is highest in the spring coinciding with maximum water recharge and detrital influx. However, a secondary P flux was observed in both 2007 and 2008 that may reflect authigenic-scavenging processes.

P fractionation was carried out on both the seston and dated sediment cores representing approximately the last 100 years of deposition. This divided the total P (TP) into organic P (OP), non-apatite inorganic P (NAIP), and apatite P (AP). On an annual basis the total concentration and fractional composition of the seston closely matched that observed in the surficial sediments. Bearing this in mind, a first rate loss coefficient was calculated for the sediments using the sestonic concentrations as the initial sediment composition. This indicated

that 9.85% of the total remaining labile P was being recycled from the sediment on an annual basis.

Of this labile P that was recycled, the remaining labile NAIP fraction was recycled at a loss coefficient of 0.073 per year, while the remaining OP fraction was recycled at a loss coefficient of 0.045 per year. Conversely, the AP fraction exhibited no long-term labile fraction and actually increased deeper in the core. In total approximately 98.5% of the initially labile P was recycled back into the lake water over a 50-year period.

Overall, the rate at which recycling was occurring in Clear Lake was similar to other studied lakes. However, the efficiency with which it is occurring is less than other lakes in the literature. In total, the sediments retained 71% of the P initially deposited to the lake bottom over the entire 100-year period of observation. 59% of the refractory P was in the form of AP.

The chemical ability of AP to permanently bind P has been previously established, however, the precipitation of this species from surface water can be kinetically inhibited. In sediments, the genesis of AP usually begins with a precursory calcium-phosphorus species that over time chemically transforms into AP. In Clear Lake the observation of elevated CSI levels and inferred  $\text{CaCO}_3$  coprecipitation of P would satisfy this requirement for precursory calcium-phosphorus species. While some fraction of the AP in the sediments likely originated from detrital sources, any that is produced by authigenic processes is preserved over the life of the sediment.

A large part of the observed P scavenging and burial increase within Clear Lake is associated with the presence of high levels of calcium and AP in the system. In response to elevated P levels and a sufficient calcium level, the lake experiences algal blooms that indirectly lead to  $\text{CaCO}_3$  precipitation. Once in association with the crystal  $\text{CaCO}_3$ , the P is then preserved allowing for the slow kinetic transformation into a refractory AP species.

## 3.2 Management Options

This research has identified the important factors and mechanisms operating within the P biogeochemical cycle. With this knowledge it is possible to begin to adjust the inputs of P and lake water management strategies to maximize the efficiency of the lake's natural processes. This could include management of inputs of point source P from the town site, and possible management of the water budget of the lake.

Outflow from the wastewater treatment facility in Wasagaming, Manitoba, represents an important point source for P in the surface waters of Clear Lake. This facility also provides managers with an opportunity to efficiently regulate the timing of P release into the lake. My research has shown that the P scavenging efficiency within the lake increases as a result of direct and/or indirect  $\text{CaCO}_3$  coprecipitation. In Clear Lake this process appears to be initiated or accelerated by blooming algae in the epilimnion. By regulating outflow from the facility to coincide with conditions that are conducive to both  $\text{CaCO}_3$  precipitation and algal growth managers would be able to maximize the efficiency of this scavenging mechanism.

Conditions that would favour precipitation of  $\text{CaCO}_3$  would include warm periods, with low inflow from surface water sources and high evaporative loss from the surface waters. The desired net result of these conditions would include high dissolved  $\text{Ca}^{2+}$  concentrations, high pH and subsequently high CSI values. During the period of large-scale limnological changes observed in July 2008, all of the conditions were present. The results appear to have been large-scale  $\text{CaCO}_3$  co-precipitation of epilimnetic P.

Conversely, high levels of surface water inflow and cooler temperatures common during the spring and early summer at Clear Lake do not favour  $\text{CaCO}_3$  precipitation. In these situations, dissolved  $\text{Ca}^{2+}$  concentrations are diluted by ion poor surface water and overall pH values are reduced. Hawryliuk (2000), noted that in previous summer seasons P concentrations far exceeded those observed during 2007 and 2008. This could suggest that the scavenging mechanisms observed during 2007 and 2008 are not always operating. Perhaps climatic variations (i.e., variability in precipitation or mean summer temperature) are impacting the

biogeochemical processes. Certainly, precipitation would compound problematic P concentrations by increasing P runoff from non-point sources around the watershed.

From a management perspective, it would be preferable to release bioavailable P during periods where it may be rapidly assimilated and scavenged from the water. Timing of these releases should coincide with extended warm periods with low precipitation during mid to late summer. Release of P during the cooler and wetter spring periods would only serve to compound elevated concentrations entering from spring runoff and internal loading from the winter period. In the case of Clear Lake the solution to pollution does not appear to be dilution.

In the event that regulating the timing of wastewater releases proves insufficient to reduce the elevated levels of P in the surface waters of Clear Lake it may be possible to artificially enrich surface water in  $\text{Ca}^{2+}$  and  $\text{CO}_3^{2-}$ . This would involve diverting a portion of the surface water inflow away from the lake and thereby increase the proportion of groundwater that enters the lake. The most obvious choice for this measure would be Octopus Creek, which would require a diversion channel traveling from South Lake directly to Clear Creek. This measure would have the secondary impact of greatly reducing the P loading to the surface water of Clear Lake. With higher concentrations of groundwater and an extended residency period within the lake basin the waters would exhibit higher ionic concentration and greater CSI values.

While these biogeochemical mechanisms continue to function in Clear Lake at the current levels it is important to note that this may not always be the case. Natural systems are filled with various activation energies and tipping points. Unfortunately, it is sometimes difficult to know where these exist until it is too late. Previously, many other lakes have succumbed to anthropogenic nutrient stresses and become eutrophic. The only way to ensure that Clear Lake is preserved in its current state is to maintain or reduce the total amount of P entering the system.

### **3.3 Future Work**

This study was posed with the task of describing and elucidating the biogeochemical processes and factors that control P within Clear Lake. As a result, data collection and interpretation was

carried out on a broad spectrum of chemical attributes and characteristics. Ideally, future studies should be more focused on the processes and factors identified in this study. This would include:

- Accurately measuring and quantifying the  $\text{Ca}^{2+}$  cycle and  $\text{CaCO}_3$  precipitation in Clear Lake;
- Investigating, with the use of microscopy and fractionation techniques, the roles of direct and indirect P co-precipitation in scavenging P from the epilimnion of Clear Lake; and,
- Synthesizing and integrating the work conducted by Hawryliuk (2000), looking at factors impacting algal productivity, into the P biogeochemical processes as they have been described here.

In the end the chemical characteristics exhibited by a lake are the result of the biological and the geological components within the watershed and the climatic processes operating on them. For Clear Lake, I have shown that the inputs of  $\text{Ca}^{2+}$  and alkalinity from the broader watershed play an important role in the biogeochemical cycling of P. The next step would be to determine what effect climate (i.e., temperature and precipitation) have on the input of these chemicals. This may provide important insight into some of the variability in P concentrations that have been previously observed.

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