Improvement of Lake Water Quality Using Sediment Resuspension

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ABSTRACT

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Lake Caron is a shallow and hypereutrophic lake situated 75 km from Montreal, QC, Canada. Phosphorus has been identified primarily responsible for lake eutrophication. Sediment acts as a source of phosphorus, so it is directly related to water quality. Phosphorus dynamics within Lake Caron were investigated, considering both water and sediments. To understand the burial and diagenesis and prediction of phosphorus, selective sequential extraction was performed for surface sediments. Core sediment samples were also collected along with surface sediment. Surface sediment resulted in 131 mg/g phosphorus whereas sediment from the bottom most layer resulted in 28.7 mg/g of phosphorus which is 64.5% less than the former one. Phosphorus distribution was also calculated on the basis of different particle sizes. Particles which are smaller than 45μm showed a phosphorus value 37% higher on average than the particles larger than 75μm. The vertical profile of the water column was also investigated and showed a 56.5μg/L higher phosphorus concentration than in the hypolimnionetic zone. To improve the water quality, a resuspension technique was applied which had gained much interest due to its contradictory results in experiments done by various researchers. Resuspension was successfully able to improve the water quality by reducing phosphorus content in water by 96.7% compared with the actual concentration before resuspension.

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CHAPTER ONE

INTRODUCTION

Any change in physical, chemical or biological properties of water that has harmful effects is named as water pollution. The entire ecosystem gets disturbed due to water pollution, because water is the most abundant natural resources on earth. Sediment plays a major role in the transport and fate of pollutants and so is clearly a concern in water quality management. Toxic chemicals and pollutants can become attached or adsorbed to sediment particles and then transported to and deposited in other water bodies. These pollutants or contaminants later get released into the water and deteriorate water quality.

Phosphorus cycle in aquatic environment has been a topic of scientific importance for several decades (Muhamed et al., 2006). Sediments actively take part in the nutrient uptake and regeneration processes. In the aquatic system, phosphorus behaves as growth limiting nutrient (Elwood et al., 1981) and also regulates the biomass and productivity of this ecosystem. Excessive phosphorus, either in total or bioavailable forms, has a negative influence on the water system. It favours the growth of phytoplankton and algae which ultimately leads to eutrophication (Devesa-Rey et al., 2009). Eutrophication was recognized as a pollution problem in European and North American lakes and reservoirs in the mid-20th century. Over 48% of the lakes were eutrophic in North America (Rodhe, 1969). Since then, it has become more widespread. Eutrophication can also occur naturally with the aging of the water body but most of the time human activities trigger the process.

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1.1 Motivation

As sediments act as source of phosphorus and the concentration of phosphorus largely depends on the concentration of sediments in the water, sediment phosphorus has been the subject of a number of studies.

Lake Caron was categorized as hypereutrophic since 2008 (ABV lacs.org). Massive algal blooms were seen in 2008 and 2009 and the Ministère du Dévelopment Durable, de l'Environnement et des Parcs (MDDEP) has prohibited the inhabitants around the lake from using the water even for recreational purposes (MDDEP, April, 2008). No industrial or agricultural effluent was accumulating inside the lake, so the reason behind this eutrophication was somewhat natural. Sediments continuously accumulate at the bottom of the lakes as they are constantly eroding from rocks and lands. Also microbial uptake, their growth and death are taking place inside the water contributing to the total phosphorus load. That is why preventing natural eutrophication is difficult.

Other than regulations regarding nutrient management in effluent and in discharge, several methods have been tried to prevent sediments' release of phosphorus inside water. Among them in situ capping, using aluminum salts and dredging were widely used. But they all have their own limitations such as cost factor, maintenance, toxicity, constraints of particle sizes, incomplete removal, etc. There should be a method which combines cost effectiveness and low maintenance with of course being effective in improving water quality.

1.2 Objective

This study aimed to evaluate resuspension of sediments in Lake Caron followed by filtration of resuspended particles with the intention to improve the water quality by removing excessive phosphorus. Sediments are the primary sources of phosphorus in lake water. Effectiveness of resuspension technique could be directly obtained by measuring phosphorus content in water before and after the resuspension was applied. Predicting future phosphorus release from the sediments and investigating the specific sediment fractions to encounter higher release of phosphorus into the water were also the focus for this project.

1.3 Thesis Organization

This study is presented in five chapters. In this chapter, the problem to be investigated for the research and the objective are highlighted.

The second chapter is the literature review. This chapter primarily includes the literature studies in regard to the present experiments done for this research. The main topics in the chapter are the phosphorus cycle, sources of phosphorus, release of phosphorus between sediments and water, selective sequential extraction, distribution of phosphorus inside the water column and resuspension of sediments.

The materials and methods used in this thesis are described in chapter three. The methods which were followed to perform this research are explained in this chapter. Along with that, site description and description of the important instruments are included.

Chapter four includes the results and discussion. The results from different experiments meeting the objectives and their analysis are well described in this section. Possible explanations are also given for all of the results which could have resulted in some other way. Certain correlations and experimental model results are also analysed.

Finally, in chapter five, the conclusions for the whole analyses of the results are included. Recommendations and suggestions for further work are also discussed.

The references cited in this thesis are listed at the list of references section.

CHAPTER TWO

LITERATURE REVIEW

2.1 Effect of Phosphorous on Aquatic Environment

Phosphorus has been recognised as the most critical nutrient limiting lake productivity (Kaiserli et al., 2002). It may exist in solution, as particles, loose fragments or in the bodies of aquatic organisms. Availability of phosphorus is regarded as the most important factor for determining the lake water quality (Søndergaard et al., 2003). Phosphorus mainly controls the trophic status of the water body. An elevated level of phosphorus can affect aquatic ecosystems in many ways, most of them can be considered negative. Important consequences can be the increased growth of algae and aquatic macrophytes and a distinct shift in species composition. The senescence and decomposition of these organisms create shortages in dissolved oxygen (DO) which results in fish kills, foul odours and high turbidity (Environment Canada, 2004). In some aquatic systems algal blooms and the presence of cyanobacteria in particular are prominent symptoms of eutrophication. Furthermore, cyanobacteria produce and release toxins that can destroy livestock and may pose a serious health issue for human beings.

Although phosphorus does not have any direct adverse effect because it is non-toxic to people or animals unless they are present in very high levels, its indirect effects are quite serious, especially for water. One of the secondary effects for example, eutrophication is a serious concern (discussed in the next section). Algal blooms can also destroy the aesthetic value for any water body limiting its use for any general purpose. So management of phosphorus requires consideration of societal values (Environment

Canada, 2004). For these reasons, phosphorus is on the list of the priority pollutants for Canadian Council of Ministers of the Environment (CCME) (Environment Canada, 2004).

2.1.1 Eutrophication

Eutrophication is a natural process that occurs in an aging lake or pond as the body of water gradually builds up its concentration of plant nutrients. Eutrophication can be cultural or artificial when human activity introduces increased amounts of nutrients such as nitrogen and phosphorus. Wastes are being produced by human activities and many of these waste products often contain nitrates and phosphates.

For any water body the trophic status is determined by the concentration of chlorophyll a and total phosphorus and secchi disk depth in water. For North American lakes, the trophic status index (TSI) is widely used (Carlson and Simpson, 1996).

Table 2-1 Trophic status index for North American lakes, adapted from Carlson and Simpsons (Carlson, 1977; Carlson and Simpson, 1996)

Trophic Index	Chlorophyll a (mg/mL)	Total Phosphorus (mg/mL)	Secchi Disk Depth (m)	Trophic class
< 30 – 40	0 – 2.6	0 - 12	> 8 – 4	Oligotrophic
40 – 50	2.6 – 7.3	12 – 24	4 – 2	Mesotrophic
50 – 70	7.3 – 56	24 – 96	2 – 0.5	Eutrophic
70 – 100[+]	56 – 155[+]	96 – 384[+]	0.5 - < 0.25	Hypereutrophic

Whether or not eutrophication is occurring naturally or as a result of anthropogenic activities, it affects the ecosystem in the same manner. The most immediate effect of eutrophication is an increase in the plant (phytoplankton and/or macrophyte) biomass.

Most water systems will respond to eutrophication by generating a greater biomass of plant material. Sedimentation of this organic material will increase food availability for benthic organisms and result in changes in benthos biomass. The increase in organic material in the pelagic and benthic systems increases the food availability for fish and can result in fish biomass (Jørgensen et al., 1996). According to Gray (1992) this stage is called as enrichment phase (Gray, 1992).

Increase in biomass can lead to a change in species composition along with advancing one or more trophic levels. Any change in species composition will change in the structure composition in phytoplankton community which in turn potentially affects the energy flow in the entire ecosystem. The increased plant biomass resulting from eutrophication will give rise to secondary effects, such as reduction in the depth to which light can penetrate in the water column and a subsequent reduction in the depth distribution of benthic plants (Gray, 1992; Jørgensen et al., 1996).

Another secondary effect of eutrophication can be exceptional. Blooms of toxic or nuisance phytoplankton (algal bloom) can be seen above water destroying the aesthetic view of that water body. As algal biomass builds during blooms it forms aggregates that sink and fuel bacterial growth in bottom waters and sediments. Bacterial metabolism consumes O_2. If the rates of aeration of water by mixing are slower than bacterial metabolism, then bottom waters become hypoxic (low in oxygen) or anoxic (devoid of oxygen), creating conditions stressful or even lethal for marine invertebrates and fish (Gray, 1992; Jørgensen et al., 1996). This extreme situation is termed as anoxia (Encyclopedia of earth).

2.1.1.1   Phosphorus management in freshwater

Phosphorus is on the list of the priority pollutants for Canadian Council of Ministers of the Environment (CCME) (Environment Canada, 2004). Releases of phosphorus into Canada's lakes and rivers can result in the over-fertilization (excess phosphorus) of these water bodies, increased plant growth, and an overabundance of algae. Highly over-fertilized systems tend to be predominated by algae that form dense, foul-smelling and noxious blooms, often as surface scum. Many species of algae produce potent toxins which can poison fish, avian waterfowl, terrestrial wildlife, livestock, pets and humans (Environment Canada, 2004; Canada Gazette, June 24, 2009).

Algal blooms are a problem across Canada, and in particular where there is urban and/or recreational development in the vicinity of water bodies. Examples of regions where algae blooms and/or over-fertilization are serious issues include: Lake Simcoe in Ontario; Lake Winnipeg in Manitoba; the Bow River in Calgary, Alberta; Saskatchewan's Qu'Appelle River System; the Okanagan Basin and other water bodies in British Columbia; water bodies in Prince Edward Island; and the Province of Quebec (MDDEP, April, 2008; Canada Gazette, June 24, 2009)

Along with the traditional guidelines, a thorough review of the scientific literature on phosphorus was conducted as part of developing a guidance framework for nutrient management in freshwater. First, the goals and objectives are defined and then the water quality for desired uses is considered. Certain 'trigger ranges' are set by comparing their trophic status. These trigger ranges are selected according to the level of phosphorus observed in the baseline condition of the lake or river. In Table 2-2, the trigger ranges for

Canadian lakes and rivers are described. If the upper limit of the trigger exceeds or likely to be exceeded, further assessment is recommended to better characterize the type and magnitude of the impact (Environment Canada, 2004).

From September, 2009, a Comprehensive Nutrient Management Plan (CNMP) developed in accordance with Natural Resource Conservation Service (NRCS) planning policy that addresses all resource aspects of an animal feeding operation. As defined by NRCS, a CNMP is a grouping of conservation practices and management activities that, when implemented, will ensure that both production and natural resource protection goals are achieved. A CNMP should identify and address natural resource concerns with regards to soil, water, air, plants, animals and people on the farm. The potential impacts of soil erosion and manure on water quality are a key natural resource concern (comprehensive nutrient management plan (CNMP), April 06, 2009).

A key objective of a Comprehensive Nutrient Management Plan (CNMP) is to document the plans of an animal feeding operation owner/operator to manage manure and organic by-products in combination with conservation practices and facility management activities to protect or improve water quality. NRCS has listed the elements that CNMP should consider during preparation of the plan such as, Manure and Wastewater Storage and Handling, nutrient and feed management, land treatment practices etc (comprehensive nutrient management plan (CNMP), April 06, 2009).

In regard to the previous Canadian Environmental Protection Act (1999), an annexe was added from June, 2009 with the existing regulations for controlling phosphorus in fresh water system, name as, "regulations amending phosphorus concentrations". This amendment will be in effect from July 2010.

The key feature of this amendment is mainly reducing the concentration of phosphorus in laundry and household cleaning detergents and other commercial and industrial cleaning agents. In Table 2-3, the key features are tabulated.

Table 2-2 Total phosphorus trigger ranges for Canadian lakes and rivers (Environment Canada, 2004)

Trophic status	Canadian trigger ranges for total phosphorus (μg/L)	
	Lakes	Rivers
Ultra-Oligotrophic	<4	-
Oligotrophic	4-10	<25
Mesotrophic	10-20	25-75
Meso-Eutrophic	20-35	-
Eutrophic	35-100	>75
Hyper-Eutrophic	>100	-

Table 2-3 Summary of phosphorus concentration effects, amendment of the Canadian environmental protection act, 1999, adapted from (Canada Gazette, June 24, 2009)

	Prior to July 1, 2010	On/After July 1, 2010
Household laundry detergents	2.2 %	0.5 %
Commercial and industrial laundry detergents	2.2 %	2.2 %
Household dish-washing compounds	None	0.5 %
Household cleaners	None	0.5 %

2.2 Phosphorus in Sediments

Sediments are loose earth materials and formed by weathering of rock. Phosphorus exists naturally in rocks and other minerals. They erode from the site of weathering and are transported by wind, water, ice and mass wasting, all operating by the influence of gravity. Eventually they settle out and accumulate after transport. This process is known as deposition (Wilkes University website).

Phosphorus is incorporated into the sediments through the deposition of suspended solids or by direct contact with water through mechanism such as adsorption, precipitation, isomorphic substitution in minerals or anionic exchange (Devesa-Rey et al., 2009). Gradually, these rocks release phosphorus as PO_4^{-3} ions in water which are soluble and the mineralize phosphate compounds breakdown. These forms of phosphates occur in living and decaying plant and animal remains, as free ions or weakly chemically bound in aqueous systems and chemically bound to sediments and soils (Lake monitoring program; Wilkes University website). The phosphorus cycle in aquatic environment is described by Figure 2-1. Phosphorus enters into the water from different discrete and diffused sources and accumulates as sediments.

The rate at which phosphorus loads enter freshwater systems varies with land use, geology, morphology of the drainage basin, soil productivity, human activities, and pollution. Products such as laundry detergents used to be a large source of phosphorus to freshwater systems. Regulations under the Canadian Environmental Protection Act now control the amount of phosphorus in these products because of the adverse effects of excess phosphorus on freshwater systems (e.g., toxic algal blooms and cyanobacteria) (Environment Canada, 2004).
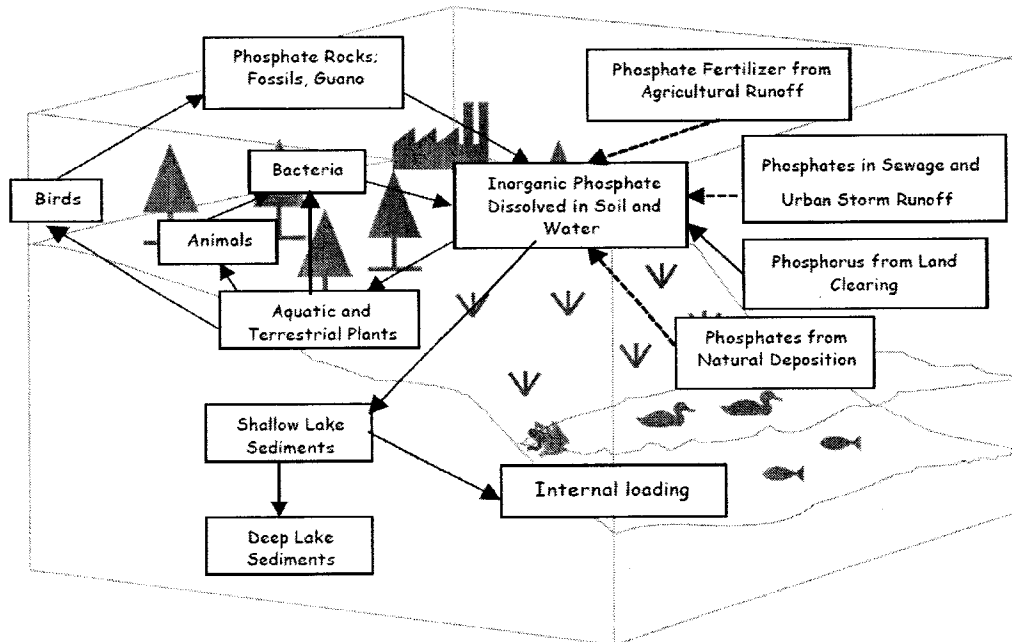
Figure 2-1 Phosphorus cycle in an aquatic environment (Environment Canada, 2004)

Phosphorus enters into the freshwater systems in four main ways (Guidelines at a glance, February, 2005):

- **Atmospheric inputs**: Enters into the freshwater system due to atmospheric activities such as wind, precipitation, dust, weathering, erosion etc.

- **Point sources**: Discrete sources or from a certain point such as effluents or wastewater from sewage treatment plants, industrial effluents, agricultural run-off, run-off from lawn mowing, grass cutting etc.

- **Non-point sources**: These sources do not enter into the fresh water from any definite point. They are diffuse sources, such as stormwater, runoff due to agricultural and land cleaning activities etc.

- **Non-point sources from within the water system**: Apart from the external inputs of phosphorus, some phosphorus come from within the system, such as, washout from riverbanks and re-suspension from sediments, internal loading etc.

Figure 2-2 describes that phosphorus is present in different stages of day to day life and hence also accumulates in the water as sediments.
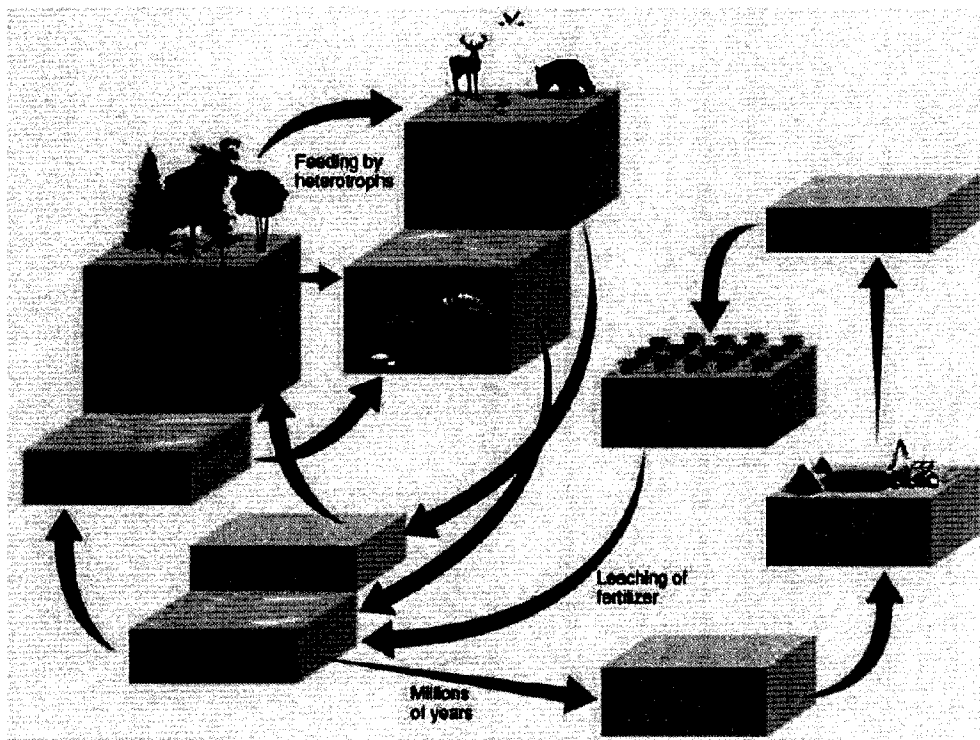
Figure 2-2 Different types of sources of phosphorus in environment (Soil & Water Conservation Society of Metro Halifax (SWCSMH), November, 2007)

There is an inverse relationship with phosphate binding or retention with sediment particle sizes. The smaller the particle sizes the higher its capacity to retain phosphorus and eventually release it into the overlying water (Selig, 2003). Selig (2003) also showed that the highest sediment phosphorus was observed for the sediment fraction 40-63 μm

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and smaller than 40 μm sizes. Devesa-Rey et al. (2009) found that the particles smaller than 63 μm have the highest phosphorus. The smaller fractions of phosphorus are also representative of the fractions that they are eroded from the soils of the basin and transported as suspended solids (Devesa-Rey et al., 2009).

Along with the surface sediment analysis for phosphorus, researchers also experimented with core samples to investigate the distribution of phosphorus in the cores. Surface sediments of shallow non-stratified lakes are exposed to a more heterogeneous environment due to the contact with circulating water mass. Microstratifications are rapidly formed and destroyed. Since, surface sediments and resuspended particles are in contact with topogenic water layers, they usually contain more phosphorus than others (Perrone et al., 2008; Devesa-Rey et al., 2009).

2.2.1 Forms of phosphorus

Phosphorus (P) is a highly reactive, multivalent, non-metal of the nitrogen group that is never found free in nature. Phosphate rock contains the mineral apatite. Mineral apatite is an impure tri-calcium phosphate and an important source of phosphorus. The main forms of phosphorus in the natural water systems are ortho-, meta-, pyro-, polyphosphates and various phosphorus containing organic compounds (Aydin et al., 2009).

The most abundant form of phosphorus in the environment is phosphate P(V). For its availability of assimilation it has been traditionally used as fertilizers. However, almost all of the phosphorus on earth is found in the form of minerals including apatites (chloro and flouro), vivianite, wavellite and phosphorites. The largest reservoir of phosphate on

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earth is apatite {$Ca_5(PO_4)$}[F, OH or Cl] which is relatively insoluble in water (Aydin et al., 2009).

2.2.2 Selective sequential extraction

To understand the burial and diagenesis of phosphorus in sediments, it is necessary to identify, separate and quantify the various solid-phase reservoirs of sedimentary phosphorus (Ruttenberg, 1992). Chemical selective sequential extraction of sedimentary phosphorus has served as a tool to predict the phosphorus binding capacity of sediments under different environmental conditions. Often, the potential internal loading is the matter of interest (Kisand, 2005). Deep lakes have a redox dependent accumulation of phosphorus in anoxic hypolimnion. Whereas, in shallow lakes the layers are usually well mixed and oxidized throughout the water column. Therefore, in order to understand the P-cycle in lakes and to predict the system's behaviour after any reduction of the external nutrient load, it is essential to know the phosphate associated within the sediment in different phosphate forms. These are the phosphates which under certain environmental conditions (during spring and summer) may be released to the overlying water (De Vicente et al., 2003).

Complete physical separation of different phases associated with phosphorus from fine grained sediment rarely can be achieved (Ruttenberg, 1992). Inorganic P can react with calcium (Ca), iron (Fe) and aluminum (Al) to form discrete phosphates. Organic P can be found in forms with varying resistance to microbial degradation. The fractionation procedure of Chang and Jackson (1957) has been widely used to investigate the forms of inorganic P and transformations of applied P fertilizers. Subsequent research indicated

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that the various extractants were not as specific as first envisioned. For example, retention of P by calcium fluoride (CaF_2), formed from calcium carbonate ($CaCO_3$) during ammonium fluoride (NH_4F) extraction, affects results when the Chang and Jackson (1957) method is used to fractionate P in calcareous soils and sediments. Since its development, modifications made by Fife (1959), Peterson and Corey (1966), Williams et al. (1967), and Syers et al. (1972) have improved extractability and allowed for use with calcareous soil (Fife, 1959; Petersen and Corey, 1966; Williams et al., 1967; Syers et al., 1972). The original fractionation procedures and the most important modifications were summarized by Kuo (1996). The inorganic P extraction performed in this report follows the procedures described by Kuo (1996).

In any selective sequential extraction or fractionation procedure, extractants are chosen on the basis of different solubilities of that component in reactive phase. For phosphorus, ammonium chloride (NH_4Cl) is used first to remove soluble and loosely bound P for non-calcareous soils or sediments. It is also referred to as the phosphate which is readily available in water. It gives an estimate of immediately available phosphorus. This fraction may contain porewater P, P released from $CaCO_3$ associated phosphorus or leached P from decaying cells of bacterial biomass in deposited phytodetrital aggregates. It also gives a seasonally variable pool of phosphorus compounds dissolved in the interstitial water (Rydin, 2000). Al-P and Fe-P were soluble in NH_4F and NaOH. These fractions are exchangeable against OH^- and they can be used up both short-term and long-term available P in sediments and a measure of algal available P (Rydin, 2000; Zhou et al., 2001). The reductant soluble P is extracted by adding CDB (sodium citrate-sodium dithionite-sodium bicarbonate). This phosphate is termed as BD-P (Buffered dithionite P)

which is mainly reductant soluble P, that releases phosphorus upon changing the redox potential. In our study, the BD-P values were not significant so the results were not documented. Finally, the apatite P (Ca-P) is more soluble in HCl than CDB (Pierzynski, 2000). The Ca-P represents phosphorus form which is sensitive to low pH and has natural and detrital traces of hydrolysable organic P. This fraction is a relatively stable fraction of sedimentary P and contributes to a permanent burial of phosphorus in sediments (Gonsiorczyk et al., 1998). Different methods were applied for calcareous sediments. The methodology is discussed in chapter-3 in "Materials and Methods" section.

2.3 Release of Phosphorus from Sediments

Phosphorus releases from the sediments into the lake water occurs by mobilization from the sediment particles and then transportation to the water column. After mobilization into the dissolved phosphorus pool in sediment pore-water, phosphorus travels upward along with other dissolved species into the water column (Boström et al., 1988).

Physical and chemical mobilization thus includes desorption, dissolution of phosphorus containing precipitates and ligand exchange mechanisms, e.g. 'ion exchange' between orthophosphate and OH⁻ or chelating agents. Biochemical mobilization includes mineralization processes ending up with hydrolysis of phosphate-ester bonds, release of phosphorus from living cells as a result of changed cellular metabolism (Boström and Pettersson, 1982).

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2.3.1 Phosphorus mobilization

Phosphorus mobilization is controlled by a number of environmental factors of which temperature, pH and redox potential are the most important.

An increase in temperature primarily has indirect effects. It increases biological activity and increases pH. Microbial activity increases the oxygen consumption and decreases redox potential. With lowered redox potentials alternative electron acceptors are used for the mineralization of organic matter, resulting in the production of reduced products affecting phosphorus release in lakes in various ways (H_2S, CH_4 etc.).

Increased pH in the water decreases the P-binding capacity of iron and aluminum compounds due to ligand-exchange reactions. In this reaction hydroxide ions (OH^-) replace orthophosphate (PO_4^{3-}) ions (Lijklema, 1977; Boström and Pettersson, 1982). Again, at high pH , if iron (II) and orthophosphate (PO_4^{3-}) are released from an anaerobic sediment and mixed into aerobic lake water, only part of the released phosphorus will be bound to the re-precipitated iron (III) compounds (Boström et al., 1988).

At redox potentials below 200 mV, part of the Fe (III) in surface sediments is reduced to Fe (II). Associated phosphorus with Fe (II) are thereby returned to the solution. Studies (Sorensen, 1982; Jones et al., 1983; Jansson, 1987) have shown that iron reduction might be partly due to the result of microbial utilization of Fe (III) compounds as an alternative electron acceptor analogous. For example, denitrification and sulfate reduction under anoxic conditions. A change in the metabolism of cyanobacterial and bacterial cells can result in a significant release of phosphorus from the cells which might contribute to the phosphorus release from anoxic sediments (Fleischer, 1983; Boström et al., 1988).

2.3.2 Phosphorus transport

Steep concentration gradients between lake water and pore water induce an upward diffusion flux of phosphorus across the sediment-water interface in most lakes. Molecular diffusion is considered the main mechanism for the transport of phosphorus from sediments superimposed by stagnant, anaerobic hypolimnetic water layer (Boström et al., 1988).

Wind-induced turbulent currents affects phosphorus exchange between sediment and lake-water in many different ways. The diffusion increases since phosphorus from the sediments is rapidly dispersed in the water column, whereby a steep concentration gradient is maintained. Again, sediment disturbance cause mechanical mixing of pore water and lake water. Wave action and wind-induced turbulence also cause re-suspension of sediment particles and release of phosphorus may occur in the water column due to different equilibrium criteria (Boström et al., 1988). However, re-suspension of particles sometimes helps to decrease phosphorus, which is discussed in section 2.6.

A. Aerobic conditions

P in non-living organic matter

O_2 Oxygen respiration H_2O

P in microbial biomass

Net immobilization

Mortality

Net mineralization

Mobilized Phosphorus (P)

P in non-living organic matter

Microbial solubilisation of ferric iron

Adsorption or precipitation with ferric iron

B. Anaerobic conditions

P in non-living organic matter

Mortality

NO_3^- Denitrification N_2

Fe^{3+} Iron (III) respiration Fe^{2+}

SO_4^{2-} Sulfate respiration H_2S

P in microbial biomass

Net immobilization

Net mineralization

Released due to changed metabolism

Mobilized Phosphorus (P)

Fe^{3+} Microbial iron reduction Fe^{2+}

Fe^{3+} Chemical ion reduction Fe^{2+}

P bound to ferric iron

Adsorption or precipitation with ferric iron

Figure 2-3 Schematic of possible phosphorous transfer process between lake-water and sediments (Boström et al., 1988)

Microbial activity in surface sediments affects phosphorus cycling in lakes in a number of direct and indirect ways. The mineralization process involves phosphorus transfers from the detritus pool to the biomass pool and possibly to the mobilized pool. The net result is variable because it depends on the type of degradable organic matter and on the prevailing type of respiration. The possible effects of microbial activity on phosphorus transfers to and from the organic and iron-bound phosphorus pools under aerobic and anaerobic conditions can be discussed on the basis of the schematic outlines given in Figure 2-3 A & B respectively. The term net mineralization implies a phosphorus transfer from the biodetrital pool to the mobilized pool. This transfer does not necessarily occur via microbial cells, because it can also result from the activity of oxyzenome (Boström et al., 1988).

Microbial metabolism produces particular gases such as nitrogen (N_2), carbon dioxide (CO_2), and methane (CH_4). If the gas production and pressure conditions allow bubble formation, the bubbles rise, inducing vertical currents. Along with the bubbles, the sediment particles and dissolved substances along with mobilized phosphorus are transported upwards to the water column. A particularly important role has been attributed to methane and 'methane convection' is considered a dominant transport mechanism in shallow and highly eutrophic lakes (Ohle, 1958; Boström et al., 1988).

2.4 Internal Loading

Sediment phosphorus release (internal loading) can be an important source of phosphorus and can maintain high water column phosphorus concentrations, even in the absence of significant external loading (Marsden, 1989; Environment Canada, 2004; Environment

Canada, erosion & sedimentation). This internal loading will often determine the eutrophication status of the lake and the time lag for recovery after reduction of the external loading. Internal loading is the most severe during the summer compared to other seasons (Pettersson, 1998).

Inorganic and organic materials are continuously stored into the sediments at the bottom of the lakes or oceans and actively take part in the transformations. Precipitation and shells of diatoms contribute to inorganic compounds in the sediment. Plankton debris, tree leaves and particulate phosphorus from the runoff sink to the bottom and enrich the sediment with organic content (Pettersson, 1998). This organic matter settles at the bottom and decomposes by aerobic or anaerobic processes resulting in low levels of oxygen and anoxic conditions at the water-sediment interface. Under conditions of low or no oxygen at the bottom layer of water phosphorus can be released from the sediments due to chemical reactions (from different fractions of phosphate) which is discussed in section 2.2.2. Release of phosphorus due to internal loading or from the sediment is regulated by many environmental factors, i.e. redox condition, oxygen availability (aerobic, anaerobic or anoxic), sorption mechanism etc. This regeneration contributes to the in lake fertilization and triggers for algal growth in the water body (Nürnberg, 1988).

All types of water systems are prone to exhibit internal load. It is clearest in stratified waters, where the build-up of anoxia and increased P concentrations in the bottom water layer can be witnessed. But even shallow, polymictic systems often have a microlayer of stagnant water above the sediment surface, e.g. in weedbeds, at certain times i.e. before dawn, and anoxic P release may occur. Internal load has been reported from many man-

made impoundments and dams as well as from rather pristine lakes, although the quantity is usually much smaller in unspoiled lakes.

2.5 Distribution of Phosphorus in Water Column

Generally, the topmost layer of the water column is termed as epilimnion. It is warmed by the sun and mixed by wind. This layer is less dense and the temperature throughout this layer remains constant. Epilimnion is always mixing oxygen from the atmosphere that helps keeping oxygen in abundance here. However, if there is excessive growth of algae, they can use up all the oxygen resulting a less amount of oxygen in this layer. Again, hypolimnion sits at the bottom and the densest layer of a stratified lake. It is typically the coldest layer in the summer and warmest in the winter. It is isolated from wind mixing and typically too dark for much plant photosynthesis to occur. Organic matter decomposes in this layer, due to increased demand of oxygen, and sometimes this layer becomes anoxic to anaerobic.

Between the epilimnion and hypolimnion, there is another layer called as metalimnion. The metalimnion is characterized by rapidly changing temperatures. This drastic change in temperature is what separates the upper reaches of the lake from the lower reaches. High density gradient in this layer prevents mixing hypolimnion and epilimnion together. Figure 2-4 schematic shows different water layers (epilimnion, metalimnion and hypolimnion) of a model lake. The oxygen availability and mixing during different season and temperature was shown in Figure 2-5.
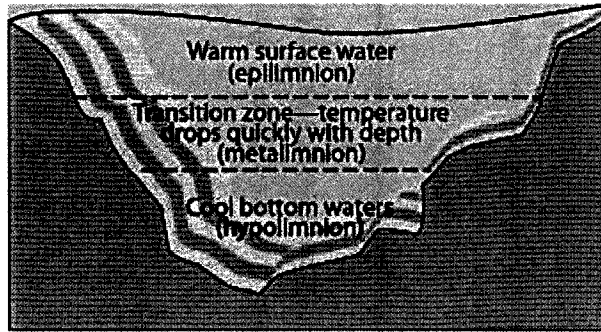
Figure 2-4 Schematic of a stratified lake, showing epilimnion, metalimnion and hypolimnion (Natural resource Canada (NRCAN))
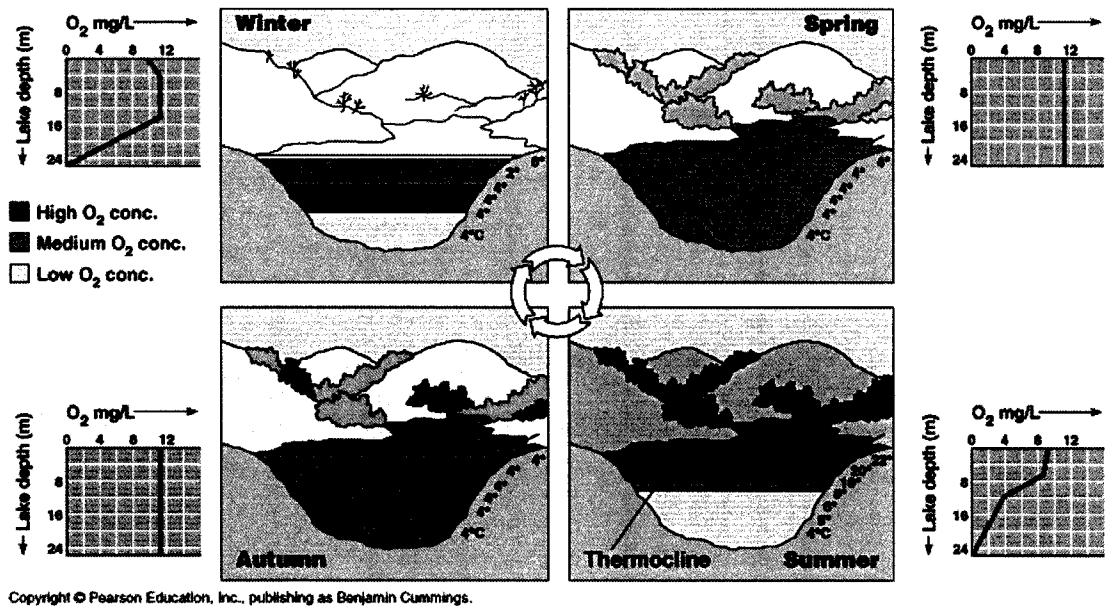
Figure 2-5 Stratification and seasonal changes in water layers, mixing and changes in concentration of water (Pearson Education Inc. website)

In spring, the lake water in the epilimnion is heated by sun, causing decrease in density of this layer. The water in the hypolimnion is cooler and remains at the bottom. The same stratification continues throughout the summer. In autumn, the epilimnion cools off by radiating the heat. When the temperature in both the epilimnion and the hypolimnion is equal, the two layers mix with each other. This mixing is assisted by autumn winds. As a

result, the thermal stratification is terminated. Thus the annual cycle brings the deep water to the surface where it is enriched with oxygen. The nutrients in the hypolimnion also get mixed with the water in the epilimnion. In winter again a stable stratification occurs.

The hypolimnion contains water at or near 4°C, which has a higher density and the epilimnion has colder, less dense water or ice above. This situation prevents turbulent mixing. Again in spring the surface water warms to 4°C leading to a mixing.

In the hypolimnion, as the sediments are anoxic, they release phosphorus and it is thereby transported to the water column (earlier discussed in 2.4). Deeper in the water column, the concentration of total phosphorus increases until the hypolimnion (Devesa-Rey et al., 2009).

In all but upper few centimetres of sediment, exchange is slow and is controlled by low diffusion rates. If the water above sediment is oxygenated, an oxidized microzone is formed below the sediment-water interface (0-5 mm), under which the sediments usually become extremely reducing. This microzone effectively prevents phosphorus from migrating upward into the water column (Environment Canada, 2004).

Total and soluble phosphorus shows little variation in oligotrophic lakes. Eutrophic lakes commonly show a marked increase in phosphorus in the lower hypolimnion. Much of this increase is from soluble phosphorus near sediment-water interface (Environment Canada, 2004). A generalized vertical distribution of total phosphorus, soluble phosphorus, oxygen and thermal profile is shown in Figure 2-6.

Oligotrophic   Eutrophic

P_S P_T θ O_2 P_S P_T θ O_2

Depth

$P, \,^{\circ}C, \, O_2$ →
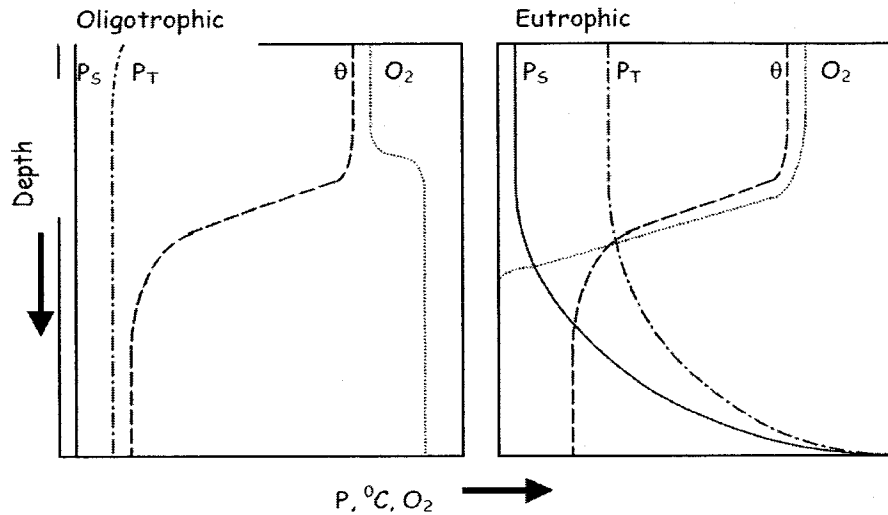
Figure 2-6 Generalized vertical distribution of soluble phosphorus (P_S), total phosphorus (P_T) in a stratified oligotrophic and eutrophic lake. Oxygen and thermal (θ) profiles are also shown (Environment Canada, 2004)

The chemical processes occurring at the sediment-water interface are operating in synergy with the dynamics of water body. The complex combination of all these processes often makes dynamics and the evolution of each lake a unique case (Perrone et al., 2008).

2.6 Resuspension of Sediments

Sediment resuspension is defined as the redistribution into the water column of sediment particles which had been settled on the lake bottom before (Bloesch, 1994). Generally, when the critical shear stress of the overlying water is strong enough, it can resuspend the sediment particles from the bottom. The critical shear stress is a function of the properties of the bottom material such as water content and grain size (Evans, 1994). For example,

recently deposited, unconsolidated material is resuspended more easily than compacted material (Bengtsson et al., 1990). Resuspension is a very common physical phenomenon for any lakes, rivers, estuaries or even in deep sea (Tengberg et al., 2003). It can be caused by natural events, such as strong winds, tidal currents and biological activities or by anthropogenic perturbations such as trawling and dredging (Graf and Rosenberg, 1997). According to Evans (1994), depending on the lake depth and morphometry and the wave base, the whole water body or only deeper layer are affected by resuspension (Evans, 1994). Resuspension is closely related to lateral sediment transportation and sediment focusing, since the driving force, such as currents and waves have a horizontal component in addition to the vertical force (Evans, 1994).

The effect of resuspension on nutrient release and carbon recycling is debated (Tengberg et al., 2003). According to Cyr (2009) and Da-Peng (2010) sediment resuspension can promote phosphorus release from surface sediments (Cyr et al., 2009; Da-Peng and Yong, 2010). This can happen due to the displacement of sediment pore water, desorption or dissolution of P bound to iron, manganese, and other inorganic complexes, as well as mineralization of organic matter (Burger et al., 2007). However, sediment resuspension can also expand the phosphate sorption sites (Noges and Kisand, 1999). In these sites the dissolved phosphorus in the water would be physically sorbed onto the sediments or chemically sorbed by phosphorus reactants including metal oxides, hydroxides, clay minerals, $CaCO_3$ particulates, aluminum and iron-complexes, and other inorganic complexes. Most of this phosphorus incorporated into these different sedimentary phosphorus fractions are transported into the sediments in these particulate forms by

sedimentation–deposition and sorption–precipitation (Selig, 2003; Loeb et al., 2008; Tallberg et al., 2008) event. Then they are again redistributed during resuspension.

Little or no effect was reported by Sloth et al (1996). "A marine system is just showing a short-term response to the resuspension and after 1 week, almost all of the measured parameters returned to the conditions that existed before the resuspension had occurred. In that laboratory study, there was a high increase in oxygen consumption, 10 times the normal, but only small changes in nutrient fluxes" (Sloth et al., 1996).

However, Tengberg (2003) has concluded that resuspension of sediment improves the water quality by reducing the nutrient level in water body (Tengberg et al., 2003). When the resuspended sediments are transported to the oxic water column, it might lead to a formation of iron oxides, which adsorbs phosphate on its surface, with a decrease in phosphate in the water column in result. If the majority of the sediments are mainly the refractory organic material, upon resuspension, they can be stirred up and be diluted in the overlying water. This makes the bacterial decomposition less efficient, thereby reducing phosphorus (Tengberg et al., 2003).

CHAPTER THREE

MATERIALS AND METHODS

This chapter contains the experimental procedure and the methodology followed in this research work. In order to understand the current problem and the solution to improve the lake quality, it is also important to know about the location of the lake and its physical parameters. Seven different stations from where the sediment samples were taken for analysis are indicated on the map. A detailed description of sediment collection procedures followed by phosphorus measurement procedures are the core of this chapter.

3.1 Site Description

Lake Caron ($45^0 50' 28''$ N $74^0 08' 50''$ W) is situated around 75 km north from downtown, Montreal in the province of Quebec in Canada. It is a shallow (average depth of 1.3m) artificial lake which lies in the municipality of Sainte-Anne-des-Lacs (municipalité de paroisse). The approximate area and average water volume of the lake are 35,300 m^2 and 46,400 m^3, respectively. It remains frozen usually from late October to the middle of May. During heavy downpours, it usually overflows to some points to maintain the water level of the lake. The watershed is dominated by wild trees and there are some privately owned houses surrounding the lake. The habitants usually do kayaking, canoeing, pedal boating on water. They also seasonally do gardening and lawn mowing on the banks.

Based on average total-phosphorus (TP) content (34 μg/L), chlorophyll a concentration (38 μg/L) and Secchi disk results (1.1m) the Ministère du Développement Durable de l'Environnement et des Parcs (MDDEP) and the municipality has classified Lake Caron

as eutrophic since 2008 (ABV lacs.org) (MDDEP, April, 2008). To avoid the situation becoming worse, they asked people to refrain from doing any recreational water activity on that zone (ABV lacs.org). The geographic location and bathymetric map indication seven stations are given in Figure 3-1. Limnological features of Lake Caron are tabulated in Table 3-1.

Table 3-1 Limnological features of Lake Caron

Limnological characteristics	
Area	35300 m^2
Volume	46400 m^3
Altitude	333m
Highest depth	2.6 m
Average depth	1.3 m
Eutrophic class	Hyper-eutrophic
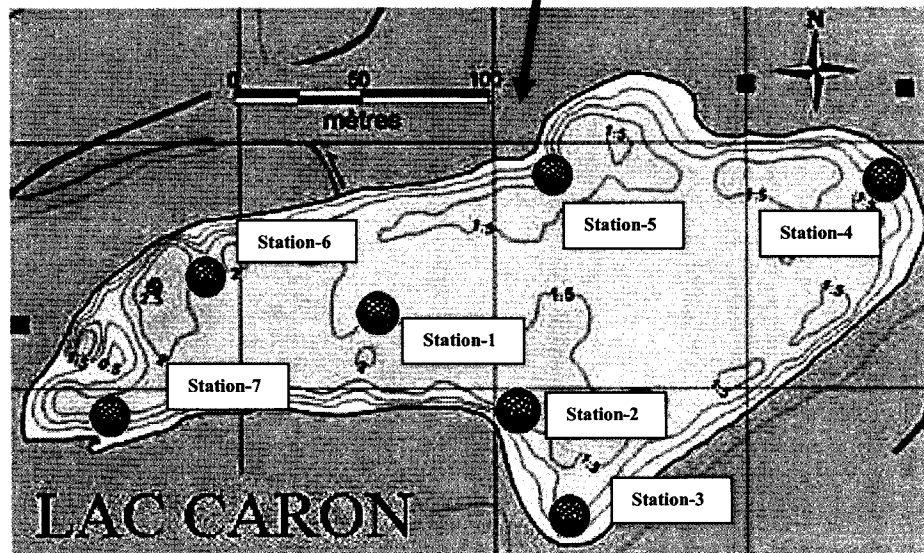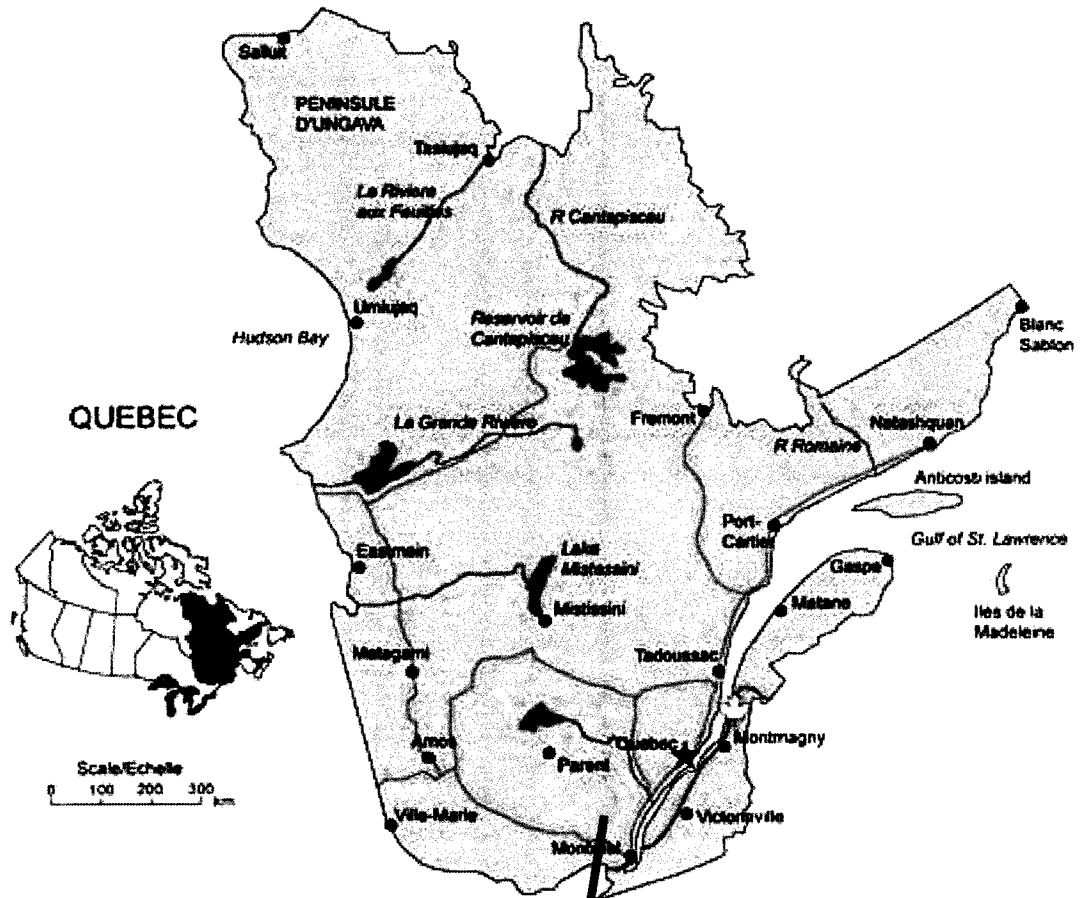
Figure 3-1 Geographic location, and bathymetric map of lake Caron, indicating seven stations (ABV lacs.org)

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3.2 Sample Collection, Storage and Air-drying

Surface sediment samples were collected in late August, 2009 by a surface sediment sampler. It was a Birge-Ekman grab type sampler from 'wildco', wildlife Supply Company. The sampler had two thin jaws, hinges, overlapping on the top, which opens during descent to let water pass through. They remained close during retrieval and were held shut by water pressure to reduce washout. There were another two hinged jaws on the side which are responsible for grabbing the sediments from the bottom surface when it closes. The working principle is called messenger-operated twin-pin scoop release mechanism. To operate, first, the jaws were set apart forcefully and set on the springs. The sampler was lower inside the water until it reached to the sediments. Messenger (in this case, a heavy object which slides along the string, attached to the sampler) was released thus releasing also the spring so that the hinged side can close and grab sediment samples. An image of the Birge-Ekman type sediment sampler is given in Figure 3-2.

Core sediments were collected using a soil sampler. Then a core tube sampler of 20cm height and 3 cm diameter was inserted from the bottom of it. The sediments were very compact, so a solid wooden piston was used to push it from the top to collect sediments at different depths.

The sediments collected were then carried to an ice cooled box inside the car and transferred to the laboratory of Concordia University, Montreal, QC, Canada.
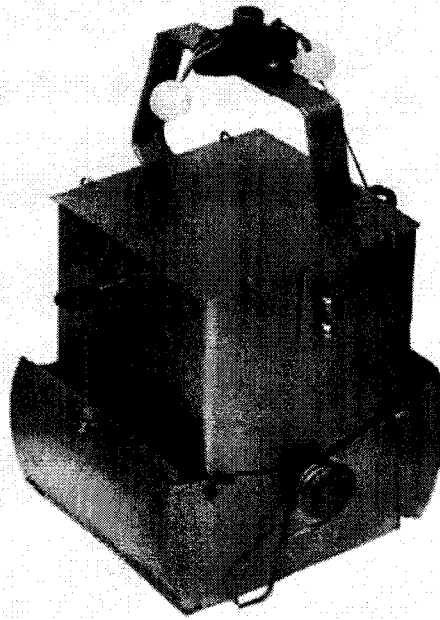
Figure 3-2 Wildco surface sediment sampler, Birge-Ekmen type, courtesy: (Wildco Company)

Upon reaching the laboratory, the sediments were placed in and kept in the refrigerator at 4^0C according to ASTM D3976-92 (Standard Practice for Preparation of Sediment Samples for Chemical Analysis). The foreign objects, which are not regarded as sediments were removed from the sediments, as they can result in inaccurate analysis. Then the sediments were sieved using a 10 mesh stainless steel sieve. Determination of water content, loss on ignition (LOI) and granulometry were performed with these wet sediments.

The sediment samples were then air dried. Large lumps or clumps were homogenized using mortar and pestle.

3.3 Methodology Used for General Characterization of Sediments

Determination of water content and loss on ignition in sediment, sediment's particle density and determination of pH were considered as the general characterization experiments for this report.

3.3.1 Water content and loss on ignition (LOI)

Water content and Loss on Ignition (LOI) were determined according to ASTM D2216-98 method (Standard test method for laboratory Determination of Moisture Content of Soil by Mass). Sediment samples were taken in pre-weighed porcelain crucibles and then the weight of each crucible was recorded using a digital scale with accuracy of 0.01g. The samples were then placed in a drying oven at $105 \pm 5^{\circ}C$ for about 12h-16 h. After that, the crucibles were placed inside a desiccator so that they do not absorb moisture from the environment. When they are cold enough as to not affect the accuracy of the digital scale by convection current, the weight of the crucible with dried sediments were again recorded.

The water content was calculated as follows:

$$w = \frac{(M_{CWS} - M_{CS})}{(M_{CS} - M_C)} \times 100 \qquad (3\text{-}1)$$

Where,

w = water content %

M_{CWS} = mass of container (crucible) and wet specimen, g

M_{CS} = mass of container (crucible) and oven dry specimen, g

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M_C = mass of container

LOI was calculated according to ASTM D2974-00 method. Oven dried (105°C) sediments were placed in furnace at 550°C for 4 hours. The sediments were cooled down in a desiccator and their weights were measured using a digital scale. The LOI was calculated based on the following equation:

$$LOI = \frac{W_{105^0c}}{W_{550^0c}} \times 100\ \%$$ (3-2)

where,

W_{105^0c} = weight of sample at 105°C

W_{550^0c} = weight of sample at 550°C

3.3.2   Determination of pH

Sediment pH was measured using a Fisher Scientific pH meter model AR25, dual channel pH/Ion meter. Sediments and de-ionized water at a ratio of 1:10 were taken. They were well mixed by a shaker for one hour and they were allowed to settle for another one hour. After that, the pH was measured using the pH meter (AR25). An image of a similar pH meter is shown in Figure 3-3.
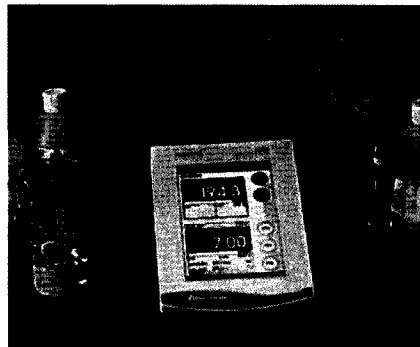
Figure 3-3 Dual channel pH meter, courtesy: (Fisher website)

3.3.3 Particle density determination

Determination of the particle density for sediments was done according to the ASTM D854-02 method. A specialty type of instrument, a pycnometer, was used for measuring density or volume for solid objects. Figure 3-4 shows a pycnometer.
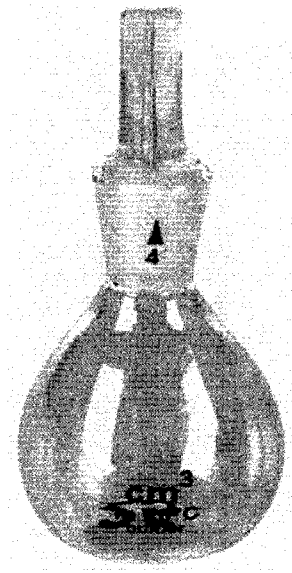
Figure 3-4 Pycnometer used for determination of density or volume of solid substances

First, sediment samples were taken inside the pycnometer and the weight of pycnometer together with inserted object is recorded, which is $m_0 + m_S$. Then, de-ionized water is added in it to determine the weight of water, m_{H_2O}' (measured weight minus $m_0 + m_S$). If ρ_{H_2O} is the density of water, then volume of added water V_{H_2O} can be obtained as per the equation,

$$V_{H2O}' = \frac{m'_{H_2O}}{\rho_{H_2O}}$$

$$(3\text{–}3)$$

The volume of measured solid object (sediment samples) V_S, is the difference between the empty pycnometer (V) and the volume of water (V_{H_2O} ').

So, the volume of the solid substance is:

$$V_S = V - V_{H_2O}' = \frac{m_{H_2O} - m_{H_2O}'}{\rho_{H_2O}}$$ (3-4)

The density of measured object ρ_s can be then calculated as,

$$\rho_s = \frac{m_s}{V_s}$$ (3-5)

3.4 Particle Size Distribution

The particle size distribution for the sediment samples was performed using the laser scattering analyzer (HORIBA, LA- 950V2) which is shown in the Figure 3-5(a). This instrument consists of two light sources and an array of high quality photodiodes. There are also sample handling system to control the interaction of particles and incident light between the light source and photodiodes. The central idea in laser diffraction is that a particle will scatter light at an angle determined by that particle's size. Larger particles will scatter at small angles and smaller particles scatter at wide angles. A collection of particles will produce a pattern of scattered light defined by intensity and angle that can be transformed into a particle size distribution result of the sample analyzed using Mie Theory (Mie theory: It is also known as Lorenz-Mie theory, which is an analytical solution of Maxwell's theory named after German physicist Gustav Mie and Danish physicist Ludvig Lorenz. This theory allows the calculation of the electric and magnetic field inside and outside of the spherical object and is generally used to calculate either how much light is scattered, the optical cross section or the form factor). In Figure 3-5(b)

a schematic is presented showing the working principle of the laser particle size analyser. The machine has the ability to measure dry or wet samples from $0.01\mu m$ to $3000\mu m$ (Horiba website).
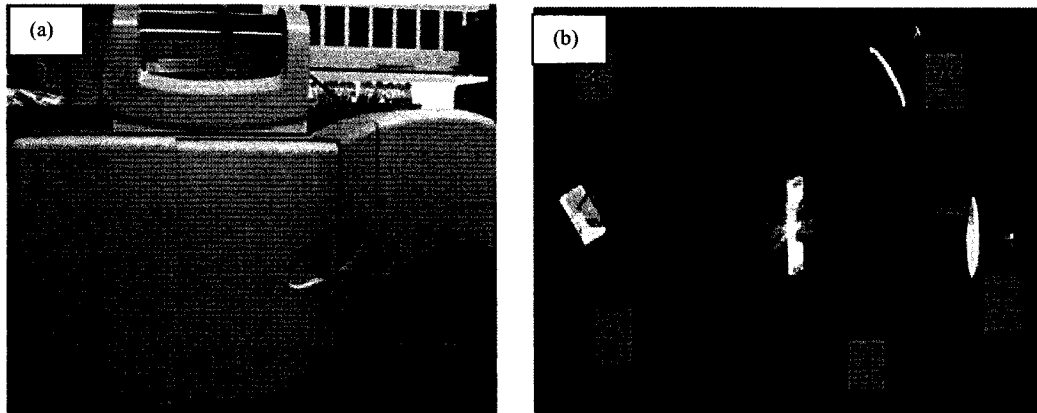
Figure 3-5 (a)HORIBA particle size analyser, (b)Working principle of the particle size analyser showing two light sources [1&2], two photodiodes [3&4] and sample handling system in the middle (Horiba website)

3.5 Water Column Experiment

To investigate the phosphorus concentration at different layers of the water body, an experiment was performed in the Concordia University laboratory. A column shaped enclosure made of transparent plexiglass was constructed having a height of 48 cm. Sediments and water were shaken using AROS-160 shaker first for 15 hours to allow them sufficient time to interchange nutrients and then put inside the column. 15 hours were allowed for shaking so that the sediments and water can be well mixed and sufficient exchange of nutrients between sediments and water can take place. According to Zaghtiti (2008) a water-sediment ratio of 20-25:1 was considered good for nutrient

sorption. After that, the mixture was transferred into the column, and the rest of the column was filled with de-ionized water.

The column (Column height=48cm, Diameter=7.62cm, Volume=2188.9cm^3) was kept inside the refrigerator at 4°C and after 24 h total phosphorus in the overlying water at different depths were measured. Particle size distribution of suspended solids at those depths were also measured. The experimental setup for the water column experiment is shown in Figure 3-6.
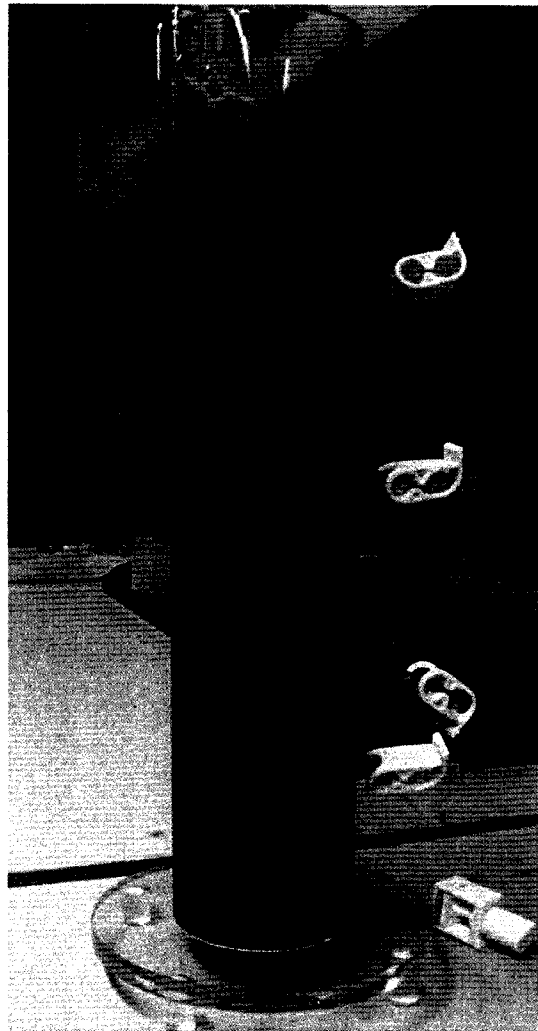
Figure 3-6 Water column made of plexi-glass, to investigate the phosphorus distribution at different water layers

To facilitate taking water samples at different heights, four holes were made at different heights/depths of the column by drilling. The first hole was at 12cm, the second, third and fourth holes were at 22cm, 32cm and 38 cm, respectively from top of the water layer. Outlets were made at those heights so that water can be drained out easily.

After 24 h, the column was taken out of the refrigerator and water samples were taken from different depths. Water samples from each depth were analysed for total phosphorus and suspended particle size distributions. The phosphorus measurements at different heights were performed using ascorbic acid method, described in section 3.7.3 and particle size distribution measurement was done by HORIBA particle size analyser (3.4).

This experiment can act as a model, representing the entire water column of Lake Caron. The average depth of Lake Caron is 1.3m, but other than the banks, which were shallower, the maximum occurring depth (Figure 3-1) of Lake Caron in 1.5m (ABV lacs.org). By dividing the depth of 1.5 m by the water column height (Sediment bed height was 5cm, so the water column height was 48-5=43cm) we get 3.5. So, by multiplying 43 cm with 3.5, a rough idea can be generated based on the phosphorus concentration at depths 42, 77, 112 and 133 cm from the top of the lake. However, it is difficult to simulate lake phenomena in the plexi-glass water column. Particles are constantly eroding from rocks and soils and accumulating at the lake bottom and releasing phosphorus causing internal loading.

3.6 Re-suspension Method

Resuspension is a very common phenomenon in nature. Naturally sediments get resuspended due to wind or wave. In shallow lakes, sometimes resuspension is a cause of increased phosphorus concentration in water. However, this is not always the case and some researchers have found artificial resuspension can also cause reduction in the overlying water (Boström et al., 1988; Tengberg et al., 2003).

The resuspension experiment was done in the Concordia University laboratory, because large scale artificial resuspension in the lake was not accessible. Sediment and water samples are taken 1:25 ratio and shaken for 15 h in a AROS 160 shaker to allow them sufficient time to exchange phosphorus. They are then taken in a beaker, for aeration and stirring. After that, they are allowed to settle down naturally under gravity and total phosphorus content in the overlying water was measured at different time intervals (1h, 6h, 18h, 24h, 48h..........216h) by the ascorbic acid method (Section 3.7.3). The concentration of suspended solids in water was also measured in the water.

For resuspension with aeration, air is passed (from the air-line in the laboratory) inside the water. Before entering the air directly into the sediment-water mixture, it was passed through a sparger to distribute the air flow evenly inside water. Air flow rate was not measured but it was controlled time to time so that the water-sediment mixture does not overflow or squirt outside of the beaker. Resuspension without aeration was without passing the air inside it. The magnetic stirrer was turned on and it mixed well the sediments and water. Figure 3-7 is an image of how the resuspension was performed with and without aeration.
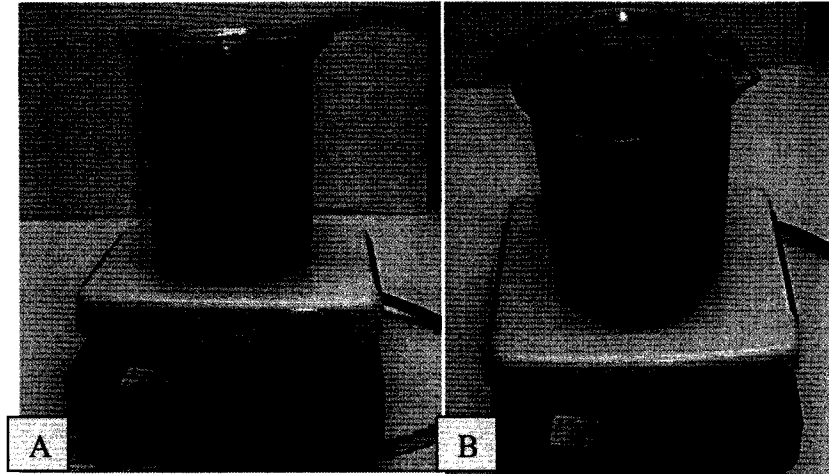
Figure 3-7 Resuspension experiment, (a) aeration, (b) no-aeration. Aeration was achieved by injecting air inside the sediment-water mixture

3.7 Measurement of Phosphorus

3.7.1 Total phosphorus content in sediment

Total phosphorus content in sediment was measured by the perchloric acid digestion method as described in method APHA 4500-P of the book 'Standard methods for the examination of water and wastewater' (American Public Health Association, 1998).

One gram of air dried sample was placed in an Erlenmeyer flask for digestion with 20 ml of concentrated nitric acid. After digestion with nitric acid, 30 ml mixture of nitric (about 10ml) and perchloric acid (about 20ml) were added in it. Then the temperature was increased to the boiling point of the mixture. The digestion was continued until heavy white fumes appeared and the particles became like white sand. The total time of digestion was approximately 45 minutes. After cooling the mixture, 1 drop of aqueous phenolphthalein solution was added, followed by 6N sodium hydroxide solution (NaOH)

until the solution just turned pink. The volume was brought to 250 mL using de-ionized water. Phosphorus in the solution was measured using ascorbic acid method, described in section 3.7.3.

3.7.2 Selective sequential extraction

Selective sequential extraction was performed for inorganic phosphorus in the lake sediments. The methodology used for this purpose was adapted from the method described by Chang and Jackson (1957). Their method is widely used for fractionation procedure, although further modified by Williams et al. (1957), Simillie and Syers (1972), Peterson and Corey (1966) and Fife (1959) for enhanced extractability and for calcareous soils. Selective sequential extraction used in this report was originally based on Kuo's fractionation scheme (Kuo, 1996).

The chemistry of soil phosphorus is complicated. Inorganic phosphorus can react with Ca, Fe and Al to form discrete phosphates. The selective sequential extraction procedures are based on the differential solubilities of the various inorganic phosphorus (P) forms in various extracts. Ammonium chloride (NH_4Cl) is used first to remove soluble and loosely bound P, followed by separating Al-P from Fe-P with NH_4F, then removing Fe-P with NaOH. The reductant soluble phosphorus (P) is removed with CDB (sodium citrate–sodium dithionite–sodium bicarbonate) extraction. The sediments analysed for this experiment in this thesis did not show any significant results for reductant soluble P, so the results were not shown in this report. The Ca-P was extracted with sulphuric acid (H_2SO_4) since Ca-P is insoluble in CDB.

Required Reagents

— 1M ammonium chloride (NH_4Cl). Prepared by adding 53.5 g of NH_4Cl dissolved in 1L de-ionized water

— 0.5M ammonium fluoride (NH_4F), pH 8.2. Prepared by 18.5 g of NH_4F in 1L de-ionized water. pH was adjusted by 4M NH_4OH solution

— 0.1M NaOH solution. Prepared by dissolving 4 g of NaOH in 1L de-ionized water

— Saturated NaCl solution. Prepared by dissolving 400 g of NaCl in 1L de-ionized water

— 0.25M sulphuric acid (H_2SO_4) solution

— 2M hydrochloric acid (HCl) solution

— 1M sodium bicarbonate ($NaHCO_3$). Prepared by adding 84 g of $NaHCO_3$ in 1L de-ionized water

— 0.8M boric acid solution. Prepared by dissolving 50 g of H_3BO_3 1L de-ionized water

— 0.25% p-nitrophenol. Prepared by adding 0.25 g of p-nitrophenol in 100 ml of de-ionized water.

Procedure

Loosely bound-P

For this extraction, 1g of soil (>2mm, passed through10 mesh) was mixed with 50ml of 1M ammonium chloride (NH_4Cl) and was shaken for 30 min. The solution was then centrifuged, the supernatant was filtered into a 50 ml volumetric flask and made up to volume with de-ionized water. This was named as extract-A.

Aluminum bound-P (Al-P)

For aluminum bound phosphorus, 50 ml of 0.5M ammonium fluoride (NH_4F), pH 8.2 was added with the residue and shaken for 1 hour for extraction. The solution was then centrifuged, the supernatant was filtered and transferred into a 100 ml volumetric flask. The soil sample was then washed with a 25ml portion of NaCl twice and added into the volumetric flask after filtration. Total volume of the extractant was made to 100 ml with de-ionized water. This extract was named as extract-B.

Iron bound – P (Fe-P)

50 ml of 0.1M NaOH solution was added with the soil residue and was shaken for 17 h to extract iron bound phosphorus. After centrifuge, the supernatant was filtered and taken into a 100 ml container combined with two washings with saturated NaCl solution and made to volume with de-ionized water. This extract was named as extract-C.

Calcium bound-P (Ca-P)

For this extract, 50 ml of 0.25M sulphuric acid (H_2SO_4) solution was added to the soil residue and shaken for 1 hour. Then it was centrifuged, supernatant was filtered followed

by two washings with saturated NaCl solution. Extract was transferred into a 100ml volumetric flask and made to the volume with de-ionized water.

A block diagram of the selective sequential extraction method is presented in the next page, Figure 3-8.

Preparation and determination of P from the extracts

50 ml from each of the extracts A, B, C, D were transferred to beaker and few drops of de-ionized water were added in it. Five drops of p-nitrophenol indicator was added in extract C and D and the pH was adjusted with 2M HCl or 2M NaOH until the solution colour just changed. 15 ml of 0.8 M Boric acid was added to extract B. Phosphorus concentrations in various extracts were analysed by ascorbic acid method (Murphy and Riley, 1962) using a spectrophotometer (DR 2800) at a wavelength of 880nm. The procedure to measure phosphorus by ascorbic acid method and spectrophotometer is described in the sections 3.7.3 and 3.7.4.

1.0 g of sediment in 100 ml centrifuge tube

50ml of 1M ammonium chloride (NH$_4$Cl), shake 30 min., centrifuge → Extract-A → Soluble & loosely bound-P

50 ml of 0.5M ammonium fluoride (NH$_4$F), shake 1 h., centrifuge, and wash with saturated NaCl → Extract-B → Al-P

50 ml of 0.1M NaOH, shake 17 hours, centrifuge and wash with saturated NaCl → Extract-C → Fe-P

50 ml of 0.25M sulphuric acid (H$_2$SO4), shake 1 h., centrifuge and wash with saturated NaCl → Extract-D → Ca-P

Figure 3-8 Selective sequential extraction for non-calcareous soils (Pierzynski, 2000). This fractionation procedure was primarily based on Chang & Jackson (1957), then improved and modified by Williams et al (1967)

3.7.3   Ascorbic acid method

Ascorbic acid method is widely used for determining phosphorus in water samples and solutions. Ammonium molybdate and potassium antimonyl tartrate react in acid medium with orthophosphate to form a heteropoly acid [i.e, a heteropoly acid is a class of acid made up of a particular combination of hydrogen and oxygen with certain metals and non-metals which should contain an addenda atom (such as tungsten, molybdenum or vanadium), oxygen, acidic hydrogen, one hetero atom (generally from p-

bloc of the periodic table, such as silicon, phosphorus or arsenic)] that is reduced to intensely coloured molybdenum blue by ascorbic acid (American Public Health Association et al., 1960).

Required reagents

— 2.5 M sulfuric acid (H_2SO_4)

— Potassium antimonyl tartrate solution ($K(SbO)C_4H_4O_6.1/2H_2O$). Prepared by dissolving 1.3715 g $K(SbO)C_4H_4O_6.1/2H_2O$ in 400 mL of de-ionized water in a 500mL volumetric flask, then diluted to volume with de-ionized water

— Ammonium molybdate solution ((NH_4)$_6Mo_7O_{24}.4H_2O$). Prepared by dissolving 20 g (NH_4)$_6Mo_7O_{24}.4H_2O$ in 500 mL of de-ionized water

— 0.01M ascorbic acid. Prepared by dissolving 1.76 g of ascorbic acid in 100 mL of de-ionized water

— **Mixed reagent** was prepared by mixing 50 mL 5N H_2SO_4, 5 mL potassium antimonyl tartrate solution, 15 mL ammonium molybdate solution, and 30 mL ascorbic acid solution by the mentioned order. All the reagents were added at room temperature

— **Stock P solution**: 219.5 mg of anhydrous KH_2PO_4 was dissolved in de-ionized water. The solution was diluted to 1 L with de-ionized water.

(In this solution, 1.00 mL = 50.00 μg PO_4-P)

— **Standard P solution**: 50 mL of stock P solution was added to 1000 mL of de-ionized water.

(In this solution, 1.00 mL = 2.50 μg PO_4-P)

Procedure

50 ml of standard P solution (mentioned in the section above) were taken in an Erlenmeyer flask. 8 ml of mixed reagent was added in it and mixed thoroughly. After 10 minutes but not more than 30 minutes, the mixture was taken in sample vials and the absorbance was measured at 880nm. These are all known concentrations, so from these all known concentrations of standard P solution, different absorbance values were obtained at 880 nm. At that wavelength, absorbance Vs. concentration was plotted (straight line passing through origin) which is called a calibration graph. Figure 3-9 is the calibration graph for the experiments for phosphorus determination.
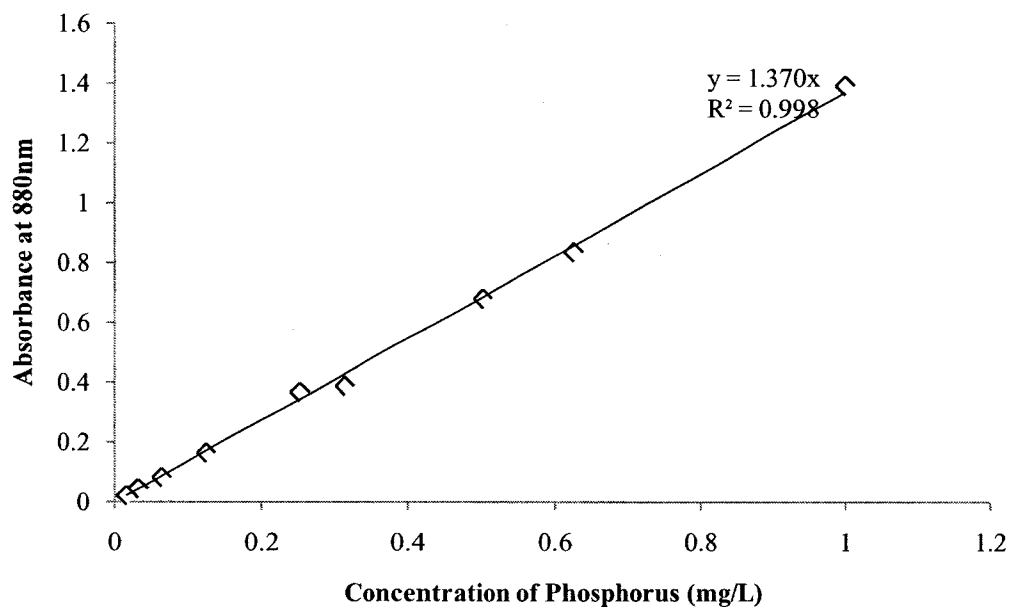
Figure 3-9 Calibration graph for determination of phosphorus by ascorbic acid method

For any solution, by measuring the absorbance at the same wavelength (880nm) one can measure the concentration of phosphorus present in the solution.

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3.7.4 Measurement of phosphorus by spectrophotometer

Absorbance was measured using a spectrophotometer (HACH DR2800). Organic free water was used as a blank for measuring phosphorus, which was ordered from HACH (via Fisher scientific). Wastewater effluent (phosphorus concentration of 2mg/L) was used as a standard solution every time starting the measurement. Figure 3-10 is an image of the spectrophotometer.

Figure 3-10 Spectrophotometer (DR 2800) and the reactor used for phosphorus measurement. Absorbance was measured at 880 nm

3.8 Measurement of Suspended Solids

Suspended solids in the water were measured using the standard method ASTM 2540-D. A vacuum filtration method was used for this determination. Measured amount of water (along with suspended solids) was passed through a pre-weighed 0.45μm microfiber filter paper. Wet filter paper was then dried in an oven at 105°C for an hour. After that, the filter paper was cooled in a desiccator and the weight was recorded. Figure 3-11 is a sample image of the vacuum filtration unit.

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Figure 3-11 Sample vacuum filtration unit

If the initial weight of the filter paper is m_i and final weight is m_f and V is the volume of water passed through the filter, then concentration of suspended solids will be,

Concentration of SS is,

$$SS = \frac{m_f - m_i}{V} \times 1000 \quad \text{mg/L} \tag{3-6}$$

Where,

m_i = mass of the filter paper before filtration (mg)

m_f = mass of the filter paper after filtration and drying in the oven (mg)

V = volume of water that was passed through (ml)

CHAPTER FOUR

RESULTS AND DISCUSSION

This chapter includes experimental results and analysis performed for the determination of phosphorus content of the sediment and water samples of Lake Caron. The first step to this result involved the characterization of the sediments based on the physical properties followed by the analysis of the result of phosphorus measurement.

The organization of this chapter is:

- Section 4.1 : This section represents the characterizations results (Water content, LOI, particle size distribution, particle density), total phosphorus content (4.1.3) and selective sequential extraction (4.1.4) results for surface sediments

- Section 4.2 deals with the results of core sediment analyses collected from station-3 and station-4. Core sediments were analysed to investigate which layer of sediments contain more phosphorus.

- The experimental results and analysis that were performed based on their different particle sizes are included in section 4.3. Although these experiments were done using surface sediments collected from station-1 to station-5, a different section is included for better understanding. The aim of this experiment was also to find the particle sizes that are responsible for containing more phosphorus.

- Section 4.4 focuses on the results of distribution of phosphorus in water column. An artificial water column was made in the laboratory and phosphorus concentrations at different levels were measured.

- Resuspension experiments were performed in lab to investigate if it is able to improve the water quality. Section 4.5 gives explanation and reasoning for the results of resuspension experiments.

All of the experiments were done in triplicate and the average values were taken. The average error was calculated using standard error and reported in the graphs. Seasonal changes and unknown reactions during experiments might be a cause of errors. The error margin was between 4.2% and 15%.

4.1 Surface Sediments Analysis

Sediments were characterized by determining the water content, loss on ignition (LOI), pH and particle density using standard ASTM methods (as described in detail in section 3.3).

4.1.1 General characterization

The results of the water content, loss on ignition and pH are tabulated in Table 4-1. Averages of the triplicates values are taken and standard deviations are presented in parentheses.

Table 4-1 General characterization of surface sediments from Lake Caron (Water Content, LOI, pH, particle density). Standard deviations are presented in parentheses

Stations	Water content (%)	Loss on Ignition (%)	Particle Density (g/cm^3)	pH
Station 1	1287 (19.25)	84.87 (0.38)	1.98 (0.01)	5.75
Station 2	937.21 (82.80)	86.07 (0.14)	2.23 (0.02)	5.56
Station 3	388.17 (4.82)	27.41 (0.18)	2.12 (0.10)	5.96
Station 4	548.57 (76.74)	45.10 (0.48)	1.80 (0.03)	5.60
Station 5	805.17 (2.28)	68.54 (1.19)	2.70 (0.02)	5.76
Station 6	43.82 (4.04)	1.36 (0.01)	2.33 (0.09)	5.71
Station 7	28.24 (0.03)	1.06 (0.01)	2.33 (0.01)	5.63

As shown in the Table 4-1, from station-1 to station-5, the sediments had very high water content and loss on ignition (LOI). High values for water content and loss on ignition indicate a higher nutrient and organic matter contents in the sediments (Ratnayke et al., 2007). Since water acts as a major transporter of nutrients, it is necessary for the cells (microorganisms and plants) to survive. In section 4.1.3, it will be found that, the sediments were enriched with organic matter and nutrient content. This fact justifies the above results of high water content and loss on ignition. Another interesting fact is that clay type soils have little macropores in them, whereas sandy soils have micropores. So clay type soils will tend to hold more water rather than percolate down the water as sand particles do. Sediments from station-6 and station-7 were sandy. So they resulted in a low water content and loss on ignition values.

In regard to the particle density, Rühlman et al (2006) has found sandy sediments range between 2.35 and 2.5 g/cm^3. Sediments from station-6 and station-7 were also sandy and they both showed particle densities equal to 2.33 g/cm^3 Smettem (2002) cited that the

soils which are high in organic matter have less particle density. It can be as low as 1.5 g/cm^3 to 2.9 g/cm^3 (Smettem, 2002). Rühlman et al (2006) also stated that for clay type particles and highly organic matter enriched soils, the particle density ranges from 1.8 g/cm^3 to 2.5 g/cm^3 (Rühlmann et al., 2006). Particle density results obtained for the sediments from station-1 to station-4 fit well in this range justifying that this group of sediments were clay particles. Sediment from station-5 was a kind of loam which is a mixture of sand, silt and clay. That might be the reason why the particle density was 2.7 g/cm^3.

Sediments or soils which are very rich in organic matter and nutrients are very fertile and good for plants. Lake Caron was a hyper-eutrophic lake (ABV lacs.org; MDDEP, April, 2008) which also means the sediments are very favourable for plant growth. A slightly acidic environment having pH range 5.5 to 6.5 is perfect for most of the plants' growth (Soil types & Testing). For all of the sediments collected from different stations (from station-1 to station-7), the average pH was 5.71, which falls in the acidic range. The lake was eutrophic (It also means over-fertilized), it supported the growth of algae which means the pH of the lake was also favourable for algae/plants' growth. Since pH 5.71 is readily considered a favourable pH for plant's growth, finding an acidic pH is quite logical in Lake Caron.

4.1.2 Particle size distribution

Surface sediments were characterized to find their size distributions. They were analysed through HORIBA LA-950 particle size analyser. Samples from every station were passed through the laser analyser three times and the data were plotted against percent finer vs. particle diameter in Figure 4-1.
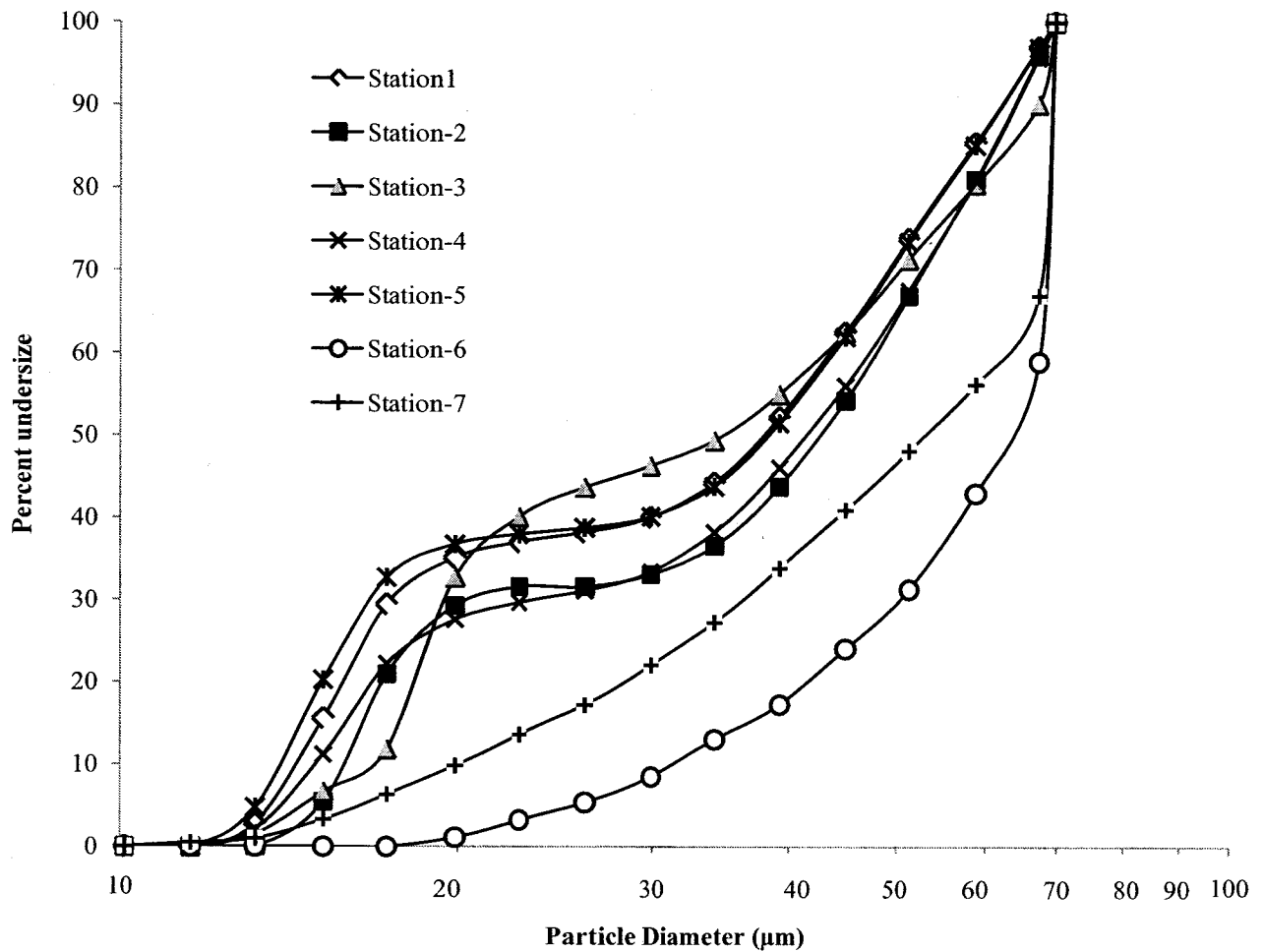
Figure 4-1 Particle size distribution of the surface sediments from Lake Caron

Figure 4-2 shows the frequency distribution of sediment particles collected from different stations. From station-1 to station-5, particles represent mainly clay and silt size fractions. The distribution gave a peak between 0-20 μm which lies in clay/silt region (0-63 μm) However, sediments from station-6 and station-7 were representing silt and fine sand size fractions. The frequency distribution showed a peak between 60-70 μm, which falls under particles' diameter (63 μm-2mm). These set of results also support the results from the water content, loss on ignition (LOI) and soil density described in section 4.1.1.
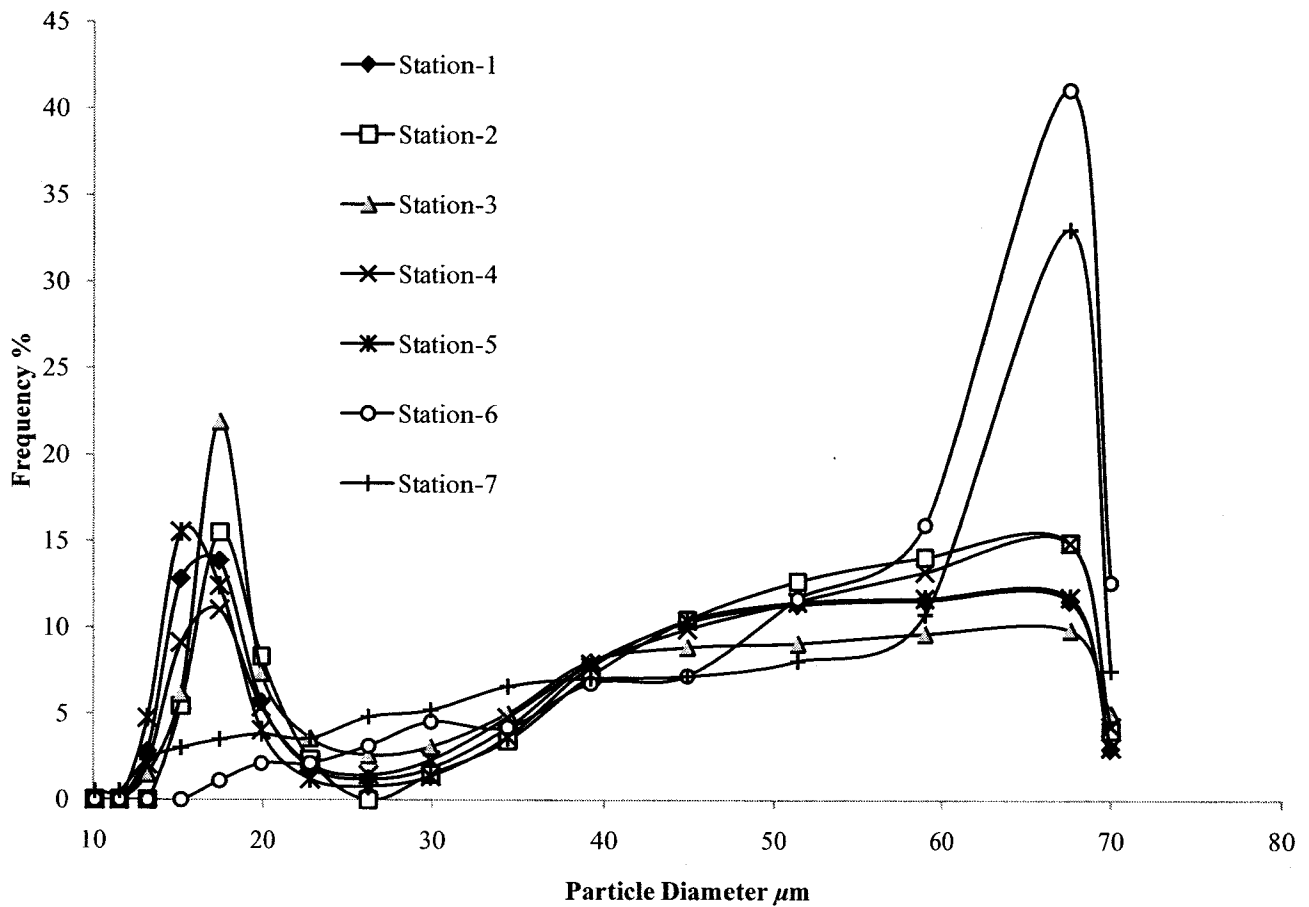
Figure 4-2 Intensity graph for particle size distribution of sediments

4.1.3 Total phosphorus content

Total phosphorus content in the sediment was determined by following the perchloric and nitric acid digestion method. All of the experiments were done in triplicate and the average values were taken.

The results of the total phosphorus measurement are illustrated in Figure 4-3.
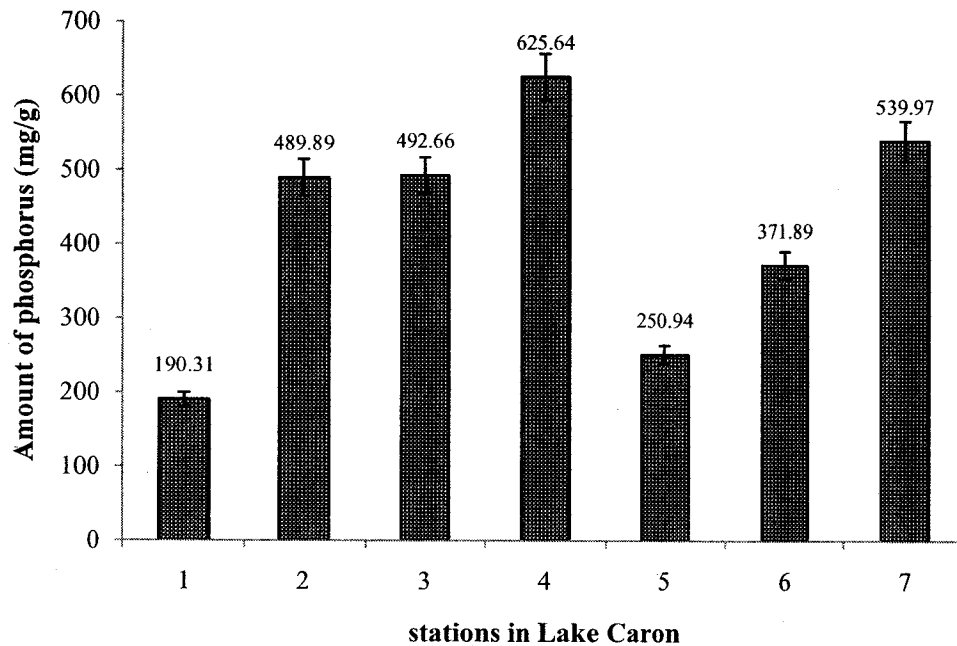
Figure 4-3 Total phosphorus content (mg/g) in sediments from all stations

As in Figure 4-3, Station-4 resulted in the highest amount of phosphorus, 625.64 mg/g (mg per gm of sediment sample). The lowest value was found in station-1, 190.31mg/g. The station-2, 3 and 4 all had higher silt and clay contents. Generally, higher clay contents can retain much phosphorus. Dead leaves and branches from the tree are mainly accumulated around these stations. This might be the reason why they are enriched in organic phosphorus which also contributed to a higher total phosphorus content.

Sediments of station-6 and station-7 were mainly sand particles, unlike station-2, 3&4 they have much less phosphorus retention capacity. However, station-7 has a high value (540.0 mg/g) of total phosphorus. It could be partly due to experimental error or due to algal bloom in 2009. An algal mat had covered the whole area from station-6 to station-7 (ABV lacs.org; MDDEP, April, 2008). It was quite possible that some algae or

microorganisms accumulated during the time of collecting the sediment samples and that is why the amount of phosphorus is high in these places.

Station-1 is located in the middle of the lake and remains undisturbed by anthropogenic activity or natural external phosphorus inputs. For the same reason, there wasn't a high level organic substance at this place.

Unlike any of the stations, the sediment from station-5 was consisted of different kinds of sediment particles. It was a mixture of sand, clay and silt forming a loam. Predicting the reason for existing phosphorus content of sediment at this station is difficult. There exists an overflow just beside this station. During the rainy season, the water drains out through this region lowering the water level of the lake. So, there is always a renewal of water and sediments at this station. This might be a possible reason for the comparatively lower (250.9 mg/g) phosphorus value at station-5.

There was a poor correlation between the loss on ignition and total phosphorus content. Figure 4-4 shows a regression constant value of 0.18.
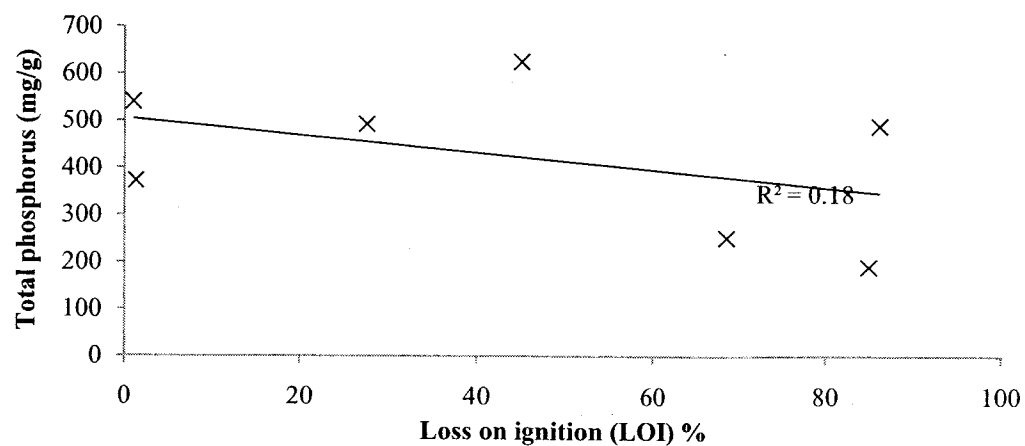
Figure 4-4 Dependency between loss on ignition and total phosphorus content of surface sediment samples

4.1.4 Selective sequential extraction

Selective sequential extractions for inorganic phosphorus were performed for all seven stations' sediment samples. Triplicate measurements were obtained for every set of experiments and the average was taken. The results of selective sequential extractions were illustrated in Figure 4-4. In regards to the total phosphorus in every station, percentage contributions of different fractions of phosphorus were also illustrated in Figure 4-5.

4.1.4.1 Loosely bound phosphorus (Loose-P)

Soluble or loosely bound phosphorus is a measure of immediately available phosphorus pool in sediments which is readily exchangeable within the water column. The average amount of loosely bound phosphorus is 8.44 mg/g. Station-6 resulted in the highest amount of this kind (10.21 mg/g). A filter was set up by another researcher at station-6 for removing the suspended solids in the water thus improving the water quality. The sediments of this station were constantly resuspended due to this filtration unit. This might be a reason for high amount of available phosphorus in the sediments compared to other stations. In regards to the relative contribution of each station, station-1 has the highest loosely bound P with respect to total P, 4.82% (9.19 mg/g). As stated earlier sections, station-1 is the least disturbed station. Benthic algae can also contribute to this phosphorus fraction (Zhang et al., 2009).

Figure 4-5 Phosphorus distribution in different fractions of sediment samples
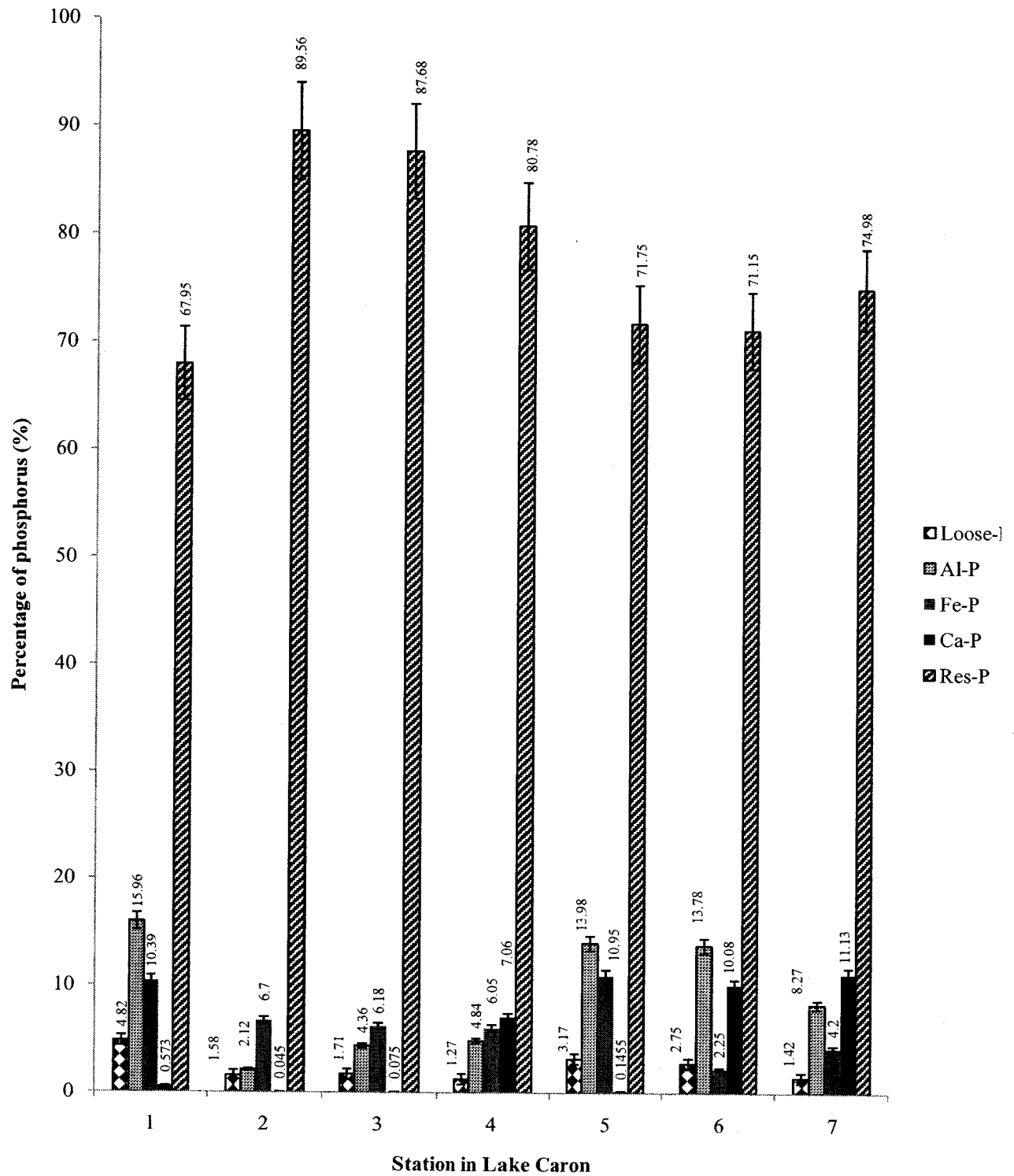
Figure 4-6 Relative contributions of different phosphorus fractions in the sediment samples

of Lake Caron

4.1.4.2 Aluminum bound Phosphorus (Al-P)

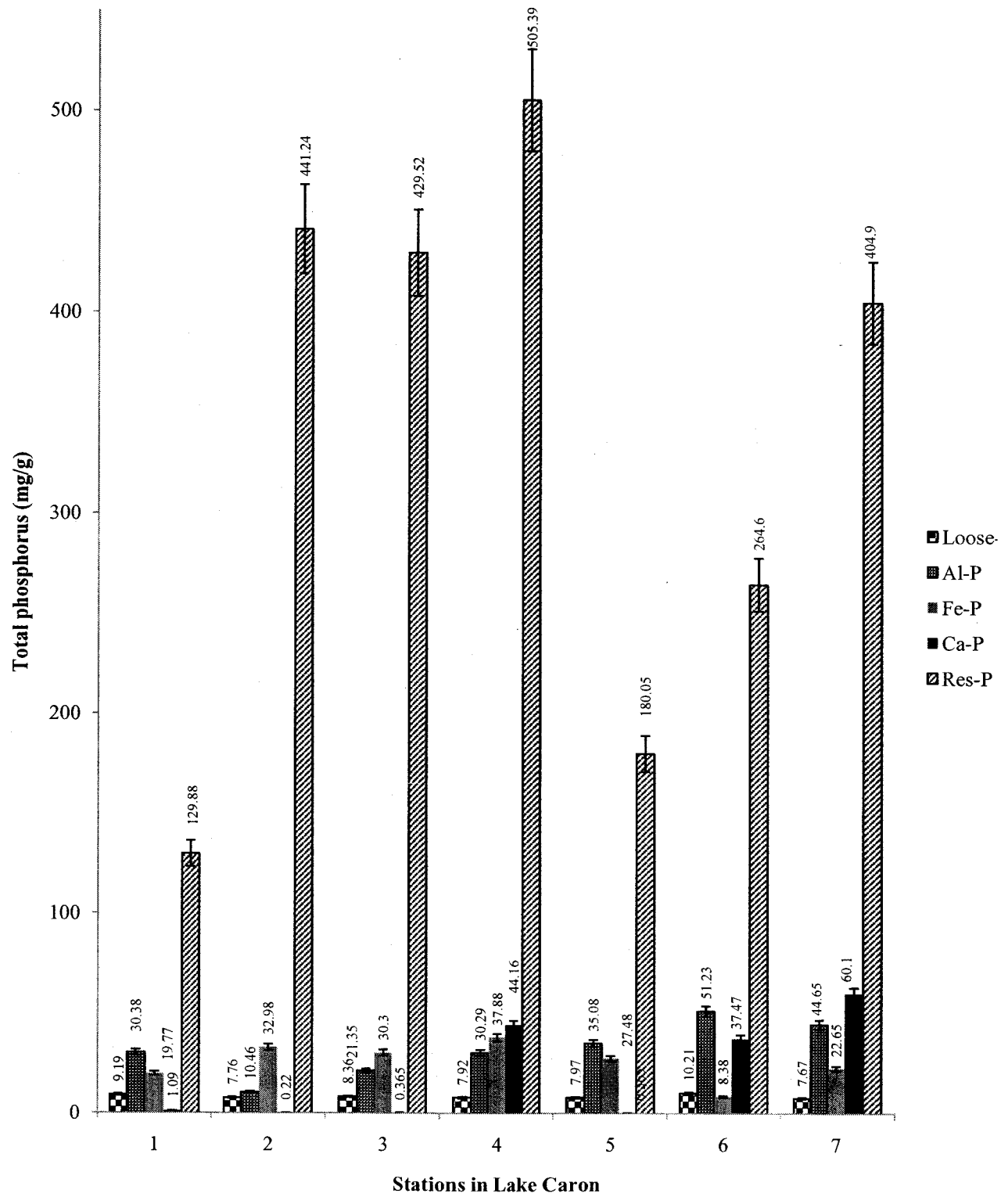Aluminum bound phosphorus comes into play when pH is in acidic range (≥ 5.0). Nature and amount of organic ligands co-precipitated in Al oxides, surface area and crystallinity of the minerals play significant role in phosphate sorption (Violante and Huang, 1989). Aluminum organic co-precipitates, which can be formed in rhizosphere and in acid soils, significantly influence phosphate sorption capacity (De Cristofaro et al., 2000).

The average amount aluminum bound phosphorus for seven stations is 31.92 mg/g.

4.1.4.3 Iron bound phosphorus (Fe-P)

Phosphorus bound to reducible forms of iron and manganese is, in general, considered as a potentially mobile pool of phosphorus in sediments. Consequently, this phosphorus pool (mainly iron bound P) becomes a potential internal phosphorus source to water bodies, for which the water body can undergo occasional oxygen depletion (Boström and Pettersson, 1982).

It was believed that phosphorus release from this reducible iron is dependant on redox potential (Golterman, 1984), but it actually happens when there are available hydrogen ions (acid medium) or hydrogen ion donors (Golterman, 1997). Thermodynamically, iron hydroxide $Fe(OOH)$ is more stable than $Fe(OOH){\approx}P$, opposite scenario can happen only in presence of hydrogen ions (Golterman, 1997).

4.1.4.4 Calcium bound Phosphorus (Ca-P)

Other than deeper lakes and water systems, calcium bound phosphates are considered as permanent burial of phosphorus in the sediments. However, according to Golterman (1997) increasing acidity can cause $CaCO_3{\approx}P$ (P adsorbed $CaCO_3$ surface) to release

phosphorus into water while some orthophosphate will be adsorbed on Fe(OOH) (Iron hydroxide) surface until saturation. As a result, orthophosphate concentration in the water can increase (Golterman, 1997). When sediments become anoxic, there is automatically a decrease in pH as a result of the produced CO_2. This decrease will dissolve the apatite, thereby dissolving also phosphorus as the pH strongly controls this solubility (Golterman, 2001; Huang et al., 2005).

4.1.4.5 Organic or residual Phosphorus (Res-P)

It has long been recognized that organic phosphorus is a source of phosphorus for phytoplankton. Strong evidence has emerged that organic phosphorus is as abundant (as often excess) as phosphates in many water and sediment systems (Turner et al., 2005). Also the organic phosphorus is less refractory that it was previously assumed (Turner et al., 2005). Furthermore, soluble organic phosphorus is bioavailable to phytoplankton and bacterioplankton (Turner et al., 2005). Studies showed that organic phosphorus released from sediments that increased water salinity and it was hydrolysed within days under typical marine aerobic conditions (Suzumura and Kamatani, 1993) (Turner et al., 2005). Parfitt et al (1994) and Martínez (1968) both found that organic phosphorus can undergo mineralisation and release phosphorus in the overlying water (Martínez, 1968; Parfitt et al., 1994). Biological activity gradually enhances this mineralization process, thus releasing phosphorus into the water column.

For station-2 and station-3, there were low amounts (0.22 mg/g and 0.365 mg/g respectively) of calcium bound P (Ca-P) and high amounts of organic phosphorus (441.2 mg/g and 429.5 mg/g respectively). According to Zhang et al (2009) a lower Calcium

bound P with the presence of very high organic P indicates the possibility of becoming highly productive in the near future since lower Ca-P indicates small amounts of burial of phosphorus and higher org-P signifies they can go mineralization (releasing phosphorus into the surface water) anytime soon (Zhang et al., 2009). The next algal blooms might occur at those areas.

4.2   Core Sediment Analysis

Core sediments were collected for station-3 and 4 in the month of July in 2010 to investigate the sediment distribution through the core. Figure 4-7 illustrates the distribution of total phosphorus with increasing depth of the sediment bed. Temperatures were warm; average temperature for July, 2010 was 17.5° C, whereas the average temperatures for September and October, 2009 were 11.2°C and 5.1°C, respectively (Weather Network Site). Retention of phosphorus usually remains low during the warmer period of the year. They release phosphorus into the overlying water. Therefore, total P concentration in sediments compared to that of the samples collected during the fall (Section 4.1.3), 2009 resulted in smaller amounts.

Amount of total phosphorus (mg/g)
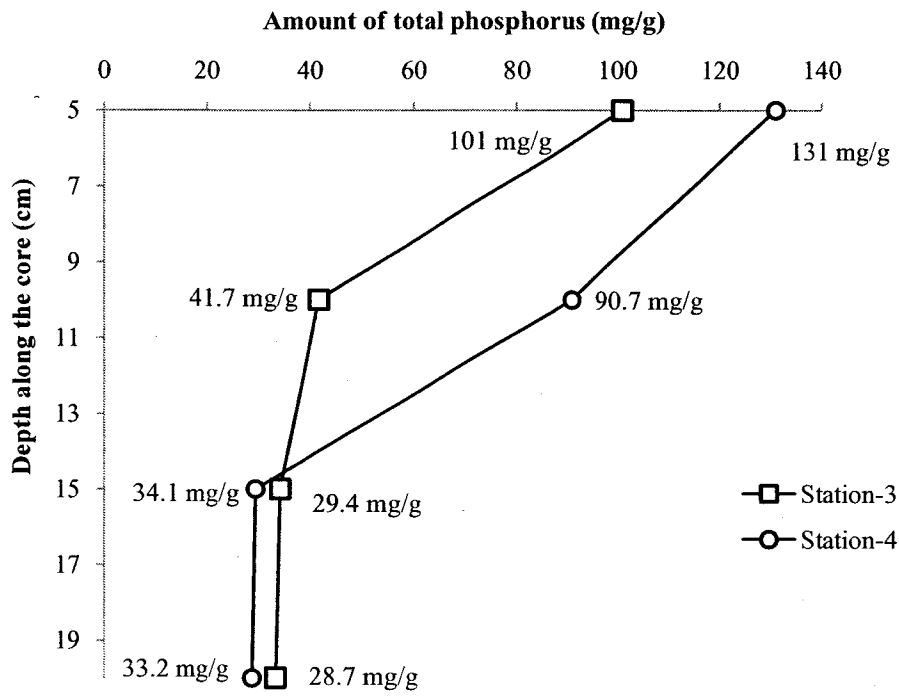
Figure 4-7 Phosphorus distribution (mg/g) along the core of the sediment for station-3 and 4

The phosphorus values showed a downward trend further inside the core of the sediments. The upper surface (0-5 cm) of the sediment bed is much influenced by human activity or anthropogenic and natural reasons (tree leaves, branches), while the layers underneath are not. The top layer of the sediment accounted for 131 mg/g whereas the lowest one resulted in only 28.7 mg/g (station-4). The similar trend is also observed for station-3.

The top layers of the sediments were recently deposited material which did not undergo much transformation or exchange of phosphorus into the water. Therefore, they contain more phosphorus than the bottom layers. Besides, on the top, mainly they are smaller

particles, so they have more surface area available. They can easily adsorb phosphorus, and upon suitable environmental condition, they release it. It is also possible that there are more recent deposits of phosphorus than earlier.

The percentage contribution of phosphorus can be explained by a bar diagram showing percentage phosphorus values at different core depths.

Figure 4-8 represents the percentage of total phosphorus at five stations of Lake Caron.

Figure 4-8 Percentage contribution of phosphorus of the core sediments

The surface layer which is 0-5 cm resulted in 32.3% more phosphorus than the bottom most layer for station-3 and 36.6% more phosphorus for station-4.

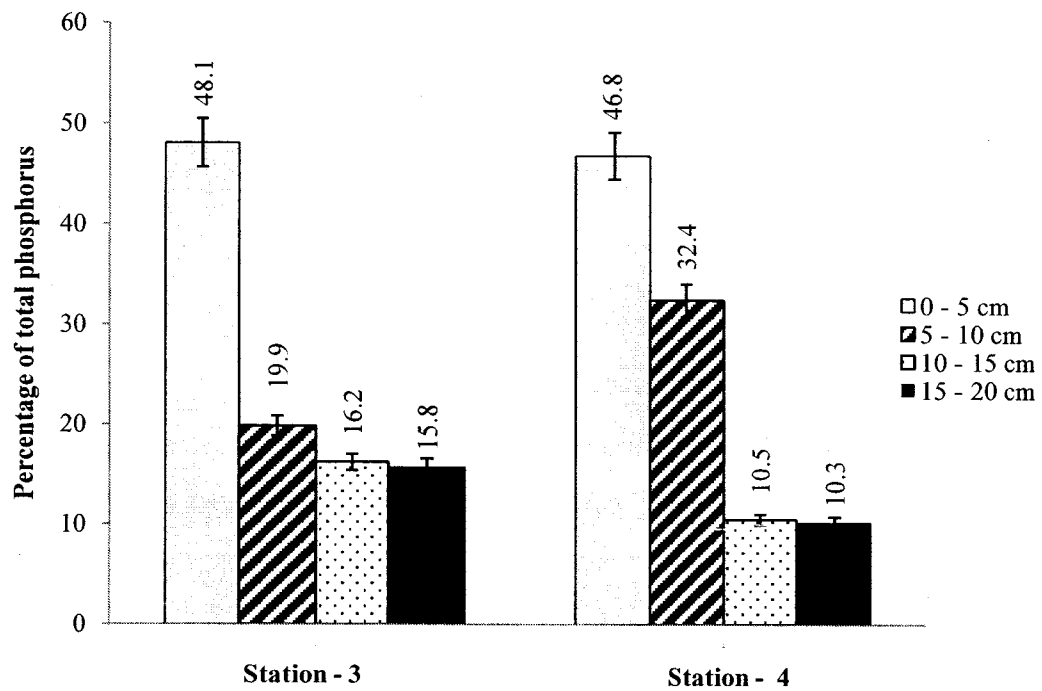## 4.3   Distribution of Phosphorus According to Particle Size

Surface sediments were subdivided into four groups according to their particle sizes. Three ASTM sieves (75μm, 53 μm and 45 μm) were used for this classification. Sediments from station 6 and 7 were sand particles, so these stations were excluded from this classification. Prior to air drying for all sediment samples, they were passed through a 10 mesh (US size) sieve. Therefore, particles larger than 75μm can also be considered in between 75μm and 2 mm.

Smaller particles exhibit the maximum amount of phosphorus in them. For smaller particles, their surface to volume ratio is larger than larger size fractions therefore, they can retain much phosphorus. On the same note, when environmental conditions change e.g.in summer, they release more phosphorus into the water. From Selig (2003) and Löfgren (1989), it is known that for shallow lakes, phosphorus is mainly released from the upper 1-6 cm layers (Löfgren and Boström, 1989; Selig, 2003). Generally, smaller particles are found on the top layers of sediment bed. Again, from the previous section, the top layer (0-5cm) of the core contains more phosphorus than the other layers which also supports the previous statement.

Figure 4-9 is a graphical representation of the phosphorus distribution for different particle sizes. They resulted in as high as 350.7 mg/g phosphorus content for station-3 for a particle size smaller than 45μm. The value of total phosphorus content decreased toward the larger particle sizes for the sediments. The lowest amount of phosphorus occurred for particles larger than 75μm, resulting in the lowest again for the same station-3 (21.97 mg/g).
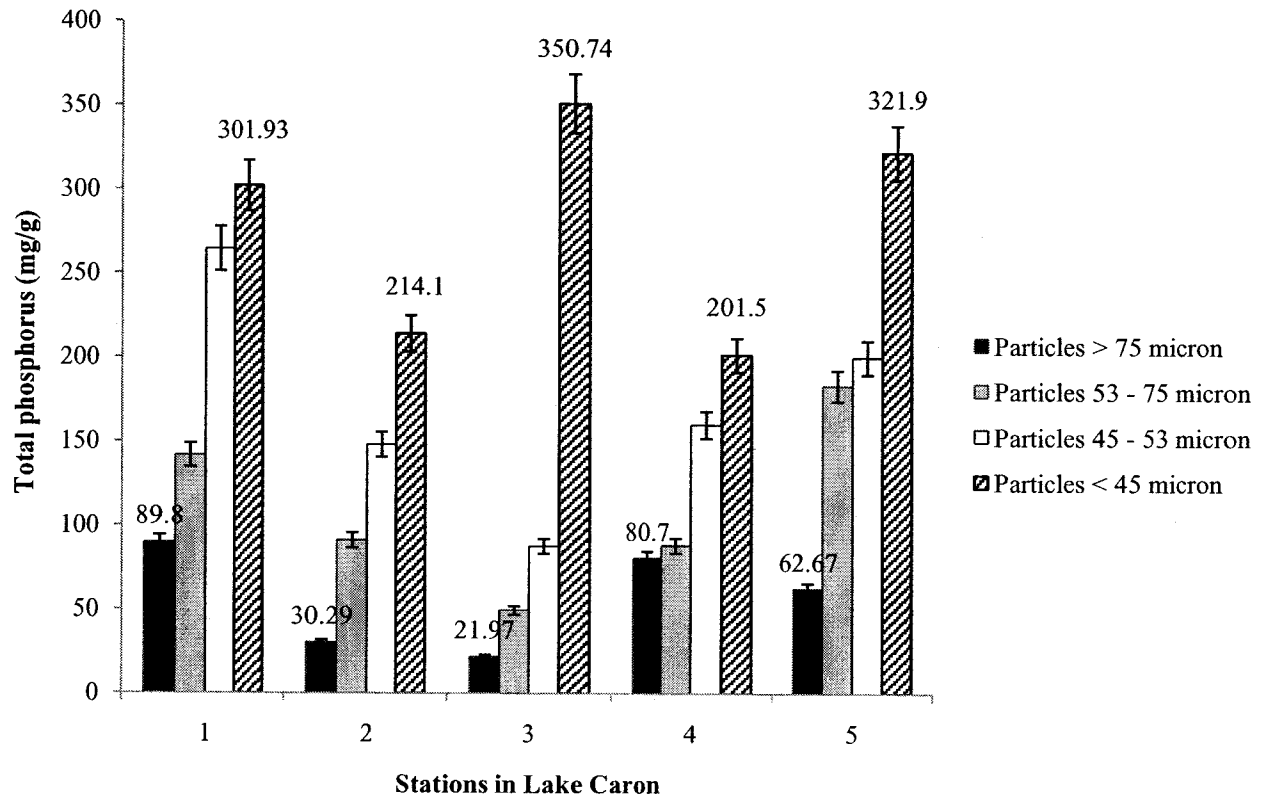
Figure 4-9 Distribution of phosphorus in four different particle sizes; >75μm, 53-75μm, 45-53μm and < 45μm

In regards to the relative contribution of phosphorus for different sizes of particles another bar chart, Figure 4-9 shows the percentage of contribution of phosphorus from different particle sizes. Figure 4-10 also illustrates the differences of the percentages of phosphorus between the largest and smallest sediment particles. For station-3, particles smaller than 45μm contained 64.5% more phosphorus concentration than particles larger than 75μm. Particles smaller than 45μm also resulted in 51.5% more P concentration than the particles between 75μm and 53μm and 59% more than the particles between 53μm and 45μm. For other stations they resulted in similar trends. Particles larger than 75μm for station-1, station-2, station-4 and station-5 resulted 26.6%, 38%, 22.3% and 33.4%

less phosphorus content compared to the particles smaller than 45μm, respectively. Researchers had also found the smaller particle sizes to be responsible having higher capacity of containing phosphorus in them. Selig (2003) showed that the highest sediment phosphorus was observed for the sediment fraction 40-63 μm and smaller than 40 μm sizes. Devesa-Rey et al. (2009) found that the particles smaller than 63 μm have the highest phosphorus. The smaller fractions of phosphorus are also representative of the fractions that they are eroded from the soils of the basin and transported as suspended solids (Devesa-Rey et al., 2009).
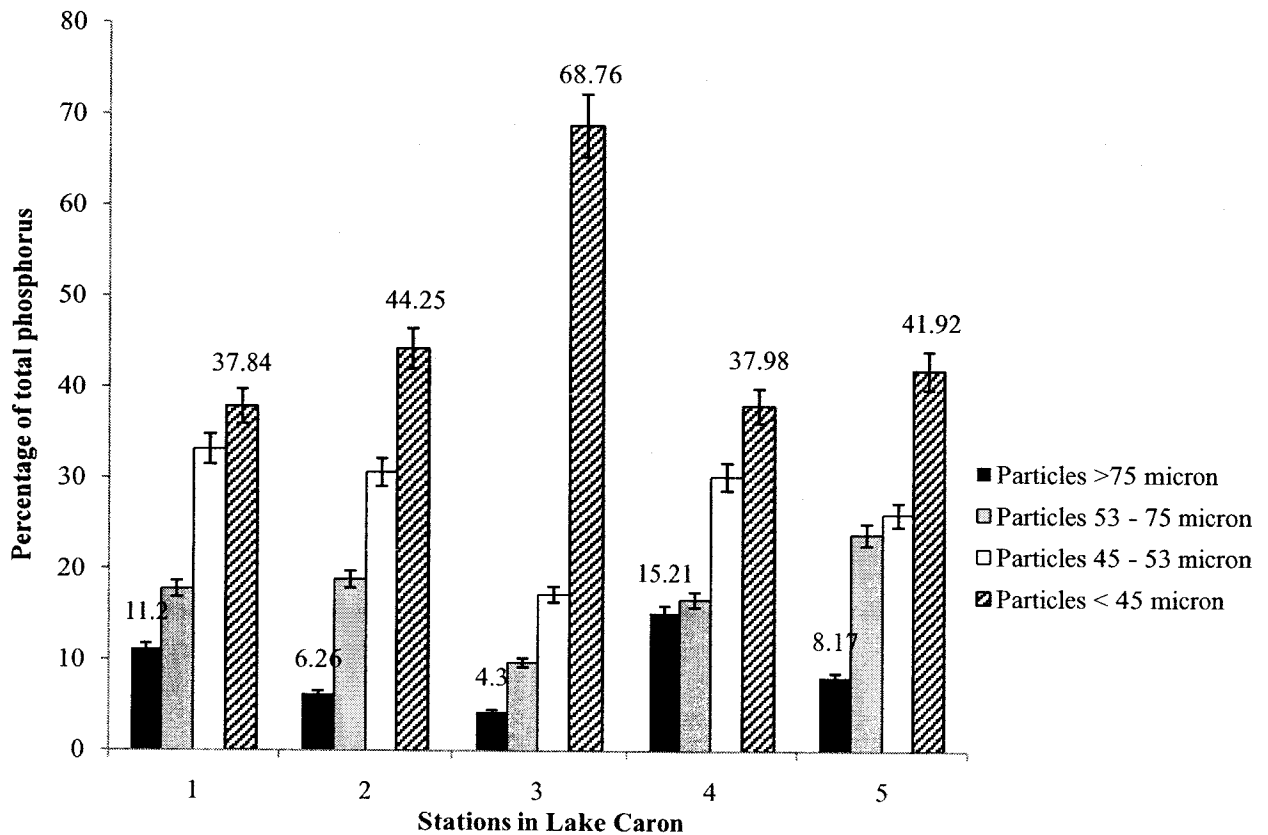

Figure 4-10 Relative contribution of phosphorus by different particle sizes

4.4 Vertical Distribution of Phosphorus in Water Column

Experiments investigating the phosphorus distribution in a water column resulted in an increase with increasing depth. According to the literature review discussed in section 2.5, the hypolimnion exhibits much more phosphorus than the epilimnion. When sediments are anoxic they release phosphorus and since the hypolimnion is cold, not oxygenated well and stagnant, this layer contains most of this released phosphorus.

Figure 4-11 illustrates the vertical distribution of phosphorus in the water column along with increasing depth for station-3 and station-4. The topmost layer has the minimum value of phosphorus (60μg/L and 87μg/L) for both stations. Both resulted in increased values of total phosphorus as the depth of water increased. The deepest height 38cm was right above the sediment bed. We can consider this layer of the water column as hypolimnion. Both sediment samples resulted in highest values of phosphorus in the hypolimnetic zone. In reality, the higher amount of phosphorus is found in the closest water layer to the sediments, which is the hypolimnion (Nürnberg et al., 1987).

When the water body become eutrophic, the sediments might become anoxic, having a lack of oxygen which enhances the release of phosphorus into the water. This phenomenon can result in surprisingly high concentration in the hypolimnetic zone. Lake Caron is a hyper-eutrophic lake, so the sediments might become anoxic thus releasing more phosphorus into the water. For anoxic sediments, oxygen becomes depleted in the hypolimnetic zone. If sediment and water become well mixed, which is resuspension, water quality could be improved by making the sediments aerobic. The resuspension results and analyses are described in the next section (4.5).

Concentration of total Phosphorus in water (μg/L)
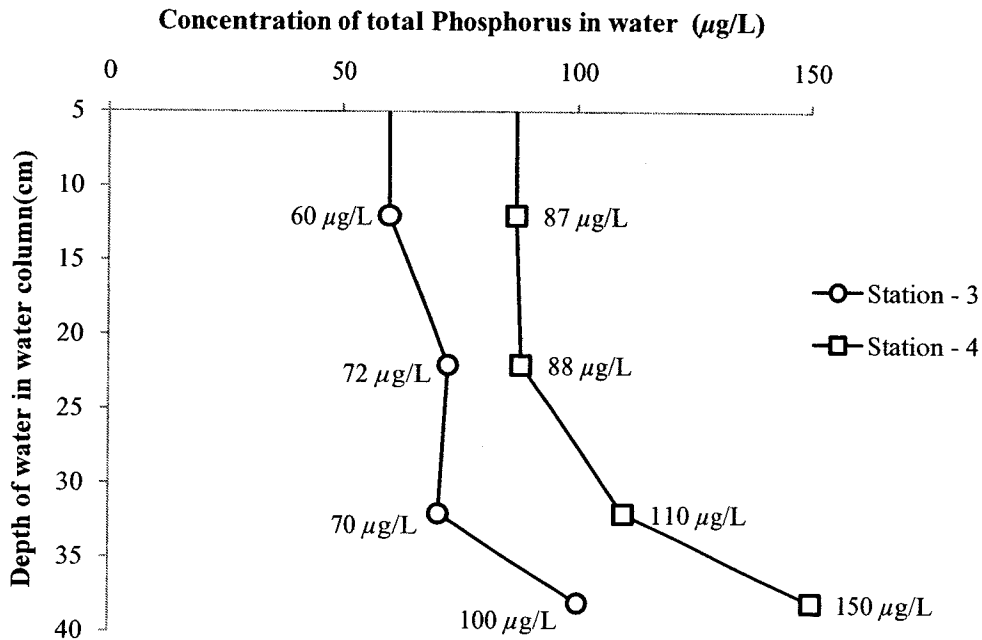
Figure 4-11 Vertical distribution of total phosphorus in water column

Particle size distributions for station-3 were illustrated in Figure 4-12. At different depths (from water column experiment, which were performed in lab), suspended solids with water were collected and particle size were analysed accordingly. The top layer which mimics the epilimnion has the least amount of particulate materials. The bottom most layer mimics the hypolimnion which has the highest amount of phosphorus also has larger particles than others. The middle layers showed similar kinds of particle distributions.

The water column experiment can also be scaled up for Lake Caron. The height of the water column (excluding the height of the sediment bed at the bottom) was 43cm and the average lake depth is 150cm. (dividing 150 by 43 we get the scale factor of 3.5). The concentrations of phosphorus resulted at different depths in the water column can be

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multiplied by scale factor 3.5 to get P distribution at different depths of Lake Caron. Figure 4-13 can be generated from this idea.
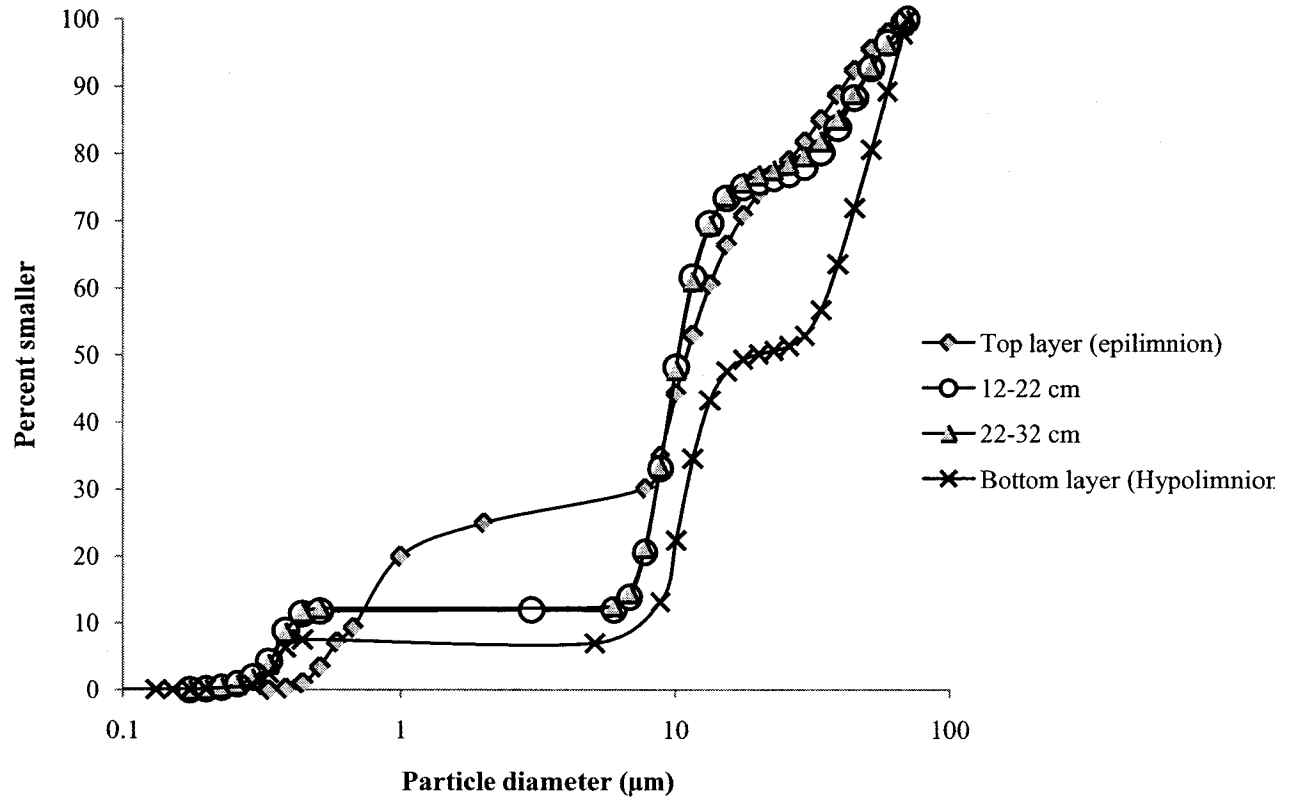
Figure 4-12 Particle size distribution at different layers of the water column
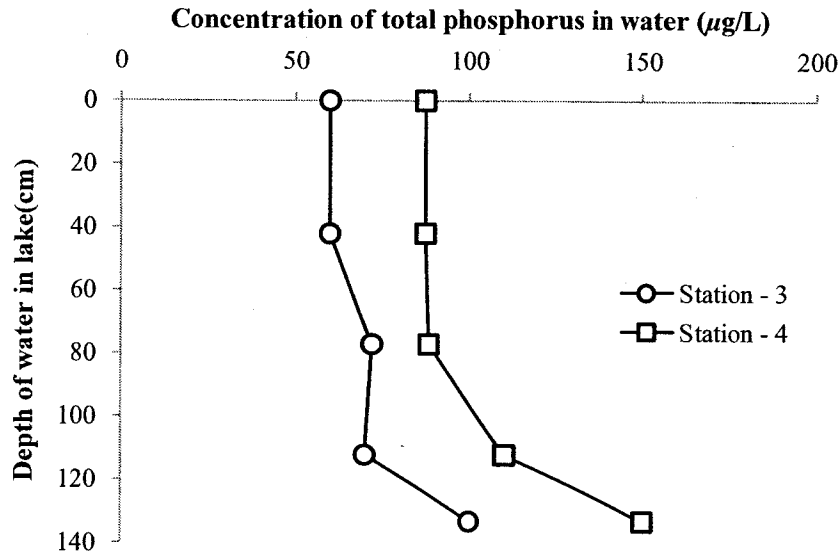
Figure 4-13 Total phosphorus distribution in the water column of Lake Caron by scaling up (scale factor of 3.5)

However, it should be kept in mind that, there are many natural and unpredictable factors inside the lake (such as benthic algae, microorganisms, wave/wind, wind induced resuspension, bioturbation etc.). Due to those factors, the results might not be same.

4.5 Resuspension Experiment

The resuspension experiments which were done in the lab resulted in lower phosphorus values. The initial concentration of phosphorus before resuspension was 900 μg/L. Immediately after resuspension, for both with and without aeration, the phosphorus values were increased. They reached 926μg/L for aeration and 782μg/L for resuspension without aeration. The effects of phosphorus concentration for these two resuspension experiments were fairly close until 5th day (120 hours). After that phosphorus value without aeration started increasing. It increased to 210μg/L from the previous

concentration of phosphorus which was 133μg/L. Therefore, the experiment was stopped and attention was drawn on aeration results.

Figure 4-14 illustrates the time series analysis of aerated and non-aerated sediment samples. For both cases, resuspension resulted in a rapid decrease in phosphorus value within 24 hours. After that, the decrease was quite slow. For non-aerated sediments, the same value was maintained during 3rd, 4th and 5th days (72h, 96h, 120h).

The resuspension experiment successfully improved water quality from the initial condition. The lowest concentration of phosphorus was seen during the 7th day (168h) which was is 30μg/L, and removed 96.7% of the initial phosphorus concentration. The experiment was continued until the 9th day (216h), resulting in a phosphorus concentration of 40 μg/L, and achieving a 95.6% nutrient removal by the resuspension (900 μg/L).
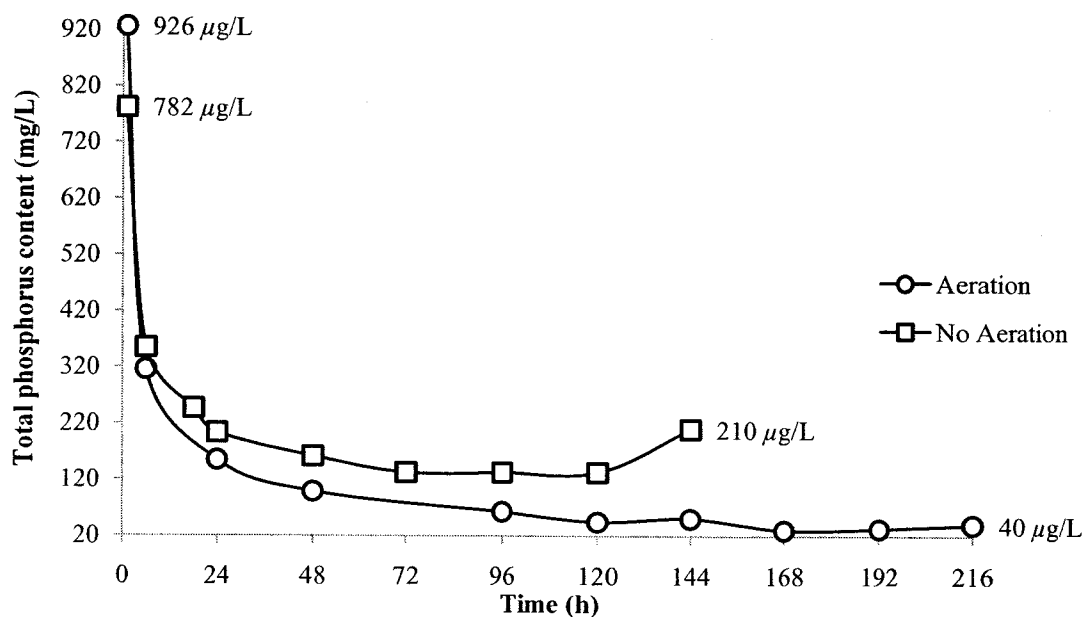
Figure 4-14 Resuspension experiment with and without aeration

When sediments were resuspended, the sediments and water are well mixed inside the water column. Sometimes it redistributes the organic content in the water evenly thereby generating a dilution (Tengberg et al., 2003). Furthermore, it might regenerate iron oxides which adsorb phosphorus (Tengberg et al., 2003). The anoxic sediments might become aerobic which also reduces phosphorus in the water column by formation of iron oxides. Biological respiration may also release phosphorus from organic fractions too (Turner et al., 2005).

The particle size distribution was also measured using a particle size analyser to investigate the sediment particle distribution at specific times. The results of the analysis are illustrated in Figure 4-15.
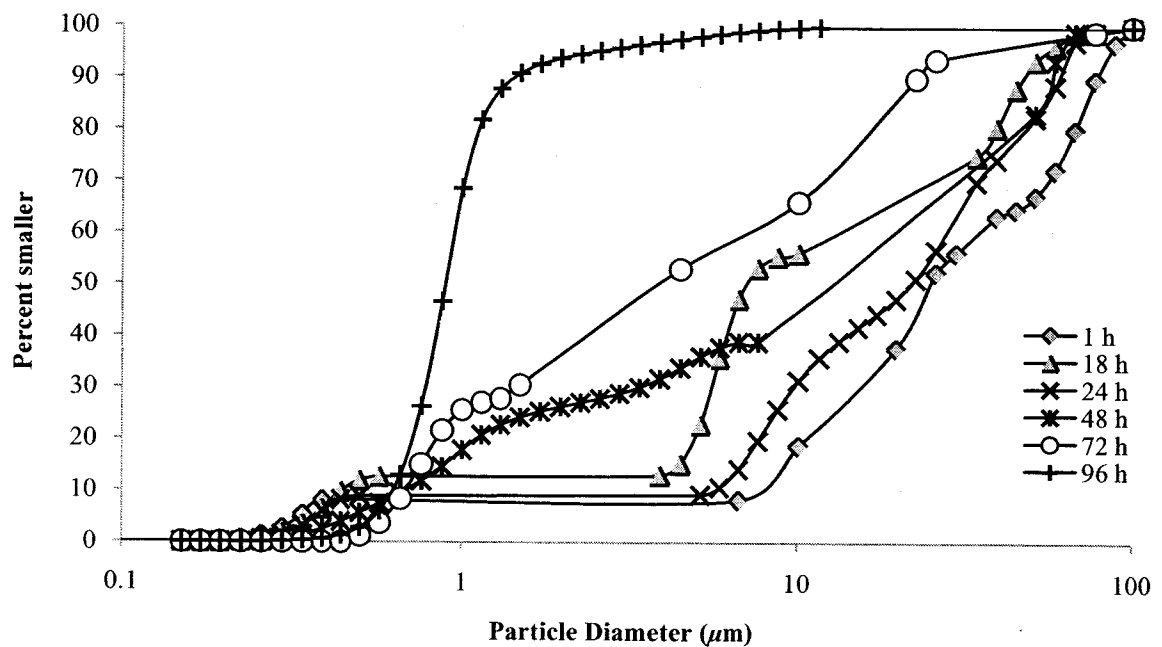
Figure 4-15 Time scale particle size distribution of the resuspended sediments (at the intervals of 1h, 18h, 24h, 48h, 72h and 96h).

Suspended solids were the smaller particles of the sediments which remain suspended even with the slightest disturbance in the water system. From sections 2 and 3 it is known that, these particles usually stay on the top and contain a higher amount of nutrients. Concentrations of suspended solids (SS) and concentration of total phosphorus with progressing time can be illustrated plotting both the concentrations vs. time in Figure 4-16.
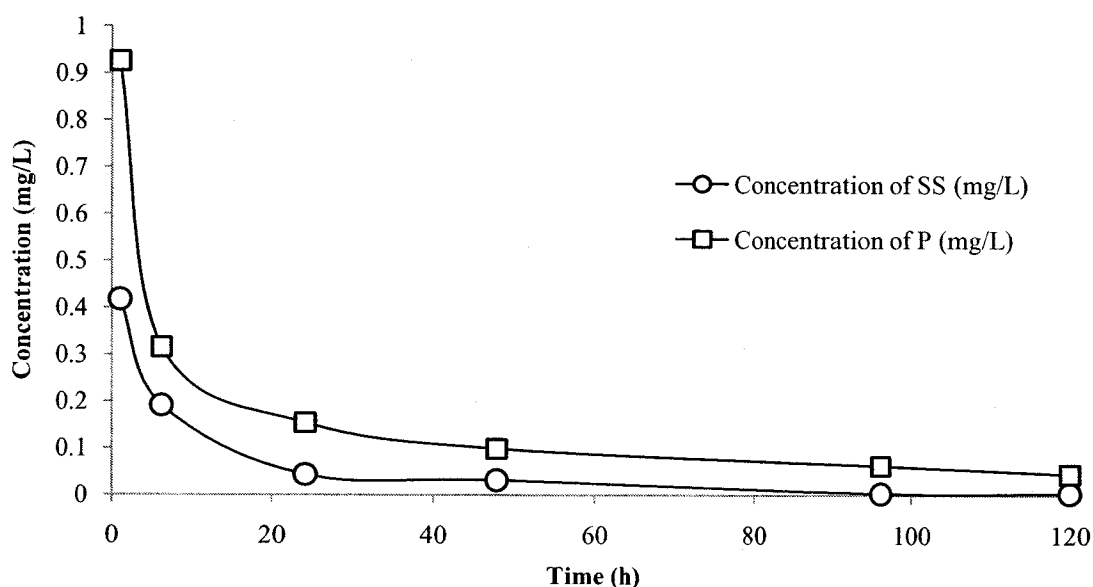
Figure 4-16 Total phosphorus and SS concentration with progressing time after resuspension

To investigate if there is any correlation between the suspended solids concentration and the amount of phosphorus, the concentration of SS was also measured. Figure 4-17 shows they are closely correlated (r^2=0.973).
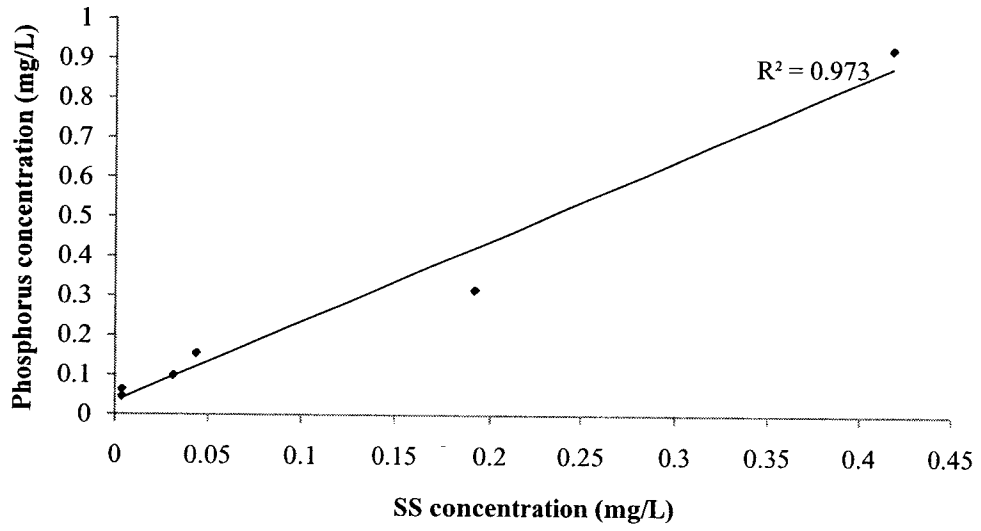
Figure 4-17 Regression analysis showing dependency of total phosphorus on suspended solids concentration in water ($r^2 = 0.973$)

CHAPTER FIVE

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

The results obtained from the resuspension experiment clearly indicated that resuspension technique could be an effective solution for improving lake water quality.

From core sediment analysis it was obvious that the surface sediments were responsible for contributing more phosphorus. Again, total phosphorus determination based on particle size also indicated that smaller particles contained higher amounts of phosphorus compared to the larger ones. Both of these findings lead to the conclusion that smaller surface sediments were the main sources of pollution in Lake Caron.

Since smaller particles remain on the sediment surface, they also remain suspended for a longer time compared to other sediment particles. When the sediments were resuspended these were the particles actually floating long after the resuspension was over. Though resuspension decreased phosphorus, the particles can again release phosphorus in water. The improvement in the lake water quality will be twofold if these particles can be removed, preferably by filtration.

Sediments of Lake Caron might became anoxic or remain anoxic during some season of the year, may be that was the reason why they showed rapid response after resuspension. By resuspension sediments and water become well mixed, preventing further release of phosphorus. Care should be taken so that the lake can be saved before the sediments become hypoxic.

In station-2 and station-3, the amount of the organic phosphorus were very high along with resulting a very low calcium bound phosphorus (Ca-P or HCl-P), which also leads to the conclusion that, in near future, these two stations might become over fertilized which also means abundance of phosphorus. Algal blooms might occur surrounding these stations.

Improving the water quality of Lake Caron might take a longer time than usual. The reason behind this lake's eutrophication is mainly the natural aging process of the lake. Another reason might be that the lake was artificially made. Unlike the cultural eutrophication (Cultural Eutrophication: the eutrophication which results from added effluent discharge into the water such as industrial effluent of agricultural runoff, etc. Sometimes, eutrophication increases fish productivity so, nutrients are added in the water body to make it eutrophic) which can be cured by stopping the effluent discharge, Lake Caron might take a longer time to respond.

5.2 Recommendations for Future Work

The study of resuspension was a lab scale, but can be employed in the case of Lake Caron (multiplying by a scale factor of 3.5). An air-water jet can be used to aerate the sediments and at the same time resuspend the sediments. This technology has already been used in Japan, developed in Tokai University, Japan (Fukue et al., 2006).

Investigation of the water and sediment quality should be monitored from time to time to check if the lake water quality is improving or not. In situ resuspension of the sediments may be feasible.

Since, hypolimnion resulted in higher phosphorus content for water column, research should be done to investigate in real case, because hypolimnetic water removal can reduce phosphorus in water. Nürnberg et al., (1987) had tried withdrawal of hypolimnetic water from eutrophic lakes and were able to reduce the phosphorus level in water.

Research should be done investigating the release or absorbance of phosphorus depending on the oxidation-reduction (E_h) potential. The change in this potential can enhance or reduce phosphorus absorbance which can be a promising technique.

Absorption desorption test with sediments might be performed in the laboratory under anaerobic condition, since sorption test under aerobic condition was already done by Zaghtiti (2008).

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