Adsorption of Phosphorus on Sediments from

Lake Caron and Huron River

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ABSTRACT

Adsorption of Phosphorus on Sediments from

Lake Caron and Huron River

Dima Zaghtiti

Sediments play an important role in the overall equilibrium conditions in eutrophic surface water, which is determined by the nutrient concentration mainly Phosphorus (P). Sorption tests were performed for sediments from Lake Caron and Huron River. By taking the originally sorbed P (S_{θ}) into consideration, the experimental data were fit to the modified Langmuir and Freundlich isotherms. The modified Langmuir isotherm was used to obtain the maximum sorption capacity (S_{max}) as its values varied between 100 to 5000 mg-P/kg. Sediments might act as a source or sink of P. The equilibrium concentration at zero sorption (EPC_0) between the water column and sediments was calculated, for the sediments from Lake Caron showed a wide range from 0.043-0.31 mg-P/L, and the sediments might act as potential source of Pinto the water, except for CS3 which might act as a sink. For the Huron River EPC_0 values are in the range of 0.15-0.18 mg-P/L. The adsorption kinetics were studied and modeled as the power function, and the half life time of P by the sediments was determined. Soluble reactive phosphorus (SRP) concentration changes in the water by resuspension was observed over a period of 4 days. More analysis for SRP changes was performed, to included the effect of sediments to solution ratio, resuspension and the background electrolyte. The effect of particle size fraction on the sorption models for CS3 was evaluated and S_{max} was 5800 mg-P/kg for a particle size less than 38μ m and 910 mg-P/kg for the particle size of 75 μ m -2mm, which indicates the smaller the particles size the more the ability to adsorb P.

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List of Abbreviations

- C : Phosphorus Concentration
- EPC₀: Equilibrium Concentration at Zero Sorption

LOI: Loss on Ignition

P : Phosphorus

SRP : Soluble Reactive Phosphorus

S₀: Originally Adsorbed Phosphorus

S': Phosphorus retained by the solid phase

 $S = S' + S_0$: Total Phosphorus Sorbed

S_{max} : Maximum Sorption Capacity

TP : Total Phosphorus

t : Time

CHAPTER ONE

INTRODUCTION

1.1. Background

The nutrient (phosphorus and nitrogen) levels in surface waters (lakes and rivers) can affect aquatic ecosystems in many ways. One of the most important consequences is the increased growth of the algae and aquatic macrophytes and distinct shifts in species composition. These symptoms are called *eutrophication* (Martin et al., 1992).

Phosphorus (P) has been identified as the limiting nutrient for algal growth in most fresh water systems, and when excessive additions of P enter water bodies, it results in algal blooms (Loehr, 1974). Over two hundred million tons of P is discharged into national surface waters each year (Leedan et al., 1990). In freshwater systems such as rivers and lakes, urban and agricultural runoffs where nutrients have accumulated are generally linked to eutrophication.

These blooms contribute to a wide range of water quality problems, as well as the senescence and decomposition of these organisms. They will also cause nocturnal oxygen consumption by community respiration hence creating a shortage of dissolved oxygen (DO) resulting in fish killing, bad odours, and high turbidity. Furthermore, certain cyanobacteria produce and release toxins that can kill livestock and may pose a serious health threat to humans (Canadian Guidance Framework 2004). Due to these environmental concerns, phosphorus is on the list of priority pollutants for the Canadian Council of Ministers of the Environment (CCME).

1.2. Phosphorus Management in Fresh Water System

To resolve the eutrophication problem, local governments set many regulations to control the quality and quantity of the contaminated influents disposed into the surface water in order to limit the external contamination with P (Martin et al., 1992). After limiting the external sources of P, in situ remediation techniques should be used further to treat the contaminated sediments and water.

The direct precipitation of phosphorus using iron, calcium and aluminum salts forms insoluble compounds (Charboneau, 2008). Chemical precipitants are generally considered non toxic and are a long lasting method; they reduce algal growth by limiting available phosphorus and trapping it as insoluble compounds that settle to the bottom of the lake (Cook et al., 1993; Cook et al., 1993). In addition, further chemical reactions prevent its release from the sediments (Charboneau, 2008).

The use of this method usually has limitations due to the cost factor (Charboneau, 2008), in most cases; treatment with iron or calcium salts may be a better option than treating with aluminum salts, especially in acidic lakes, and lakes with pH higher than 9.0 due to potential aluminum toxicity (Cook et al., 1993).

Fly-ash could be added to eutrophic lakes to control P released from sediments (Cooke, 1980). Fly-ash consists of small airborne particles from coal combustion usually used to treat acid mine drainage to increase the sorption capacity (Agyei et al., 2002). This method is disadvantageous to the environment as it leads to high pH, oxygen depletion, and metal and toxin accumulation (Cooke 1980, Charboneau 2008).

Another type of removal technique is the inhibition of the phosphorus release by in situ capping of the sediments. This technique uses active barriers such as sand, gravel and geotextile materials to isolate sediments from the overlaying water column (Berg et al., 2004, Kim et al., 2008). This method has some limitations due to the cost factors, resuspension during placement, long term erosion, and the deposition of new pollutants on the capped layer which will reinstate the initial problem.

Recently a new economical, environmentally friendly technology was developed at Tokai University, Japan for removal of hazardous materials (heavy metals and nutrients) from water and sediments by filtration. This technique is based on the removal of the suspended solids (SS) from the water column. The contaminants tend to adsorb onto the surface of the suspended solids therefore removing them improves the water quality (Fukue et al., 2006).

By resuspending the sediment particles, the concentration of the SS will increase and the ability of these SS to adsorb the contaminants will increase. This will change the sorption capacity of the sediments. This resuspension can be achieved by using a stirring tank at the bottom of the water body, or stirring by emitting water jets or mechanical disturbing using rotating blades as shown in Figure 1-1.

This study is part of this project to evaluate the sorption of P onto the sediments in order to improve the water and sediments quality and prevent the release of phosphorus from the sediments.



Figure 1-1 Schematic for the total filtration system to improve the water quality using the resuspension technique (adapted from Fukue et al., 2006).

1.3. Objectives

The objectives of this study are to:

- 1. Characterize the sediments from Lake Caron and Huron River;
- Determine P-sorption isotherm parameters for sediments from the proposed water bodies and sorption isotherm for selected sites in regards to the sediment particle size;
- 3. Determine the equilibrium concentration at zero sorption;

- 4. Determine adsorption kinetics, and uptake of P with time (removal time);
- 5. Evaluate changes in soluble reactive phosphorus (SRP) concentration in water after resuspension of sediments;
- 6. Determine the optimal sediment solution ratio for the P sorption for selected sites in order to design the stirring tank.

1.4. Thesis Organisation

This thesis consists of four chapters:

Chapter one: Introduction

Chapter two: Literature Review

Chapter three: Site description, methods and material for sampling and analyzing

Chapter four: Results and discussion

Chapter five: Conclusions and recommendations for further work

References

Appendices

CHAPTER TWO

LITERATURE REVIEW

2.1. Background

Phosphate, nitrogen and silica are generally considered the most critical nutrients for autotrophic production in freshwaters. The principle nutrients are usually nitrogen (N) and phosphorus (P) as they exist in nature at relatively high concentrations (Pierzynski et al., 1994).

Phosphorus (P) is an essential nutrient of life and has no known toxic effects. P is a highly reactive, multivalent, non-metal of the nitrogen group in the periodic table, and is never found free in nature (Segal, 1989). It is usually found in soil, rocks, water body sediments, and in water. Under normal conditions phosphorus in soil, water and sediments appear only in the form of chemical compounds. Usually phosphorus oxidized either ions of inorganic orthophosphate occurs in the state, as (HPO_4^{-2}, H_2PO_4) or inorganic compounds (Reynolds, 1984). From the analytical chemical point of view it is usual to define natural fractions as outlined in Figure 2-1 (Holton et al., 1988). Particulate P can be composed of many minerals, amorphous precipitates, and sorbed reaction products. The following list includes those forms most likely to be environmentally significant. Since much of the sediment in fluvial systems is of pedologic origin, the terminology used to describe these forms of particulate phosphate are consistent for soil and sediment systems:

- Adsorbed, exchangeable P.

- Organic P

- Precipitates; fertilizer, reaction products with Ca, Fe, Al and other cations.
- Crystalline minerals and amorphous P.





Phosphorus in solution is normally considered to be orthophosphate, inorganic polyphosphates, and organic phosphorus compounds dissolved in the water phase. Both inorganic and organic forms of phosphorus are involved in the transformations. The results are the release of water-soluble phosphorus from the solid phase or uptake of dissolved phosphorus by the solid phase. These reactions play major roles in influencing the bioavailability of phosphorus in soil and in determining if eroded soil particles or sediments are contributors of dissolved phosphorus to surface waters or sinks for soluble phosphorus present in stream or lake waters. Complex or condensed phosphates (polyphosphates, metaphosphates) which are mainly man-made for use in detergents, material from water treatments and so on, are discharged with domestic and industrial

wastewaters. These condensed phosphates are also generated by all living organisms. They are unstable in water, where they are slowly hydrolysed to the orthophosphate (Holton et al., 1988). In most surface waters such as lakes, rivers and ponds, the growth of algae or aquatic plants is controlled by the levels of P. The increase in the P levels will lead to an increase in the aquatic biomass usually referred to as eutrophication (Jarvie et al., 2005).

According to the Canadian framework for phosphorus management in surface water, the concentration of P in the water determines the trophic status of the water body as shown in Table 2-1. This table shows the total phosphorus (TP) concentration and the eutrophic status.

 Table 2-1 Total phosphorus trigger ranges for Canadian lakes and rivers (Environment Canada, 2004)

Trophic Status	Canadian Trigger Ranges of Total Phosphorus (µg/L)	
	Lakes	Rivers
Ultra-oligotrophic	<4	-
Oligotrophic	4-10	<25
Mesotrophic	10-20	25-75
Meso-eutophic	20-35	-
Eutrophic	35-100	>75
Hyper-eutrophic	>100	· · · · · · · · · · · · · · · · · · ·

Typically, rivers can sustain higher loads of phosphorus than lakes without observable changes in community composition and biomass as phosphorus is often flushed from the system before it can be utilized (Jarvie et al., 2005). Usually the inorganic phosphorus is considered the most available phosphorus form to the aquatic plants and animals and is often considered the most critical P-fraction contributor to eutrophication.

Soluble Reactive Phosphorus SRP This phosphorus fraction should consist largely of the inorganic orthophosphate form of phosphorus.

Orthophosphate PO₄ is the phosphorus form that is directly taken up by algae (Pierzynski et al., 1994). The concentration of this fraction constitutes an index of the amount of phosphorus immediately available for algal growth. Measurement of SRP can be used as an indicator, albeit a potentially inaccurate one, of the degree of phosphorus limitation of the algae. At one time SRP was called "dissolved inorganic phosphorus." This terminology was changed to "soluble reactive phosphorus" (Rigler et al., 1964) to reflect a more realistic interpretation of what forms of phosphorus were found in this fraction. The terms "soluble" and "reactive" were chosen instead because this form of filtered phosphorus was neither necessarily dissolved nor necessarily inorganic. The term "reactive" is used to indicate that the phosphorus in the SRP fraction is not solely inorganic phosphorus, but could include any form of phosphorus, including some organic forms, that react with the reagents (Rigler et al., 1964). Typically, a 0.45 micron cellulose (Millipore) filter is used. This filter excludes most particulates, but colloidal phosphorus may be present in the filtered fraction. Some analytical protocols use glass fiber filters instead of a membrane filter. Using a glass filter increases the amount of particulate material that passes through the filter and therefore increases the amount in the "soluble"

fraction. Small particulates, including very small algae and bacteria will be present in the filtered sample. Whether or not they become represented as SRP will depend on the extent that they react with the reagents (Holton et al., 1988).

Suspended Solids (SS) are organic matter, fine particles, plankton and other materials which adsorb bacteria, heavy metals, nutrients and other hazardous substances (Fukue et al., 2006).

Sediments by definition are materials that have accumulated by deposition in water. Some of the sediments particles were suspended solids. Virtually all sediments are composed of variable quantities of organic matter, mineral grains, rock fragments, and carbonates and other precipitates, such as oxides of iron, magnesium and aluminum. When the SS and sediments settle, they form the sediments layer at the bottom of the water body and they accumulate the contaminants. These contaminated sediments are toxic for the aquatic life and for humans (Fukue et al., 2006).

Generally, sediments that enter a lake or reservoir are derived from rivers, shoreline erosion, sub-aqueous erosion and atmospheric deposition. Rivers are normally the most significant source of sediment to a lake (Pierzynski et al., 1994). Bank erosion may be accelerated in non-protected regions and animal access to the waterway may result in increased bank erosion and direct addition of animal wastes and pathogens. Urbanization of watershed results in a reduction of the land surface area available for infiltration of rain and surface water leading to increased runoff and river flow. Therefore the river level responds to precipitation. In most river systems, the largest percentage of the total sediment delivered to a lake or reservoir occurs in a small number of storms (United Nations Environment Program, 2005).

The physical and chemical characteristics of the river sediments reflect the geologic and geomorphologic composition of its watershed (Cooke et al., 1993). Modification of the land surface by man due to deforestation, intensive agriculture and animal husbandry has a large impact resulting in the exposure of bare soil susceptible to erosion by both air and water, and extra loads of soil into rivers.

Soil particles from the atmosphere are of fine-grain size and may have high concentrations of organic carbon, phosphorus, nitrogen and organic micro-pollutants derived from herbicides and pesticides used for both fertilizing and pest control in agriculture. These airborne deposits are major sources of nutrients to remote lakes with little urbanization, and also account for the build up of pollutants in remote parts of the globe.

The size of sediment's particles is the most important property in understanding of sediment-water interactions leading to eutrophication of lakes and reservoirs. Most commonly used particle size fractions for characterization of sediments are as follows and shown in Figure 2.2:

- 1. Clay-size fraction, which contains particles smaller than $2 \mu m$;
- 2. Silt-size fraction, which contains particles of size between 2 µm and 63 µm;
- Sand-size fraction, which contains particles of size between 63 μm and 2.00 mm, and;
- 4. Gravel-size fraction, which contains particles larger than 2.00 mm.

The most important particle size fraction in eutrophication is the clay-size fraction (Stone et al., 1989), which consists mainly of organic matter and clay minerals (such as; hydrous aluminum, phyllosilicates, sometimes with variable amounts of iron, magnesium, alkali metals, alkaline earths and other cations). Some clay minerals are usually present in the silt-size fraction. Under specific conditions in lakes and reservoirs, iron and manganese precipitate on the surface of clay mineral particles usually as oxyhydroxides. This phenomenon generates a coating on the particles. Coating of fine-grained particles with organic matter is also common. The coatings provide a highly active physicochemical site for both adsorption and desorption of phosphorus and a wide range of trace metals and organic pollutants of low solubility. Iron oxyhydroxide coating is most important due to its capacity to adsorb phosphorus (Carter et al., 1993).



Figure 2-2 Textural triangles (adapted from Carter et al., 1993)

2.2. Sources of Phosphorus in the Aquatic Environment

Phosphorus enters the fresh surface water from many sources and in different forms. Figure 2.3 gives a quick view over the source and transport of P in nature. Phosphorus sources can be classified into two major groups:

External Loading : can be divided into two sources:

- Point source (direct input): including sewage treatment plant and industrial discharges.
- Non-point sources (such as storm water, agriculture and urban runoff, air deposition of fine particles, river bank erosion, hydromodification and wetlands).



Figure 2-3 Sources and fate of P in nature (adapted from Pierzynski et al., 1994)

Non-point sources such as agricultural and urban runoff are considered the main contributors to the phosphorus into the water bodies, especially after reducing or limiting the discharges of the point source loadings directly into the water without treatment and nutrient removal. Fertilizers used in agricultural activities in the watershed of the water body contributed in the past to the large amounts of phosphorus entering the aquatic system either from the surface runoff directly or after leaching into the ground water and then to the surface water (Baker 1992). Figure 2-4 shows the external sources of phosphorus into surface water.





Lately, the effect of the fertilizers as a source of nutrients was regulated or limited by the local governments to improve the environment quality. They have introduced a new concept, Nutrient Management Plans (NMPs), in some parts of Canada (Environment Canada, 2008), which consider issues such as; method and timing of nutrient application, and other considerations including the carry-over of nutrients and the distance to waterways. The rates of loading vary according to the land usage, urban activities, soil productivity, and other factors.

Internal Loading: Sediments play an important role in the phosphorus cycle. It may act as a source or as a sink (Bostrom et al., 1988). Usually the sediments act as a sink for the phosphorus during low loading periods. Unless the mass balance changes, sediments will act as a source for the phosphorus (during the recovery period after the external loading is limited). This is called internal loading (Petterson, 1998).

The loading rates of phosphorus vary according to the morphology of the water body, the equilibrium conditions, and the sediments ability to release or adsorb the phosphorus.

Environment Canada defined the TP concentration in sediments as [refer to Appendix (A-1)]:

LEL (lowest effect level) = 600 mg-P/kg

SEL (severe effect level) = 2000 mg-P/kg

The release of phosphorus is controlled by many factors, for example, the anoxic conditions, the microbial activities, and the specification of each water body such as: dry weight, organic content, the content of elements (iron, aluminum, manganese, calcium,

clay) and other elements with the capacity to bind and release phosphorus. All of the above may influence the water-sediments interaction (Pettersson, 1998). Sediments accumulate and desorb nutrients. Organic matter produced by algae in the lake settles to the sediment and decomposes by aerobic or anaerobic processes during which different carbon, nitrogen and phosphorus compounds are produced (Nurnberg, 1978). Further, decomposing organic matter affects changes in oxygen concentrations and redox potential and can generate anoxic conditions at the sediment-water interface. This in turn affects nitrogen and phosphorus release from the sediments to the overlying water. One of the most important processes, which occur under anoxic conditions, is the solubilization of iron and manganese oxyhydroxide coatings on fine-grained sediment particles. Under anoxic conditions, non-soluble trivalent iron and tetravalent manganese change to soluble divalent iron and manganese, with substantial release of adsorbed or co-precipitated elements and compounds, particularly phosphorus (Jensen et al., 1992). In lakes where the external loading has been reduced, the internal phosphorus loading may prevent improvement in the lake water quality especially during summer concentration rise.

The total quantity of phosphorus in a lake or other surface water body is controlled by the balance between the inputs from the external sources of P, and the outputs as water drains from lakes into rivers, streams, or other water courses. A net increase in P will increase eutrophication; however, the cycling of P between soluble, organic, and sediment bonds phosphorus form within the lake and regulates the bioavailability of P, thus the extent of eutrophication. Figure 2.5 shows the phosphorus cycle in water and sediments.



Figure 2-5 Phosphorus cycle (Adapted from Wikipedia, the free encyclopedia)

The net retention of the phosphorus is the difference between two processes (Sondergaard et al., 2003):

- The down-ward flux caused mainly by the sedimentation of the particles continuously entering the lake or produced in the water column (algae, detritus, etc...) and;
- The up-ward flux or gross release of phosphorus driven by the decomposition of organic matter and phosphorus gradients and transport mechanisms established in the sediments.

2.3. Phosphorus Retention and Distribution in Sediments

Bostrom et al. (1988) discussed the exchange of phosphorus (P) in lakes across the sediments-water interface; they recognized six major transfer mechanisms in regards to the deposition of phosphorus in lake sediments:

- Sedimentation of the detrital phosphorus minerals derived from the watershed; a large portion of this fraction consists of rapidly settling material, and deposition occurs mainly near the shore area.
- 2. Adsorption (to clays and amorphous oxyhydroxides) or precipitation of phosphorus (with iron and manganese).
- 3. Sedimentation of phosphorus with allochtonous (rocks, deposits, etc. found in a place other than where these allochtonous and their constituents were formed) or organic matter.
- 4. Sedimentation of phosphorus with autochtonous (rocks, deposits, etc.; found where these autochtonous and their constituents were formed) or organic matter.
- 5. Direct uptake by assimilation of phosphorus from the water by periphyton (a complex mixture of algae, cyanobacteria, heterotrophic microbes, and detritus that is attached to submerged surfaces in most aquatic ecosystems) and other biota in surficial sediments.
- 6. Direct adsorption of dissolved phosphorus in lake water onto sediment particles.

After the reduction of the external loads, the lakes start to respond to this reduction but it requires a period of time to equilibrate with the new loading rates. In order to understand the eutrophication in lakes, and how to reverse it, the mechanism of exchange should be well understood.

Figure 2-6 shows the changes of phosphorus fluxes due to the seasonal variations in the lake. During the winter and early spring, the external loads are high especially from

surface runoffs during and after storms. In consequence, the sediments accumulate the phosphorus by sedimentation since the biological activities and consumption of phosphorus by the aquatic life is minimal. This is due to the stratification of the lake which leads to anoxic conditions and low temperatures at the interface layer between the sediments and water.

The critical time for P impact in rivers is during the spring/summer low flows when eutrophication risk is greater. Under low flow conditions, the contact time between the water and the bed sediments is relatively high and the sediments surface area to water volume ratio is extreme (Jarvie et al., 2004). At this critical time, diffused associated P sources of sediments stored on the river bed may potentially release SRP, the main dissolved bioavailable form of P. The sediments also act as a net source of P into the water (Jenson and Anderson, 1992). In late summer, the external loads are reduced but the sedimentation of the phosphorus will increase after the death of the periphyton which will settle. Some precipitated inorganic forms (Fe and Al oxides) will settle and accumulate at the bottom of the lake. In most well mixed lakes, the redistribution of P (released and settled) is mostly controlled by temperature changes.



Figure 2- 6 Changes of P fluxes due to seasonal variation in a lake (adapted from Canadian guidance framework for the management of phosphorus in fresh water, 2004).

In rivers, P enters from diffuses catchment sources particularly agricultural and point effluent sources. However, the system has an important internal capacity to remove or release P from/to the water column and to transform P forms (Jarvie et al., 2004) [Figure

2-5]. This occurs due to physical, chemical, and biological processes. The transfer mechanism of P in rivers is not different than what happens in the lakes except for the contact time between the sediments and the water which is relatively low due to the flow pattern in the rivers.

2.4. Theory

Natural attenuation is the use of the natural processes to reduce the concentration of the contaminants in the contaminated sites (soil or aquifer) without interference of manmade recovery processes (Mulligan and Yong, 2004). These natural processes involve degradation of contaminants into non- or less toxic pollutants, or complete removal by biological activities, dilution, dispersion, radioactive decay, and adsorption onto the surface of the soil minerals and organic matter. All these lead to remediation of the contaminated sites.

Adsorption is, in general, a process that occurs when a gas or liquid solute accumulates on the surface of a solid or a liquid (adsorbent), forming a film of molecules or atoms (the adsorbate). It is different from absorption, where a substance diffuses into a liquid or solid to form a solution. The term **sorption** encompasses both processes (adsorption and absorption), while **desorption** is the reverse process i.e. the release of the adsorbate from the adsorbent (Cussler, 1997).

Mulligan and Yong (2004) have identified several mechanisms involving the sorption of contaminants onto the surface of the solid phase:

- Ion exchange reactions: ion exchange is a reversible chemical reaction wherein an ion (an atom or molecule that has lost or gained an electron and thus acquired an electrical charge) from solution is exchanged for a similarly charged ion attached to an immobile solid particle (Helfferich, 1995).
- 2. Electrostatic interactions of charged molecules with charged sites on the surface (also known as physisorption): Van der Waals electro-static forces which is the attractive or repulsive force between molecules or between parts of the same molecule other than those due to covalent bonds or to the electrostatic interaction of ions with one another or with neutral molecules (Segal, 1989).
- 3. Chemisorption: adsorption in which the forces involved are valence forces of the same kind as those operating in the formation of chemical compounds due to the surface reactions. Chemisorption usually is very slow (Mulligan and Yong, 2004).

2.4.1. P Adsorption

P adsorption is a term that is used to describe any process in which phosphate ions in solution react with atoms on the surface of soil or sediments (Holtan 1988, Barrow 1978). In other words, adsorption refers to the removal of ionic P ($H_2PO_4^{-}$, HPO_4^{-2} , PO_4^{-3}) from a solution by the sediments (Pierzynski et al., 1994; Holtan, 1988). Sediments with different characteristics and different conditions might have different P sorption profiles. In general, sediments that are low in P, acidic, and high in clay or Fe and Al oxides have

the greatest P adsorption capacities. On the other hand, high sandy content sediments tend to desorb P (Pierzynski et al., 1994).

The main concept about sorption or in other words, the sorption mechanism is, when the sediments contact with the water, P will be exchanged until the equilibrium is reached (Zhou et al., 2005). This property is usually measured by shaking samples of the sediments with phosphate solution, measuring the change in phosphate concentration in the solution and calculating the phosphate adsorbed. The information is then summarized by plotting the adsorbed P versus the equilibrium concentration of P. This plot is known as Quantity to Intensity Q/I (Barrow 1978). Several factors may affect the adsorption of P (Zhou et al., 2005, Zhou et al., 2001; Barrow, 1978):

1) the method of shaking,

2) soil or sediment solution ratio,

3) temperature changes,

4) pH, oxidation-redox potential ORP,

5) soil mineral's ability to retain or release P,

6) and supporting electrolyte used.

2.4.2. P Desorption

P desorption refers to the release of P from the sediments when the sediment-bound P interacts with water at very low P concentration. Usually this case happens when the
sediments or soil is placed in a free or very low P concentration, the soil or sediments tends to release some P from its surface. Eutrophication problems are related to the P desorption (SRP release from sediments the bioavailable form of P that leads to eutrophication).

The adsorption isotherm is the mathematical formula to describe the Q/I plots, which relate to the amount of P retained by the solid phase, to the equilibrium concentration in a solution at equilibrium, when the adsorption depends only on the temperature and concentration. When the temperature is constant, the relation between the adsorption and the concentration can fully describe the system (Barrow, 1978).

2.5. Adsorption Isotherms Types and Parameters

An adsorption isotherm is a curve that relates the concentration of a solute on the surface of an adsorbent, to the concentration of the solute in a liquid with which it is in contact. Sorption experiments are all based on the validity of the fundamental equation:

S = f(C)

where S is the quantity of sorbed phosphorus and C is the concentration of phosphorus in solution (Holtan, 1988).

There are basically two well established types of adsorption isotherm, the Freundlich adsorption isotherm of 1894 and the Langmuir adsorption isotherm of 1914. The Langmuir adsorption isotherm describes quantitatively the build up of a layer of molecules on an adsorbent surface as a function of the concentration of the adsorbed

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material in the liquid in which it is in contact. The shape of the isotherm (assuming the (x) axis represents the concentration of adsorbing material (P) in the contacting liquid (water)) is a gradual positive curve that flattens to a constant value. The Freundlich isotherm curve is the opposite and is exponential in form. It often represents an initial surface adsorption followed by a condensation effect resulting from extremely strong adsorbent-solute interaction (Cussler, 1997).

The experimental data generally fit relatively well with the sorption equations for narrow concentration ranges. To cover wider concentration ranges efforts have been made to improve the sorption equations by expanding them with new variables and constants. Some researchers have tried to explain the nature of the sorption mechanisms by interpretation of the sorption equations, but others have been very critical of these attempts. Because of assumptions made in the equation derivations, the 'goodness-of-fit' does not necessarily correspond to 'correctness' of the equation (Holtan, 1988).

2.5.1. Langmuir Isotherm

In 1916, Irvin Langmuir introduced an isotherm for describing the adsorption (in general) based on the four following assumptions (Cussler, 1997):

- 1. The surface of the adsorbent is uniform, that is, all the adsorption sites are equivalent.
- 2. Adsorbed molecules do not interact.
- 3. All adsorption occurs through the same mechanism.

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4. At the maximum adsorption, only a monolayer is formed: molecules of adsorbate do not deposit on other, already adsorbed, molecules of adsorbate, only on the free surface of the adsorbent.

The linearity of the adsorption isotherm is, however, limited to a certain low concentration range. At higher concentrations, the adsorption isotherm becomes non-linear and often has a convex (downward) shape. It is customary to describe this non-linearity with a Langmuir adsorption isotherm.

The non-linear Langmuir equation:

$$S = \frac{CkS_{\max}}{1+Ck} \tag{1}$$

And the linearized Langmuir equation is:

$$\frac{C}{S} = \frac{1}{kS_{\max}} + \frac{C}{S_{\max}}$$
(2)

$$\frac{1}{S} = \frac{1}{kS_{\max}C} + \frac{1}{S_{\max}}$$
 (2*)



Figure 2-7 Langmuir adsorption isotherm

Where:

 $S = S' + S_0$, the total amount of P retained, mg/kg,

S' = P retained by the solid phase, mg/kg,

 $S_0 = P$ originally sorbed on the solid phase, mg/kg,

C = Concentration of P after 24 h equilibrium, mg/L,

 $S_{max} = P$ sorption maximum mg/kg,

k = Constant related to the bonding energy, L/mg P.

"Bond energy is the energy required to break a covalent bond homolytically (into neutral fragments generating two free radicals, that is, two electrons that are involved in the bond are distributed one by one to the two species)" (Segal, 1989).

2.5.2. Freundlich Isotherm

This isotherm gives more explanation about the adsorption than the Langmuir. The main assumptions are (Cussler, 1997):

1. There are infinite sites for adsorption.

2. Most favourable sites are filled first.

3. Free energy of adsorption decreases.

The Freundlich equation:

$S = KC^{n}$ (3)

When $n \neq 1$; qualitatively, it can be said that the extent of adsorption S does not increase rapidly with the increase in concentration C, as shown in Figure 2-8.

The Freundlich equation can be transformed into a linear form by taking the logarithms on both sides of the equation (3).

The linear formula is:

$$Log S = Log K + n Log C$$
(4)

Where:

S and C as defined earlier in the Langmuir isotherm;

K is the adsorption constant, expressed as mg P/kg;

n is a constant expressed as L/kg.

K and n are empirical constants that vary according to the sediment properties.



Figure 2-8 Freundlich adsorption isotherms

2.5.3. Originally adsorbed P (S_o)

Referred to also as the previously adsorbed P, this case can be noticed when the adsorption test is performed while the initial P solution concentration is zero or very low. The soil or sediments tend to release or desorb P into the solution and after the equilibrium; detectable amounts of P can be measured in the solution higher than initially (Fuleky et al., 2007).

Adsorption data should be corrected for the S_0 before fitting the Langmuir or the Freundlich isotherm (Nair et al., 1984). The procedure for calculating S_0 using the least square fit method is based on the linear relation between S and C at low equilibrium P concentration (Villando 1997; Zhou et al., 2001). The relation can be described by:

$$S' = K'C - S_0$$
 (5)

Where K' is the linear adsorption coefficient and all the other parameters are as defined earlier. (It is recommended that the linear portion of the isotherm has an r^2 value of 0.95 or better).

Therefore, after considering the originally sorbed P, the modified Langmuir adsorption isotherm is:

$$S' = \frac{CkS_{\max}}{1+Ck} - S_0 \tag{6}$$

And the modified Freundlich adsorption isotherm:

$$S' = KC^{n} - S_{0}$$
(7)

2.5.4. Maximum Sorption Capacity S_{max}

The Langmuir isotherm defines maximum sorption capacity S_{max} which is the solid phase's (soil or sediment) P retention ability (Cucarella et al., 2007). It is also the start of the saturation condition (Zhou et al., 2005). S_{max} is closely related to the sediment composition (clay minerals and iron, aluminum, and calcium content). Phosphate adsorption is a linear process when phosphate concentration in the overlying water is at a lower level than in the sediments. The slope of the Langmuir adsorption isotherm equation represents the adsorption efficiency of phosphate onto sediments (Liu et al., 2002). From the linearized Langmuir plot using Eq (2*); [1/ S_{max}] is the intercept and [1/ S_{max} k] is the slope.

2.5.5. Equilibrium Concentration at Zero Sorption EPCo

The "Equilibrium P Concentration at Zero Sorption" (EPC_o) represents the P concentration maintained in a solution by the solid phase (soil or sediments) when the rates of P sorption and desorption are the same (Pierzynski et al., 1994). Jarvie et al. (2005) explained EPC_o as the concentration of the SRP which, when placed in contact with the sediment, produces no changes in SRP in solution over a 24 h period.

The usefulness of the EPC_o is that it gives the information on whether sediments release or extract SRP when placed in contact with water (Zhao et al., 2005; Jarvie et al., 2005). When the EPC_o > SRP in water, the sediments release SRP to the water column. When $EPC_o < SRP$, the sediments will take up the SRP from the water. If the EPC_o is close to the SRP from the water column, the bed sediments and the water is approximately in equilibrium. Values for EPC_o can be determined graphically from the linear isotherm plots of P sorbed vs. P in solution at equilibrium. Using Eq. (5), EPC_o is the value of C when S' = 0. EPC_o values are controlled by the contact time between the boundary layer and sediment, and the mixing time and pattern.

Jarvie et al. (2005) showed that EPC_o values are correlated to the SRP concentration in the overlaying water. River bed sediments that have a high TP have a higher SRP fraction concentration available for exchanging between water and sediments. The equilibrium conditions will be affected by the SRP concentration values, so the higher the SRP in the water column is, the higher the EPC_o will be. Their results also showed that sediments with low EPC_o concentration have a higher affinity to uptake SRP. In other words, these sediments have a higher affinity to adsorb P at low EPC_o values.



Figure 2-9 Sorption parameters and EPC_o (adapted from Zhou et al., 2005)

2.6. Adsorption kinetics

Adsorption kinetics is a term used to describe the removal rate of P, in other wards, the half-life of uptake on the soil or sediments particles when they interact with a solution containing P (Zhou et al., 2005). Different functions are used to describe these kinetics such as the power function or the simple Elovich model and the parabolic diffusion model (Jin et al., 2005). In this research, the power function modeling will be used to describe the adsorption kinetics since the other two models need special software for calculation.

The power function model is described by the general formula:

$$\mathbf{y} = \mathbf{a} \ \mathbf{x}^{\mathbf{b}} \tag{8}$$

Or in other words, to describe the amount of P sorbed in regards to time

 $S = a \cdot t^{b}$ (9)

Where,

S = P sorbed (mg-P/kg)

T = time(h)

a and b are the adsorption constants can be obtained from the following formula:

Log S = Log a + b Log t(10)

From the linear fit using the Eq (10), and the least squares method, the value of the power function constants (a) and (b) can be obtained.

In general, certain chemical processes such as adsorption or radio active decay, are described by first-order kinetics. In the absence of any other chemicals, first order decay

may lead to exponential decay or first order decay of the chemical concentration (i.e., the concentration of the parent compound decreases exponentially with time) (Hemond et al., 2000):

$$-\frac{d[C_t]}{dt} = k[C]$$
(11)

Where; t the time

C concentration of the chemical at time t

k is the first order rate constant, which has units of 1/time.

The integrated first-order rate law is:

$$Ln[C_t] = -kt + Ln[C_0]$$
(12)

$$C_t = C_0 e^{-kt} \tag{13}$$

 C_0 the initial concentration of P in the solution.

A plot of Ln [C] vs. time t gives a straight line with a slope of -k.

The half life of a first-order reaction is independent of the starting concentration and is given by the following formula:

$$t_{1/2} = \frac{\ln(2)}{k}$$
(14)

2.7. Effect of Environmental Factors on P Sorption

Many factors might affect the sorption of P onto the sediments surface such as pH, ORP, temperature, sediments composition. Nair et al. (1984) noted from laboratory work that P sorption varies with:

1. soil/solution ratio,

2. ionic strength and cation species of the supporting electrolyte,

3. time of equilibration,

4. range of initial P concentration,

5. volume of soil (sediments) suspension to head space volume in the equilibration tube,

6. rate and type of shaking, and

7. method of separating liquid from solution after equilibration.

2.7.1. Effect of pH

It is found that P adsorption is determined by the surface charge and the protonation state in the bulk solution (Zhou et al., 2005). Laboratory studies on sediments from eutrophic lakes show that P sorption varies with pH changes. Zhou et al. (2005) found that the most preferable form of P to be sorbed is $H_2 PO_4^-$ for the pH range of 2-8, but in the range of pH of 1-2 the originally sorbed P will be released. On the other hand, studies for SRP concentration changes with pH by Jenson et al. (1992) from disturbed sediments by resuspension show that SRP will increase with an increase of pH.

2.7.2. Effect of ORP

The reduction potential (also known as redox potential, oxidation / reduction potential or ORP) is the tendency of a chemical species (Fe^{3+} , Mg^{2+}) to acquire electrons and thereby their charges will be reduced. Each cation has its own intrinsic reduction potential; the more positive the potential, the greater the species' affinity for electrons and tendency to be reduced.

Lake sediments contain much higher phosphorus levels than water. Under aerobic conditions, inorganic exchange at the sediments- water interface is strongly influenced by redox conditions (Wetzel, 2001). According to that, ORP is one of the most important parameter to describe the P adsorption onto the iron minerals in sediments. The iron-bound-phosphorus or magnesium is very sensitive to ORP changes (Zhou et al., 2005), When ORP is very high which in turn produces high P adsorption affinity onto Fe^{3+} , Mg^{2+} (Jenson et al., 1992).

2.7.3. Effect of Sediment Composition

Sediment composition is usually referred to the organic and mineral (iron and aluminum...) content. These components are related to the morphology and chemistry of the water body. Researchers have concluded that sediment composition was more

significant on P sorption than the pH on natural sediments (Zhou et al., 2005). The higher the concentration of Fe^{3+} , Mg^{2+} , Al^{3+} , the higher the intensity of the sediment for sorption, due to the positive discharge on the surface of the sediments particles. Jensen et al. (1992) found that release of SRP from sediments into the water column is also controlled by the Fe: P ratio. This ratio indicates the free sorption sites for P sorption in the sediments. It also indicates an inverse relation between sediment Fe: P ratio and sediment P release.

Another reason for the difference in sediments adsorption-desorption could be the organic content. Fukue et al. (2006) considered the organic matter as an important adsorbent in the aquatic system. Sediments from wetlands which have relatively high values of organic content are more capable of adsorbing dissolved P from solution at equilibrium after 24h. For other samples with less organic content to adsorb the same amount of dissolved P, the sediments need more time (Schwemm et al., 2004).

2.7.4. Effect of Temperature

Experiments show that the impact of temperature affects P sorption on natural sediments from lakes and river (Mamo et al., 2005). Liu et al (2002) found by experimental simulation on sediments from Yangtze Estuary, China, that P adsorption increases linearly with the rise of temperature, because the rise of the temperature enhances the ionic exchange on the sediments-water interface layer. In the nature, the release rates of SRP increases with temperature rise during hot summer days due to the increase of the biological reactions, especially under aerobic and anoxic conditions (Jensen et al., 1992).

2.7.5. Effect of Salinity

Salinity refers to the dissolved salt content of water body, mainly sodium, potassium, calcium and magnesium salts. When these salts dissolve in water they give negatively charged ions such as; Cl^- , OH^- , Br^- and SO_4^{2-} (Sundareshwar et al., 1999). Results from Liu et al. (2002) showed that P adsorption on the sediments increases at low salinity, whereas it decreases with higher salinity (>5%). This might be due to the enhanced ionic strength and increased competition for ionic adsorption with increasing salinity in the water–sediment system. Table 2-2 shows the classification of water types according to the salinity.

Table 2-2 Levels of salt in various types of water

	Water	Salinity	
Fresh water	Brackish water	Saline water	Brine
< 0.05 %	0.05 – 3 %	3 - 5 %	> 5 %

The amount of P sorbed increases as a result of particle aggregates in low salinity water. When salinity reaches a certain amount, anions, such as Cl^- , OH^- , Br^- and SO_4^{2-} , competes with PO_4^{3-} to take up available exchange sites on the sediment surfaces. As a result, the rate of P adsorption on sediments decreases.

2.7.6. Effect of Nitrogen: Phosphorus Ratio

The phosphorus to nitrogen ratio is the most important factor related to the presence of other nutrients. This ratio control the shift from lesser to more productive state of P sorption in the system. Jenson et al. (1992) found that a high NO₃⁻ concentration will increase the PO₄³⁻ sorption during winter and early spring, and it might be due to high external loads during winter to keep the equilibrium conditions. In summer, no significant influence of NO₃⁻ concentration on P sorption or desorption was noticed, but during the late summer when NO₃⁻ concentration >35µg/L, NO₃⁻ has an effect on SRP release. They also suggested that NO₃⁻ will cease SRP release by oxidizing the sediments.

2.7.7. Effect of Particle Size

The P sorption is highly affected by the surface area of the sediments. The smallest adsorbent sizes offer comparatively larger surface areas, hence higher phosphate removal and more available sites for sorption-desorption processes (these processes are controlled by the equilibrium state between sediments and water; Özacar, 2003).

Stone et al. (1989) explained that sediments show a general pattern. With an increasing concentration of P in water, the amount of the adsorbed P increases and particles between 34 and 500 μ m exhibit the lowest adsorption. The finest particle size less than 13 μ m was the most active in phosphate adsorption/desorption, and subsequently may play an important role in influencing the availability of this nutrient for biotic uptake in lakes.

In consequence, the primary reactive elements in sediments are the clay particles and iron/manganese hydroxides. These hydroxides usually precipitate on the surface of clay minerals which will generate a coating on the clay particles that leads to more available sites for adsorbing P onto clay particles (Jensen et al., 1992).

Modeling of the Langmuir and Freundlich isotherms on sediments from Lake Caron and Huron River is studied in this research, and so is the effect of particle size for selected sediments. Also analysis for the SRP uptake with time and EPC_o is considered.

CHAPTER THREE

METHODOLOGY

3.1. Study Site Description

In this study, two water bodies are studied:

- Case I: Lake Caron
- Case II: Huron River (Rivière des Hurons).

Case I: Lake Caron

Lake Description and Morphology:

Lake Caron (Fig. 3-1) is a part of the municipality of Ste-Anne Des Lacs, Québec, 75 km north of downtown Montréal in the Laurentian Mountains. The coordinates of the site according to the Canadian Atlas are 45 50'30,155" N and 74 8' 54.577" W.

Lake Caron is an artificial lake. It used to be a natural shallow pond that collected rain water and snow melt (the only source of water). The annual precipitation is approximately 1000 mm and the snow depth reaches up to 226.9 cm (Environment Canada, 2008). The lake starts to freeze by the end of October until May when the snow starts to melt during the warm spring days.

In the 1960's, the municipality of Ste-Anne Des Lacs increased the surface area of the pond and considered it as a lake with an approximately 35,400 m² surface area and capacity of 50,200 m³. The average depth is 2.25 m in most parts of the lake and 0.5 m in the shallow parts. The lake is surrounded by wild trees and there are some private

properties around the lake shores. Some owners live all year-round but most of them use their properties as country summer houses. There are some agricultural activities around the lake during the summer by the house owners.



Figure 3-1 Lake Caron (adapted from, http://abvlacs.org/leslacs/Lac-Caron.html)

Lake Caron is a closed water body and the only water source is the natural precipitation and the surface runoff from the surrounded area. During the summer days, the discharge from the lake involves two natural phenomena which are; the infiltration and the evaporation. In some cases, when the water level in the lake exceeded a certain level, the water will flow out of the lake at some points by lowering the height of the lake walls.

Problems of Lake Caron:

The Lake Caron association asked to investigate the lake water quality after they noticed the presence of blue-green algae blooms during summer 2007. During the primary visual observation of the water on May 24th 2008, it was noticed that the water becomes cloudy with shades of green, yellow and brown and loses its transparency due to high suspended solids concentration. On July 4th, in addition to the previous situation, there was a bad odour and some aquatic plants were floating on the surface of the water in the shallow parts of the lake.



Figure 3-2 Lake Caron (July 4th 2008), blue green algae blooms

According to the inspection of Ministère du Développement Durables de l'Environnement et des Parcs Québec on June 25th 2008 [refer to Appendix A-2], in this report, blue green algae were classified as category 1, the total count of cyanobacteria was 5,000 - 10,000 cell/mL and the potentially toxic cyanobacteria count range 5,000-10,000 cell/mL. This is an indicator of the high nutrient concentrations in the water, mostly due to the surface runoff from the lake banks and forest around the lake. The runoff contributes to high loads of organic material (wood pieces and dead leaves) which settle at the bottom of the lake and form rich organic sediments. There might be a possible contamination with household detergents from the septic tanks.

Case II: Huron River

The Huron River is a tributary of the Richelieu River that joins the river on the eastern bank of the Chambly basin. It is located about 40 km east of downtown Montréal in the municipality of Saint-Jean Baptiste Quebec . The river streams in to the Chambly Lake (35-40 km north).

The area of the Huron River is an intensive agricultural area for corn and wild plants. There is a camping ground around the right banks of the river near the Chambly basin and some dairy processing facilities.

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Figure 3- 3 Huron River location and sampling sites in the summers of 2007-2008 (Google Earth 2007).

Problem of the Huron River:

The intensive use of the fertilizers and pesticides in farms around the river causes an increase in the nutrient and toxic chemical concentrations in the river water due to surface runoff after the rain storms. Also the erosion of the river banks leads to high loads of soil into the river water which leads to a great amount of nutrients in the river bed. When the water of the river is very turbid, especially during the warm summer days, it is the ideal conditions for the bacteria to act. That leads to a high concentration of the suspended solids in the river.



Figure 3-4 Huron River, HS5 (May 10th 2008).

In the past, disposal of the wastewater from the industrial facilities and the wastewater treatment plant in the area into the river contributed to high concentrations of heavy metals and nutrients.

Investigations during the summer of 2007 for water quality, primary visual observation and laboratory analysis for water samples have concluded high concentration of the suspended solids and nutrients in both sediments and water. These concentrations were relatively high in comparison to the Canadian guidelines for the water and sediment quality.

3.2. Methods and Materials

3.2.1. Sampling and Storing

Samples were collected during the summer of 2008 for both Lake Caron and the Huron River.

Lake Caron: The Lake was divided into 6 stations from the shallow parts of the lake: CS2, CS3, CS4, CS5, CS6, CS7, as shown in Figure 3-5, and one station in the middle of the Lake CS1. Samples were collected on May 24th, July 4th, and August 12th. The samples were collected from the seven stations using 500 mL glass bottles (Fisher brand) which were initially cleaned several times with lake water. The sediments were collected using a sediment messenger (Wildco brand) to get the samples from the bottom of the lake, then from each station two glass bottles of 500 mL capacity were filled with the sediments and labelled.

Core samples from Lake Caron CS6 were obtained at a depth of 30 cm, and were divided into 6 sectors (each 5 cm) to characterize the sediments properties with depth. The samples were collected by inserting a graduated cylinder in the sediments in the shallow part of CS6. The length of the cylinder was 75 cm and the diameter was 2.54 cm, both ends were open to allow the water to flow out without disturbing the sediments.

After the sampling, the samples were kept in a dark cooler to prevent the temperature changes or the sun light interactions, as they may provoke chemical and biological reactions. Then samples were transferred to the laboratories of Concordia University, and then they were stored in the incubator at a temperature of 4°C before further use. The water samples were tested within the next 24 hours for water quality. Sediments samples

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were divided into two portions; the first portion was used for characterizing the sediment (water content, specific gravity, loss on ignition (LOI), particle size). The second portion was used for air-drying for further tests (total phosphorus (TP), adsorption tests). The fume hoods were used for air-drying at room temperature of $22^{\circ}-24^{\circ}$ C. The dried samples were ground to pass through a 2 mm sieve. Then the samples were stored in a plastic container in the dark at room temperature for further use. Standard test methods according to the ASTM D3976 – 92 (Standard Practice for Preparation of Sediment Samples for Chemical Analysis) were performed.



Figure 3-5 Lake Caron sampling stations, (Summer 2008).

Huron River: The River was divided into 7 sampling stations for water and sediments where public access is allowed as shown in Figure 3-6.



Figure 3-6 Huron River sampling stations.

Samples were collected on May 10th and August 4th, 2008. For the sediment samples, it was possible to collect from HS1, HS5, HS6 and HS7 stations. The same procedures for storage and handling were used as for Lake Caron samples.

3.2.2. Sample Testing

3.2.2.1. Sediment Properties

Water Content (ASTM D 2216):

The water content of the 11 samples from Lake Caron and Huron River was measured in the lab within 24h from the sampling according to the ASTM standard test methods. For each sediment sample, triplicate measurements were performed. Samples were placed in pre-weighed porcelain crucible and the wet weight of each sample was measured using a digital scale accuracy of 0.01 g. Then the samples were placed in the oven at a temperature of 105°C for a minimum of 18 h. Thereafter, the oven dried samples were kept in the desiccators to prevent absorption of humidity while cooling. Finally, the dry weight was recorded.

The water content was measured according to the following equation:

Water Content =
$$[W_{w} - W_{d(105^{\circ}C)})] / W_{d(105^{\circ}C)} * 100\%$$

 W_{w} : Wet weight of the sample (g).

 $W_{d(105^{\circ}C)}$: Dry weight of the sample at 105°C (g).

The water content final value was considered as the average of the three replicates.

Loss on Ignition (LOI) (ASTM D 2974-00):

LOI was tested according to the ASTM method. Oven-dried sediments from each sample were divided into three parts and placed into incinerated porcelain crucibles for ignition at 550°C for 4h. Then the samples were placed in desiccators until cooling. The weight of the samples was recorded using a digital scale accuracy of 0.01 g.

LOI was calculated using the following equation:

$$LOI = [W_{d(105^{\circ}C)} - W_{d(550^{\circ}C)}] / W_{d(105^{\circ}C)} * 100\%$$

 $W_{d(105^{\circ}C)}$: Dry weight of the sample at 105°C (g).

 $W_{d(550^{\circ}C)}$: Dry weight of the sample at 550°C (g).

The final LOI value is the average of the triplicate readings for each sample.

Specific Gravity and Particle Density (ASTM D 854-02):

This method was performed to measure the specific gravity of the sediments using the water pycnometer. For each sample, three replicates were done and the average of the three readings was determined as the specific gravity of each sample.

The average weight of the three readings for the dry empty pycnometer and the pycnometer with water weight at calibration temperature was recorded to calculate the volume V_p of the pycnometer using the following equation:

$$V_p = \frac{(M_{pw,c} - M_p)}{\rho_{w,c}}$$

 V_p = volume of the pycnometer at calibration temperature (mL),

 $M_{pw,c}$ = the mass of the pychometer and the water at the calibration temperature (g),

 M_p = the average mass of dry pycnometer at the calibration temperature (g),

 $\rho_{w,c}$ = the mass density of water at calibration temperature (g/mL).

After getting the V_p , the mass of the pycnometer at the test temperature $M_{pw,t}$ was calculated using the following equation

$$M_{pw,t} = M_p + (V_p \cdot \rho_{w,t})$$

Where:

 $M_{pw,t}$ = mass of pycnometer and water at testing temperature (g),

 $\rho_{w,t}$ = the mass density of water at testing temperature (g/mL),

 M_p = the average mass of dry pycnometer at the calibration temperature (g).

Then the specific gravity G_t at testing temperature can be found using the equation:

$$G_{t} = \frac{\rho_{s}}{\rho_{w,t}} = \frac{M_{s}}{(M_{pw,t} - (M_{pws,t} - M_{s}))}$$

 ρ_s = the density of the soil solids mg/m³ or g/ cm³,

 $\rho_{w,t}$ = the density of the water at testing temperature (from tables provided by the ASTM D 854-02 method) kg/m³ or g/cm³,

 M_s = the mass of the oven dry soil solids (g).

After calculating G_{ℓ} , the particle density ρ_{s} can be found.

Total Phosphorus (TP):

To determine the TP in the sediments, digestion of the sediments was done using 60% perchloric acid $HClO_4$ as recommended by Olsen and Sommers (1982). Two grams of air dried sediments were placed in 250 mL volumetric flasks for digestion with 30 mL of

acid till boiling and the sediments color changed into white. The total time of digestion was approximately 40 minutes. After cooling the mixture, the volume was brought to 250 mL using distilled water.

The reagent used to analyze the TP was ammonium paramolybdate-vanadate. This dissolving of reagent prepared by 25 g ammonium molybdate was $(NH_4)_6Mo_7O_{24}.4H_2O$ into 400 mL of distilled water, then ammonium metavanadate NH₄VO₃ to be dissolved into 300 mL of boiling distilled water. After cooling the previous solution, 250 mL of concentrated nitric acid HNO3 was added, then after cooling the mixture of NH4VO3 - HNO3 to room temperature, add ammonium molybdate (NH₄)₆Mo₇O₂₄.4H₂O solution.

The final volume of the reagent was 1 L by diluting the mixture with distilled water. To analyze the TP, 35 mL of the aliquot (diluted digested sediments with perchloric acid) was transferred to 50 mL volumetric flasks. Thereafter, 10 mL of the reagent was added and the final volume was brought to 50 mL with distilled water. The optical density of the sample was measured after 10 minutes using a spectrophotometer (*HACH DR-2800*) at a wavelength of 450 nm.



Figure 3-7 HACH-DR 2800 Spectrophotometer used for analyzing TP and SRP.

The calibration curve was obtained by analyzing blank and different standard solutions as KH₂PO₄ (standard solutions were prepared by dissolving 0.4393g KH₂PO₄ into 1L of distilled water to obtain a stock solution of 100 mg-P/L)[Appendix B-1].

TP (mg/kg) = [concentration of P in initial 250mL dilution, mg/L] * [0.25/mass of soil, kg]

Particle Size Distribution:

The particle size distribution for the sediment samples was determined using the Laser Scattering analyzer (*HORIBA*, *LA-* 950V2). This instrument has the ability to measure the particle size of dry or wet samples within a range of 0.5 μ m-3000 μ m. Triplicate measurement for each sample was done and the distribution of the particle size was generated using *EXCEL Microsoft Office* by plotting the accumulated percentage finer to the particles diameter on a semi log scale.



Figure 3-8 Laser Diffraction Scattering Analyzer (HORIBA, LA- 950V2)

3.2.3. Phosphorus Sorption and Isotherm Determination

Since the contamination with P is common in the labs, all the glassware and centrifuge tubes used in analyzing the TP and SRP were washed with 2% nitric acid (trace metal grade) solution and phosphate free detergent to minimize the contamination.

Sorption Test:

The upcoming procedures are recommended by the SERA-IEG 17 group (Southern Extension and Research Activity Information Exchange Group for phosphorus management USA) as a standard method for the sorption test in soil and sediment. A 2 g sediment sample was weighed into 50 ml centrifuge tube. 50 mL of 0.01M CaCl² solution containing 0, 0.01, 0.1, 1, 2, 5, 10, 25, 50, 100 mg P/mL as KH₂PO₄ to produce a sediment: solution ratio of 1:25.

Samples were shaken in a mechanical shaker (AROS 160) at room temperature (22°-23°C) for 24h. After settling for 1 hour, samples were filtered through a 0.45 μ m membrane (Millipore filter paper, Fisher Scientific Brand). The filtrate was analyzed for soluble reactive phosphorus SRP (as the equilibrium P after 24h) according to the Murphy and Riley (1962) method using spectrophotometer at wave length of 880 nm. For each sediment sample, two sorption runs were performed and the final values for the equilibrium P concentration were considered as the average of the two readings.

The same procedures were performed for samples CS2 and CS3, after separating their particles using standard sieves (Fisher brand). The sieves used were:

- No 200, opening size of 75 μm,
- No 400, opening size of 38 μm.

In consequence, the particle sizes used for the tests were:

75 μ m -2mm, 38 μ m, -75 μ m - and less than 38 μ m.

Some researchers use toluene or chloroform as microbial inhibitors during performing the sorption test. Results from different research studies have shown that toluene or chloroform increase the SRP in solution after equilibrium due to lysis of microbial cells, thus some researchers do not try to inhibit microbial growth (Reddy et al., 1998). In this research, toluene or chloroform was not used due to the previous mentioned issues and safety concerns. A 0.01 M KCl solution may be used as an electrolyte background to prevent Ca precipitation in neutral and alkaline soils.

Analysis of SRP in Water (Murphy and Riley 1962):

This method is also known as molybdenum blue to measure the soluble reactive phosphorus SRP in water (SRP called also "Orthophosphate" is the inorganic form of P, mentioned earlier in Chapter Two). Water samples and solutions obtained from the sorption tests must pass through a 0.45 μ m membrane prior to the test. To prepare 100 mL from the reagent,15 mL (NH₄)₆ Mo₇O₂₄.4H₂O ammonium molybdate solution (this solution was prepared by dissolving 20 g from (NH₄)₆ Mo₇O₂₄.4H₂O in 500 mL of distilled water) should be added to 50 mL of 2.5 MH₂SO₄ sulfuric acid (trace metal grade), then 5 mL K(SbO)C₄H₄O₆.1/2H₂O potassium antimonyl tartrate solution (dissolving 1.3715 g of K(SbO)C₄H₄O₆.1/2H₂O in 500 mL distilled water), and finally 30 mL 0.1 M C₆H₈O₆ ascorbic acid (by dissolving 1.76 g of the ascorbic acid in 100 mL, this solution is stable for about a week).

The reagent is stable for 8 hours only; therefore the reagent was freshly prepared for each test. For a 50 mL of the water samples, it requires 8 mL of reagent. The optimal density of the sample is after 10 minutes but no longer than 30 minutes, using spectrophotometer on wave length of 880 nm. The minimum detectable P concentration limit is approximately 10 μ g/L. The calibration curve was obtained by analyzing blank as a reference and different standard solutions as KH₂PO₄ in distilled water [refer to Appendix B-1].

Sorption Isotherm Determination

The amount of P sorbed by the sediments was calculated from the difference between P concentration in the initial solution and equilibrium P in the filtrate solution after 24 h. Sorption parameters were calculated using linear Freundlich and Langmuir isotherms as explained earlier in Chapter Two.

The linearized Langmuir isotherm is: Add equation numbers after equations

$$\frac{C}{S} = \frac{1}{kS_{\max}} + \frac{C}{S_{\max}}$$
(2)

And the Freundlich linear isotherm is:

$$Log S = Log K + n Log C$$
(4)

The experimental data was fitted into the modified Langmuir and Freundlich isotherm using Eqs. (6) and (7).

Modified Langmuir adsorption isotherm:

$$S' = \frac{CkS_{max}}{1+Ck} - S_0 \tag{6}$$

Modified Freundlich adsorption isotherm:

$$\mathbf{S}' = \mathbf{K}\mathbf{C}^{n} - \mathbf{S}_{0} \tag{7}$$

3.2.4. Uptake of Phosphorus with Time

Two grams of sediments were placed into 50 mL centrifuge tubes with $0.01M \text{ CaCl}_2$ standard phosphorus solutions as KH₂PO₄. The standard solution initial concentrations were 1 mg-P/L and 2 mg-P/L. Then samples were shaken at room temperature using a mechanical shaker (AROS 160). SRP concentration was measured after a period of time of 1, 2, 3, 6, 12, and 24 h to determine the percentage of P uptake with time and the efficient time of shaking. The initial and final SRP concentrations were measured using the Murphy and Riely (1962) method. The adsorption kinetics was modeled using the power function model using Eq (9) and Eq (10).

$$S = a.t^{b}$$
(8)
Log S = Log a + b Log t (10)

The first order kinetics and the rate of adsorption were calculated using Eq (12) and the linear plots of Ln [C] vs [t] to obtain k values using Eq (13) are as follows:

$$C_t = C_0 e^{-kt} \tag{12}$$

$$Ln[C] = -kt + Ln[C_0]$$
(13)

The half life time was determined using Eq (14):

$$t_{1/2} = \frac{\ln(2)}{k}$$
(14)

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3.2.5. SRP Changes by Resuspension

Two grams of sediments from Lake Caron and Huron River were placed into 50 mL centrifuge tubes at room temperature. Water from the lake and the river was added to the sediment with a ratio of 1:25. The samples were shaken using a mechanical shaker (AROS 160) for periods of 24, 48, 72, and 96 hours. The initial and final SRP concentrations were determined by the Murphy and Riley (1962) method as explained earlier.
CHAPTER FOUR

RESULTS AND DISCUSSION

4.1 Sediment Properties

Table 4-1 gives a summary of the sediment physical and chemical properties from Lake Caron and Huron River. Water content and LOI were determined within 24 hours from sampling, following the ASTM D 2216 for the water content and ASTM D2974-00 for the LOI as described earlier in Chapter Three. Particle density was obtained from the specific gravity test method for the wet samples using the pycnometer as described in Chapter Three following the ASTM D854-02 method.

Total Phosphorus TP was measured after digesting the air dried sediments using the 60% perchloric acid as recommended by Olsen and Sommer (1982), mentioned earlier in the Chapter Three. The TP values were compared to the Canadian Sediment quality guideline mentioned earlier in Chapter Two [Appendix A-1].

LEL = 600 mg-P/kg and SEL = 2000 mg-P/kg

Sampling depths for the different sampling stations were measured directly during the sampling, and were validated for the lake samples from the lake description provided from Center d' Expertise Hydrique Quebec [Appendix A-3].

Sample	Water content	LOI	Particle density	ТР	Sampling depth
No.	(%)	(%)	(g/cm³)	(mg-P/kg)	(m)
CS1	1365.5±11.0	73.70±0.1	2.12±0.04	187±40	2.56-2.92
CS2	166.1±1.5	13.69±0.1	2.52±0.03	408±37	0.32-0.65
CS3	162.2±4.1	14.66±0.1	2.53±0.02	420±17	0.65-0.97
CS4	99.9±1.5	8.72±0.2	2.63±0.01	286±11	0.32-0.65
CS5	44.6±3.4	4.48±0.0	2.68±0.01	303±15	0.65-0.97
CS6	34.4±0.5	0.93±0.2	2.74±0.01	298±9	0-0.32
CS7	52.0±0.8	1.92±0.2	2.72±0.01	502±12	0-0.32
HSI	72.93±2.2	3.78±0.1	2.72±0.01	1033±132	0-0.30
HS5	56.23±1.4	4.55±0.2	2.68±0.01	782±14	0-0.30
HS6	61.82±3.9	2.81±0.1	2.73±0.01	741±11	0-0.30
HS7	65.48±1.1	4.82±0.1	2.67±0.01	653±19	0-0.30

Table 4-1 Lake Caron and Huron River sediment properties

Note: C refers to the samples from Lake Caron and H refers to samples from the Huron River

For the core sample obtained from CS6, the sediment properties are in the following figures. Figure 4-1 represents the water content changes in the sediments in the different sectors according to the depth. Figure 4-2 represents LOI changes. Figure 4-3 represents the particles density, according to the sediments properties it is clear that the sediments at the depth of approximately 20 to 30 cm, have different properties since it is mainly composed of organic material, this might be the result of reconstruction of the lake to increase the lake basin and build its walls. Figure 4-4 represents the TP concentration in

the sediments which in turn gives an idea about the history of loading; i.e. the accumulation of the phosphorus compounds in the sediments.





depth in the core sample from CS6

Figure 4-1 Water content changes with Figure 4-2 LOI changes with depth in the







From the previous graphs it can be possible to correlate the water content with the LOI values; the higher the LOI values the higher the water content. The organic matter (resulting from decomposed aquatic organisms) tends to retain water. The presence of the

organic materials in the sediments leads into lower density since it increases the volume of the sediments. TP values are related to the LOI values. The increase of the organic materials will contribute to the increase of the TP.

4.2 Particle Size Distribution

The analysis of the sediments from Lake Caron and Huron River was performed using the HORIBA LA- 950V2 Laser scattering analyzer (particle size detectable range for this instrument between 0.5 μ m to 3000 μ m) and the graph was generated using Excel. The particle distribution curve is obtained by plotting the percent of total material less than certain sizes. These sizes are determined by couple laser emissions, and classified according to the wave length of the laser provided by the instrument. Data were presented to describe the relation between the percentages of particles under size (percent finer calculated from the initial sample amount) versus particle diameter. Data were provided from the instrument [AppendixB-4].

Figure 4-5 represents the particle size distribution for Lake Caron samples and Figure 4-6 represents Huron River samples. According to these graphs, the classifications of the sediments according to their particle size as mentioned earlier in Chapter Two were according to Carter et al. (1993):

For the CS1, it was impossible to consider the fractionation of the sample according to the particle size due to the sediment properties as shown in Table 4-1, high organic content (LOI= 73.7%) and low density (2.12 g/cm³).

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Figure 4-5 Particle size distributions for sediment samples from Lake Caron



Figure 4-6 Particle size distributions for sediment samples from the Huron River

4.3 Adsorption Isotherm Parameters

All of the P adsorption experimental data shown in the following figures were fitted to the modified Langmuir and Freundlich isotherms, Eq (6) and (7) respectively, with the least squares method (the correlation coefficient values varied as $0.78 < r^2 < 0.99$). Also refer to Appendix B-2 and B-3 for further clarification. Table 4-2 shows a summary of the Langmuir and Freundlich adsorption isotherm parameters for the samples from Lake Caron and the Huron River.

	S _o	EPCo	Langmuir	Freundlich		
NO.	(mg- P/kg)	(mg-P/L)	S _{nux} k r²	n K f ²		
CSI	14	0.31	2000 0.034 0.95	0.883 56.70 0.97		
CS2	39	0.17	3333 0.083 0.99	0.949 241.32 0.99		
CS3	20	0.043	5000 0.142 0.98	0.813 562.34 0.98		
CS4	52	0.19	1428 0.233 0.95	0.886 259.77 0.97		
CS5	54	0.17	910 0.407 0.93	0.596 179.10 0.94		
CS6	5	0.07	100 0.390 0.98	1.08 58.4 0.97		
CS7	9	0.19	770 0.127 0.96	0.937 79.78 0.94		
HSI	11	0.15	5000 0.014 0.78	1.049 88.26 0.95		
HS5	14	0.16	2500 0.039 0.99	1.06 56.70 0.97		
HS6	20	0.18	454 0.511 0.95	0.846 56.70 0.91		
HS7	14	0.16	467 0.671 0.94	0.953 276.7 0.97		

 Table 4-2 Adsorption isotherm parameters

The described parameters in this table are:

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 S_0 , the originally adsorbed phosphorus, expressed as (mg-P/kg) in the sediments calculated using Eq. (5) explained in Chapter Two, and the EPC_o equilibrium concentration at zero sorption expressed as (mg-P/L) calculated from Eq.(5).

Calculated Langmuir isotherm parameters using Eq (2*) are S_{max} the maximum sorption capacity in mg-P/kg, k is the equation constant related to the bonding energy in L/mg-P and the r^2 value from the linear fit. Calculated Freundlich isotherm parameters using Eq (4) are K and n to present empirical constants that vary according to the sediment properties K is the adsorption constant, expressed as mg P/kg, and n is a constant expressed as L/kg.

The objective of these models is to fit the experimental data generally for narrow concentration ranges to cover wider concentration ranges.

HS1: The modeled isotherm Freundlich and Langmuir gave a good fit with the experimental data over a range of equilibrium conditions between 0-3 mg-P/L as shown in Figure 4-7.



Figure 4-7 Langmuir and Freundlich Adsorption isotherms HS1.

HS5: Both Freundlich and Langmuir isotherms fit well with the experimental data over a range of 0 to 3 mg-P/L of equilibrium conditions as shown in Figure 4-8.



Figure 4-8 Langmuir and Freundlich Adsorption isotherms HS5.

<u>HS6</u>: The Langmuir model gives a good fit for the behaviour of P sorption over a wide range of equilibrium conditions (0-3 mg-P/L). The Freundlich model gives at low equilibrium condition (0-0.5 mg-P/L a good fit with the experimental data, but not at a wider range. Figure 4-9 shows the Langmuir and Freundlich isotherms.



Figure 4-9 Langmuir and Freundlich Adsorption isotherms HS6.

<u>**HS7</u>**: by looking at Figure 4-10 it is possible to recognize the Langmuir model which gives a good explanation about the P sorption behaviour at low range of equilibrium conditions (0-1 mg-P/L), but on a wider range this model did not fit well due to low value of S_{max}. On the other hand, the Freundlich model gave a better explanation about the P sorption behaviour on wider range of equilibrium C concentration. By looking at the value of n = 0.953, it shows that the adsorption behaviour is closer to linear and that it agrees with the assumptions of modeling and fitting.</u>



Figure 4-10 Langmuir and Freundlich Adsorption isotherms HS7.

<u>CS1</u>: At low equilibrium conditions, the Langmuir model fits the experimental data, but not on higher equilibrium conditions. The Freundlich isotherm gave a closer fit with the experimental data for the adsorption behavior than the Langmuir isotherm, mostly due to the sediment properties (high organic content LOI =73.3%) and more available sorption sites on the organic material surface. These factors agree more with the Freundlich than the Langmuir isotherm assumptions (Figure 4-11).



Figure 4-11 Adsorption isotherms for sample CS1.

<u>CS2</u>: Both Freundlich and Langmuir isotherms fit well with the experimental data over a range of (0 to 5 mg-P/L) of equilibrium conditions. These models will give a good explanation of the sediments behavior when interact with a solution contains P. The Freundlich might be better than the Langmuir since n=0.949 which is very close to 1. This agrees with the linear fit for the Freundlich isotherm (Figure 4-12) this might be due to the presence of clay particle in the sediments and the organic content, which in turn will provide more surface area and more exchangeable sites for sorption /desorption processes and that agrees with the main assumption of the Freundlich isotherm.



Figure 4-12 Langmuir and Freundlich adsorption isotherms for sample CS2.

<u>CS3</u>: Both Freundlich and Langmuir isotherms fit well with the experimental data over a wide range of equilibrium conditions (0-6 mg-P/L) as shown in Figure 4-13. The presence of the clay particles in these sediments supported the Freundlich isotherms assumption; these particles provide large specific surface area and more available sites for exchange, so is the organic matters in the sediments which might enhance the adsorption by providing more sites for exchange. The Langmuir model fit the experimental data and gave a good estimation of the sorption capacity as provided in Table 4-2. CS3 sediments have the highest sorption capacity which might be due to the presence of the organic matter and the clay particles.



Figure 4-13 Langmuir and Freundlich adsorption isotherms for sample CS3.

<u>CS4</u> By looking at Figure 4-14, both Freundlich and Langmuir isotherms fit well with the experimental data and gave good explanation of the sediments behavior for the sorption test on a range of 0 to 3 mg-P/L of the equilibrium conditions.



Figure 4-14 Langmuir and Freundlich adsorption isotherm for sample CS4.

<u>CS5:</u> By looking at Figure 4-15, the Langmuir isotherm shows a better fit than the Freundlich isotherm on the range between 0 to 1 mg-P/L at the equilibrium conditions, but the experimental data was not enough to plot the curves fitting over the range between 1 to 8 mg-P/L of the equilibrium conditions.



Figure 4-15 Langmuir and Freundlich adsorption isotherms for sample CS5

<u>CS6:</u> In Figure 4-16 the Langmuir isotherm shows a better fit than the Freundlich isotherm over a wide range of equilibrium conditions (0-4 mg-P/L). At low equilibrium conditions ranging between 0 and 1.2 mg-P/L, the Freundlich isotherm fits better with the experimental data.



Figure 4-16 Langmuir and Freundlich adsorption isotherms for sample CS6.

<u>CS7</u>: Figure 4-17, the Langmuir isotherm shows a better fit than the Freundlich isotherm over a wide range of equilibrium conditions (0-5 mg-P/L). On the other hand, when the low equilibrium conditions are low (0 -2 mg-P/L), the Freundlich isotherm gives a good fit with the experimental data over the range between 0-0.5 mg-P/L.

Phosphate adsorption is a linear process when phosphate concentration in the overlying water is at a lower level. The slope of the Langmuir adsorption isotherm equation (1/k S_{max}) represents the adsorption efficiency of phosphate onto sediments. By comparing all adsorption isotherms for the 7 samples from Lake Caron, samples that contain clay particles (approximately 4%) tend to have higher sorption capacity as in CS3 and CS2. CS3 had the highest S_{max} at 5000 mg-P/kg and CS2 at 2500 mg-P/kg. On the other hand, CS6 and CS7 sediments are mainly sand particles (approximately 92%) and there is no

significant amount of clay. These sediments fit the Langmuir isotherm better than the Freundlich isotherm.



Figure 4-17 Langmuir and Freundlich adsorption isotherms for sample CS7.

Observations show that the clay content of the sediments plays an important role in determining the simulated model, which is the Freundlich isotherm; in this case the clay minerals offer a wide surface area and non limiting sorption sites which agrees with the observations of Stone et al.(1989) and Jensen (1992). The sand particles in CS6 and CS7 do not support this assumption of the Freundlich isotherm, but agree with the Langmuir model; hence the main assumption is that there are limited sorption sites for the sorbent on the surface of the particle which in turn forms a monolayer on the sorbate particles.

For samples from the Huron River, since the sediments have a relatively good gradation with regards to the particle size, it can be noticed that both the Langmuir and Freundlich isotherms are close to each other. Also the samples contain reasonable fractions for sand and clay to support the assumptions for both models.

The organic content in the sediments plays also an important role to determine the sorption capacities as explained by Fukue et al. (2006). By comparing the values of LOI for the sediments of Lake Caron (summarized in Table 4-1) and by looking at Figure (4-18), we can see that CS3 and CS2 samples have the highest LOI value (approximately 14.6 % and 13.7% respectively), these samples also offered that highest sorption capacities (5000 mg-P/kg and 3333 mg-P/kg) according to the Langmuir plots.



Figure 4-18 Relation between sorption capacity and LOI values for samples from Lake Caron and Huron River.

On the other hand, CS6 and CS7 with the lowest organic content (0.93% and 1.92% respectively) have the lowest sorption capacities For CS1 samples, these sediments are composed mainly from organic materials (LOI = 73 %), that doesn't means it will have

the highest sorption capacity (2000 mg-P/kg) the sorption desorption behavior is controlled by many factors such as the clay and the hydroxides contents and the equilibrium conditions between the sediments and the overlaying water. Also the decomposition of the organic materials might contribute to SRP concentration changes and the equilibrium conditions. In conclusion, there is a proportional relation between the sorption capacity and LOI values.

For samples from Huron River samples, HS5 and HS7 both samples offered the highest LOI values respectively (4.55% for HS5 and 4.82% for HS7) and their sorption capacities varied between (2500 mg-P/kg and 467mg-P/kg). But HS1 had the highest sorption capacity (5000 mg-P/kg) due to its high clay content and relatively good LOI value (3.78%). For HS6 samples, it has relatively the lowest LOI value (2.81%) and the lowest sorption capacity at 454 mg-P/kg.

The usefulness of the EPC_o is that it gives the information on whether sediments will release or extract SRP when placed in contact with water according to Zhao et al. (2005) and Jarvie et al. (2005). When the EPC_o > SRP in water, the sediments will release SRP to the water column. When EPC_o < SRP, the sediments will take up the SRP from the water. If the EPC_o is close to the SRP from the water column, the bed sediments and the water is approximately in equilibrium.

Figures 4-19 and 4-20 show the concentrations of SRP in Lake Caron and the Huron River respectively, water during summer 2008 samplings. For the Lake Caron water samples which were taken by July 4th the SRP concentrations were less than the average SRP concentration observed in the lake water, since the sampling took place by the day

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after a storm which might contribute to the dilution of the SRP concentrations in the water.



Figure 4-19 SRP concentrations in Lake Caron, summer 2008.



Figure 4-20 SRP concentration in the Huron River, summer 2008.

Figure 4-21 gives a summary of the EPC_o for all samples after calculating them from the linear isotherm using Eq 5. [Refer to Appendix B-1]. The minimum EPC_o for Lake Caron

was obtained from CS3 = 0.04 mg-P/L by comparing with the other EPC_o values for the other samples. CS3 sediments might act as a sink for P at relatively low SRP concentration in water. The equilibrium concentration of CS3 sample is very close to the concentration of SRP in the lake water which might be an indication that the lake water and the sediments in CS3 are very close to the equilibrium as observed by Jarvie (2005), but for the other samples as CS1 the EPC_o (0.31 mg-P/L) is very high, therefore these sediments will act as a potential source of P into the lake water.



Figure 4-21 EPCo for samples from Lake Caron and the Huron River

For the Huron River, the EPC_o ranged between 0.15 and 0.18 mg-P/L and these sediments therefore might act as source of P due to the SRP concentration in the river water which is in most cases less than EPC_o values. High EPC_o values might be due to the high initial TP in the sediments and high SRP fraction as mentioned earlier (EPC_o

description in Chapter Two by Jarvie et al., 2005). EPC_0 did not vary considerably for the four samples i.e. the equilibrium state of the river in its different parts is almost the same.

At HS7 and HS6 upstream the EPC_o values are a bit higher than EPC_o along the river at HS5, might be due to the high TP concentration in the river bed sediments in HS6 and HS7, which results in higher SRP in the river water and in turn, higher EPC_o values. At HS1 it has the lowest EPC_o value could be due to the high dilution of the SRP in the estuary where the river meets the Chambly Lake downstream [Refer to Table 4-1 for sediment properties and TP values]. Many factors might be involved in the overall equilibrium conditions in the river due to the dilution and flow pattern, and also the loading rates after the storms.

<u>Note</u>; The Selective Sequential Extraction (SSE) for the total phosphorus in the sediments in order to determine the SRP fraction in the sediments, was difficult to perform due to a lack of equipment in the laboratory (The head space should be filled with purified N_2 when sampling for this test to prevent oxidizing, and the samples should be kept in a glove bags). The SRP fraction in the sediments would be the exchangeable fraction between the sediments and the overlaying water.

4.4 Adsorption Kinetics, Phosphorus Uptake with Time

Standard solutions of concentrations of 1 mg-P/L and 2 mg-P/L were used for this test and the concentration of SRP was measured using the Murphy and Riley method (1962) after 1h, 2h, 3h, 6 h, 12h and 24 h. The adsorption kinetics parameters for the concentrations 2 mg-P/L and 1 mg-P/L were determined using the power function model. (a) and (b), the power function constants, were calculated from the linear fit and the least squares method using Eq.(9) and (10) as explained earlier in Chapter Two. Table 4-3 shows the values for (a) and (b) using the least squares method.

No	$S = a.t^{b}$ (2mg-P/L)			$S = a_i t^b (Img-P/L)$			
	a	b	r²	а	b	r ²	
CS1	18.64	0.2634	0.92	10.11	0.2209	0.94	
CS2	7.29	0.605	0.81	10.13	0.2233	0.93	
CS3	36.75	0.1179	0.65	15.63	0.0793	0.95	
CS4	13.19	0.3472	0.98	5.15	0.7116	0.84	
CS5	9.38	0.3847	0.93	2.82	0.6973	0.83	
CS6	9.62	0.3815	0.96	2.46	0.6817	0.66	
CS7	9.81	0.321	0.88	2.39	0.419	0.94	
HSI	26.80	0.0888	0.98	5.14	0.4345	0.83	
HS5	16.41	0.2751	0.91	6.79	0.4004	0.89	
HS6	20.13	0.2408	0.94	2.17	0.6676	0.95	
HS7	19.66	0.2359	0.96	7.83	0.3475	0.87	

Table 4-3 Adsorption kinetic parameters

Figures 4-22 to 4-32 show the adsorption kinetics of phosphorus adsorption in the sediments from Lake Caron and the Huron River. Initial phosphorus concentrations were 2 mg-P/L and 1 mg-P/L. The power function model shows a good fit ($0.66 > r^2 > 0.95$) for the sediments behavior to describe the uptake rates.

Results from the Jarvie et al. (2005) studies also show that sediments with low EPC_o concentration have a higher affinity to uptake SRP. In other words, these sediments have a higher affinity to adsorb P at low EPC_o values. This can be seen in the sediments from CS3 and HS1, approximately 70 % of the SRP will be sorbed within the first 2 hours.



Figure 4-22 Adsorption kinetics CS1



Figure 4-23 Adsorption kinetics CS2



Figure 4-24 Adsorption kinetics CS3



Figure 4-25 Adsorption kinetics CS4







Figure 4-27 Adsorption kinetics CS6



Figure 4-28 Adsorption kinetics CS7



Figure 4-29 Adsorption kinetics HS1



Figure 4-30 Adsorption kinetics HS5



Figure 4-31 Adsorption kinetics HS6



Figure 4- 32 Adsorption kinetics HS7.

In general, all the samples have almost the same behavior. For the first three hours, the average removal rate accelerated up to 65% of the total removal. It reached up to 95%

after 12 hours and then it varied at a very slow rate between 12 to 24 h to reach 100% equilibrium.

The first order kinetics and the adsorption rates were calculated using Eq (14) and Eq (13) as mentioned earlier in Chapter Two using the least squares methods, so is the half life time which was determined using Eq(14). Table 4-4 shows the adsorption first order rates K, the half life time $t_{1/2}$ and r^2 values for the sediments samples from Lake Caron and Huron River. The adsorption rate is independent of the initial concentration; it most likely depends on the sediments' ability to uptake P when interacting with a solution containing P.

No	2 mg-P/L			I mg-P/L		
	K(1/h)	t _{1/2} (b)	r ²	K(1/h)	t _{1/2} (h)	r²
CS1	0.061	11.3	0.78	0.055	12.6	0.75
CS2	0.052	13.3	0.78	0.054	12.8	0.75
CS3	0.041	16.9	0.44	0.139	04.9	0.59
CS4	0.056	12.4	0.91	0.066	10.5	0.86
CS5	0.031	22.3	0.78	0.051	13.6	0.76
CS6	0.032	21.6	0.79	0.028	24.7	0.55
CS7	0.022	31.5	0.66	0.014	49.5	0.55
HŠI	0.028	24.7	0.38	0.042	16.5	0.79
HS5	0.043	16.1	0.70	0.067	10.3	0.81
HS6	0.035	19.8	0.84	0.057	12.2	0.74
HS7	0.058	11.9	0.77	0.055	12.6	0.74

Table 4- 4 First order adsorption kinetics of samples from Lake Caron and Huron River

4.5 Resuspension of Sediments Using the Natural Water from Source

Two grams of sediments from Lake Caron and Huron River were placed into 50 mL centrifuge tubes at room temperature. Water from the lake and the river was added to the sediment with a ratio of 1:25. The samples were shaken using a mechanical shaker for periods of time of 24, 48, 72, and 96 hours. The initial and final SRP concentrations were determined by the Murphy and Riley (1962) method as explained earlier in Chapter Two.

The purpose of this test was to verify the behavior of the sediments when interacting with the lake water by resuspension. In other words, this test is an indication of the sorption desorption behavior of the sediments and the water after equilibrium, and also to determine the required time to reach equilibrium during resuspension.

4.5.1 Lake Caron Sediments

The initial SRP concentration in lake water was 0.015 mg-P/L. Figure 4-33 shows the changes in SRP concentration in the solution after 24, 48, 72, and 96 h. Sediments tend to retain the equilibrium concentrations after resuspension (Figure 4-20 for EPC_0 values). During the 4 day test period, for sample CS3, SRP increased after one day to 0.08 mg-P/L. After 2 days, the concentration started to decrease until it reached its equilibrium over the test period.



Figure 4-33 SRP changes for samples from Lake Caron by resuspension.

A similar observation was noticed for CS2. In regards to samples CS4, CS5, CS6, and CS7, there was no significant state to describe the sorption-desorption behaviors for these samples. If the test was performed over a longer period of time, we would have been able to obtain better understanding of the sediment behavior. Lastly, for sample CS1, results showed increased SRP concentrations over the test period time. This might be due to its high EPC₀ which equals 0.31 mg-P/L, or it might be related to the degradation of the organic matter which leads to higher SRP values in the solution.

4.5.2 Huron River sediments

The initial SRP concentration in river water was 0.023 mg-P/L. Figure 4-43 shows the changes in SRP concentration in the solution after 24, 48, 72, and 96h. The equilibrium concentrations for the samples from Huron River have almost the same values (an

average of 0.16 mg-P/L, as shown earlier in Figure 4-21). Figure 4-34 shows that these samples tend to have almost the same behavior for SRP concentration changes in water. Probably the period of time for this test wasn't enough to show actual changes in SRP concentration and therefore equilibrium wasn't reached.



Figure 4-34 SRP changes for samples from Huron River by resuspension.

4.6 Sensitivity Analysis

4.6.1 Sorption Isotherm According to the Particle Size

Sediments from CS3 were separated using the standard sieves as mentioned earlier in Chapter Three. After that, the sorption isotherms for each particle size were calculated using the modified Langmuir and Freundlich isotherms, as shown in Figures 4-35 and 4-36 respectively. P sorption is highly affected by the surface area of the sediments. The smallest adsorbent sizes offer comparatively larger surface areas, hence higher phosphate removal and more available sites for sorption-desorption processes, this observation was concluded also by Özacar (2003) studies mentioned earlier in Chapter Two.



Figure 4-35 Langmuir adsorption isotherms CS3 according to particle size



Figure 4-36 Freundlich adsorption isotherms CS3 according to particle size.

It is clear that the fractions from the same sample with different particle sizes showed various behaviors unlike the original sample. The finest particle size less than 38 μ m (which contains clay and silt particles according to the classifications mentioned earlier in Chapter Two) was the most active in phosphate adsorption/desorption, this was also observed by Stone et al. (1989) study. The Langmuir plots according to the particles size gave S_{max} at 5800 mg-P/kg which is higher than the original sample at 5000 mg-P/kg. The other values are shown in Figure 4-37.



Figure 4- 37 Smax changes according to particle size.

Particles between 75 μ m and 2 mm (the sand particles) exhibit the lowest adsorption capacity at 909 mg-P/kg. Particles between 75 μ m and 38 μ m are classified as silt and sand particles, these sediments offers less surface area than the silt and clay particles (less than 38 μ m particles) and less available sits for sorption / desorption processes, its adsorption capacity was about 1428 mg-P/kg.

Jensen (1992) explained that the primary reactive elements in sediments are the clay particles and iron/manganese hydroxides. For this test the clay content of the sediment from CS3 was determined using the separation methods, and the adsorption capacities were calculated, this test proved that the clay size content plays as an important factor in determining the adsorption capacity of the sediments. The element contents and the organic content of the sediments were not evaluated, so it might be recommended to determine its contents for further studies.

4.6.2 Effect of Sediment to Solution Ratio

This test was performed using sediments from CS3 and CS2. The sediments were mixed with lake water using different ratios of 1:10, 1:20, and 1:25 for 24 h. The SRP concentration was measured using the Murphy and Riely method. From Figure 4-38, the ratio of 1:25 and 1:10 gave almost the same value of SRP released into the water column. On the other hand, the ratio of 1:20 shows less SRP released. As a conclusion, the ratio of 1:20 might be the best option to design the volume of the stirring tank.



Figure 4-38 SRP concentration in water using different sediments to solution ratios.

4.6.3 Effect of 0.01M CaCl₂ as a Background Electrolyte on a Sorption Test.

In this test, the sediments from Lake Caron were mixed with the lake water and the sediments from Huron River were mixed with the river water for 24h. Two cases were evaluated:

• In the first case all the sediment samples from Lake Caron were mixed with its water, as the initial SRP concentration in the lake water was 0.022 mg-P/L, and for the Huron River samples, the initial SRP in the river water was 0.023 mg-P/L. The sediment: solution ratio during the test was 1:25, since this ratio was used during the sorption tests. The final concentrations of SRP for the different samples after shaking for 24 h at the room temperature, the initial and final SRP concentration were measured using the Murphy and Riely (1962) method as explained earlier in Chapter
Two. Figure 4-39 shows the initial and final SRP concentrations after shaking for 24 h without adding $CaCl_2$ as electrolyte background for the sorption tests.



Figure 4-39 SRP initial and final concentration (Case 1 without adding 0.01M CaCl₂)

For case 2, water from the sources was mixed with a sufficient amount from CaCl₂ to produce a 0.01M CaCl₂ solution to match the conditions of the adsorption tests since CaCl₂ solution was used as a background electrolyte in the adsorption tests. Then the sediments were mixed with water using the same ratio 1:25 at the room temperature. The initial SRP concentration in the solution for Lake Caron was 0.013 mg-P/L, and for the Huron River was 0.015 mg-P/L. After 24h the SRP concentrations for all samples were measured using the Murphy and Riely (1962) method, and the final concentrations are shown in Figure 4-40.



Figure 4- 40 SRP initial and final concentration (Case 2 with 0.01M CaCl,)

By comparing Figures 4-39 and 4-40, the initial and final SRP in case 2 are less than the SRP concentrations in case 1. This might be due to the precipitation of the calcium compounds, and some of the P probably was sorbed on the surface of these compounds. Also during this test in the lab, it was noticed that the resuspended solutions for case 2 used to settle faster than the solutions for case 1, it might be due to the precipitation to the calcium compounds which might accelerate the settling of the particles due to coagulation forming larger particles which might settle faster, this observations were remarked by Nair (1982) and Reddy (1998), so they recommended to use 0.01 M KCl solution as a background electrolyte to avoid the precipitation of Ca in neutral and alkaline soil and sediments. Finally the sorption of the P by the sediments which might occur naturally, when the sediments interact with the water should be evaluated in situ under natural conditions to obtain better explanations.

CHAPTER FIVE

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusion

Although the sedimentary P cycle has been the topic of many previous studies, the dynamics controls and effects on P sorption in natural sediments are still not completely understood. Taking into account the originally sorbed P (S_0) when applying the modified. Langmuir and Freundlich isotherms, explains well the sorption-desorption phenomena. Also, the equilibrium concentration EPC₀ gave a good understanding in regards to the ability of the sediment, whether it will act as a potential source of P or as a sink. For Lake Caron in most of the cases, sediments will act as a source of P due to the high EPC₀ value comparing to the concentrations of SRP in the water, except for CS3 which might act as sink. For the Huron River, the sediments and the overlaying water look to be close to the equilibrium state, since the values of the SRP in the water close to the EPC₀ values and might act as a sink for the P.

The variation in the sediments particle size and distribution results in different behaviors regarding P sorption. The higher the clay content and the organic content, the higher the ability to sorb P is observed, unless the sediments contain a high TP concentration as in Huron River samples where the TP content in the sediments affects the sorption capacity. It is also important to mention that sediments with a relatively high sand content tend to fit with the Langmuir isotherm more than the Freundlich as in CS6 and CS7. On the other hand, sediments with significant clay content tend to fit the Freundlich isotherm. At low equilibrium conditions, the experimental data from samples fit well with the linear

portion of the isotherm, which supported the main assumption of the linear relationship between concentration of P in the solution and P sorbed.

5.2 **Recommendations for Further Work**

To evaluate the behaviour of the sediments in natural systems, i.e. Lake Caron and Huron River, more studies should be done to perform the filtration and resuspension techniques to improve the water quality. This might be achieved by:

- In situ resuspension of the sediments and monitoring of the SRP concentration over time, to see whether these sediments will act as a source or sink of P.
- Study the other environmental factors effects on P sorption such as pH, ORP, temperature, etc., in the laboratory and in situ.
- Selective Sequential Extraction (SSE), to estimate P fractions in the sediments.
- Perform the sorption test in the laboratory under anaerobic conditions (in the dark at temperature of 25 C° and under N₂ atmosphere) as they more closely represent the natural condition, i.e. free of oxygen atmosphere.
- Evaluate the advantages and disadvantages of the resuspension technique as a remediation process for eutrophication in surface water.
- When the laboratory sorption tests are performed, the use of fractionated P concentrations is recommended to obtain more accurate data hence improving estimation when modeling.

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- ASTM D3976- 92 Standard methods for preparation of sediments for chemical analysing.
- ASTM D 2216 Standard method for measuring the water content of sediments.
- ASTM D 2974-00 standard methods for measuring the specific gravity using a pycnometer.
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Appendix A

(A-1) Ontario Sediment Quality Guidelines (Environment Canada 2008)

Table 7 Sediment quality benchma	rks				
Substance	Ontario Sedin Guide (pp LEL ^{TV}	nent Quality lines ¹ m) SEL ^V	Canadian Freshwater Sediment Quality Guidelines ¹¹ (µg/kg)	Probable Effect Leveis ^{II} (µg/kg)	Ontario Guideline for Use at Contaminated Sites Sediments- LEL ^{III} (mg/kg)
Nitrogen (total kjeldahl) (TKN)	550	4800			
Nonyiphenol and its ethoxylates			1.4 mg/kg		
Oil and Grease		0.15% ^{VI}			
PAH (total)	4	10000			
Phenanthrene	0.56	950	41.9	515	0.56
Phosphorus (total)	600	2000			
Polychlorinated biphenyls	(total) 0.07	530	(total) 34.1	(total) 277	(total) 0.07
(PCBs)			(Aroclor	(Aroclor	
			1254) 60	1254) 340	
Pyrene	0.49	850	53	875	0.49
Silver		0.5 ^{VI}			0.5
Toxaphene			0.1		
Zinc	120	820	123 mg/kg	315 mg/kg	120

¹Ontario Ministry of Environment and Energy, "Guidelines for the Protection and Management of Aquatic Sediment Quality in Ontario," August 1993, <u>Hhttp://www.ene.gov.on.ca/envision/gp/B1-3.pdfH</u>.

[#] Canadian Council of Ministers of the Environment, "Canadian Sediment Quality Guidelines for the Protection of Aquatic Life," 1999, updated 2002, H<u>http://www.ccme.ca/assets/pdf/sedog_summary_table.pdf</u>H.

¹¹¹ Ontario Ministry of Environment and Energy, "Guideline for Use at Contaminated Sites in Ontario," Appendix 2, Table E, Sediment Quality Criteria, February 1997, Appendix revised September 1998, H<u>http://www.ene.gov.on.cu/envision/gp/3161e01_1.pdf</u>H.

^{IV} Lowest Effect Level.

^V Severe Effect Level.

(A-2) Blue-green algae report for Lake Caron Summer 2008

Ministère du Développement durable, de l'Environnement et des Parcs Québec EJ EJ

Région administrative : Bassin versant : Nom du plan d'eau : Coordonnées géographiques : Carte ci-jointe 15-Laurentides Rivière du Nord Lac Caron UTM NAD 83 18T 566 032; 5 076 719

Destinataires du mén	no d'information
Municipalité(s)	Nom du destinataire, fonction
Sainte-Anne-des-Lacs	René, Jean-François, d.g.
Observations visuelles et résultats d'a	analyses du laboratoire (CEAEQ)
Date : 2008-06-25	Lieu : Station d'échantillonnage A
Observations visuelles (fleur d'eau visible, apparen Fleur d'eau d'algues bleu-vert de catégorie 1 observe toute la superficie du lac.	ce, présence d'écume, étendue, etc.) ée en suspension dans la colonne d'eau sur
Échantillon d'une colonne d'eau d'une hauteur de 1	mètre prélevé dans le secteur ouest du lac.
Résultats d'analyses : (certificat émis le 2008/06/2' Cyanobactéries totales : 10 000 - 20 000 cellules/m Cyanobactéries à potentiel toxique : 5 000 - 10 000 4	7) al celtutes/m1
Microcystine-LR (toxicité équivalente) : 0,74 µg/l	Anatoxine-a: <0,02 µg/l

http://www.sadl.qc.ca/database/Image usager/2/Avis%20Algues%20Bleues/Lac%20Car

on.pdf

Δ.

(A-3) Lake Caron

Centre d'expertise hydrique QUÉDEC

Bureau du directeur général

Nom du barrage:	Barrage numéro 1577035029 - Lac Caron
Remarques :	Par la rue Godetroy, Pinson et des Pétunias

Nom du réservoir: CARON

Municip 77035 Sa	alité(s) ainte-Anne-des-	Lacs				M.R.C. Les Pays-d'en-Haut	Région(s) administrative(s) Laurentides						
Carte to	pographique		Co	ordonné	es UTI	W NAD 83	Coordonnées degrés, minutes, secondes NAI						
Numéro 31G18	Échelle	Feuillet	Zon 18	e X (1 56612	Est) 21,800	Y (Nord) 5076813,115	Lat 45° 50	ti tude 1 [°] 30, 155"	Longitude 74° 8' 54,577"				
Hydrogr	aphie												
Туре	Numéro	Nom				Numéro	Nom bassii	n primaire					
Bassin	04017000	BONNIEI	BROOK			04300000	OUTAOUAI	S, RIVIÈRE DES					
Lac	F3219	CARON,	LAC			04300000	OUTAOUAI	S, RIVIÈRE DES					
Catégorie	administrative	9:	Forte cont	enance		Année de	modification:	1960					
Année de	construction:		1960			Longueur	(m):	90,00					
Année de	modification:					Revanche	(m):	0,20					
Hauteur d	lu barrage (m):		8,4										
Hauteur d	le retenue (m):		7,2										
Superficie	e du réservoir (ha):	3,54										
Superficie	ə bassin vərsar	nt (km²):	1,0										
Capacité	de la retenue (i	m"):	50 200										

(A-4) Lake Caron



Appendix B

(B-1) Calibration Curve



Calibration Curve Standards for TP





(B-2) S_0 Calculations: using E.q (5) S' = K'C - S₀



So calculation CS1



So calculation CS2

So calculation CS3







So calculation CS5



C mg-p/l















So calculation HS5











Linear langmuir isotherm CS1

Linear langmuir isotherm CS2





Linear langmuir isotherm CS4



Linear langmuir isotherm CS3





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Linear langmuir isotherm CS5





Linear langmuir isotherm HS5







Linear langmuir isotherm HS7



(B-4) Freundlich Isotherm



Linear freundlich isotherm CS2



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freundlich adsorption isotherm CS5





Linear freundlich isotherm HS1



Linear freundlich isotherm HS5



Linear freundlich isotherm HS6



Linear freundlich isotherm HS7



Appendix C

(Particle size distribution CS1)

HORIBA Laser Scattering Particle Size Distribution Analyzer LA-950

Sample Name	: lake caron	Median Size	: 141.32735(µm)
ID#	: 200811031511095	Mean Size	: 268.53891(um)
Data Name	: lakecaronS12	Variance	: 73480(um ²)
Transmittance(R)	: 90.7(%)	Std.Dev.	: 271.0728(um)
Transmittance(B)	: 91.7(%)	Mode Size	: 556.1606(um)
Circulation Speed	: 5	Span	: OFF
Agitation Speed	: 2	Geo.Mean Size	: 145.1685(µm)
Ultra Sonic	: OFF	Geo.Variance	: 1.8734(µm ²)
Form of Distribution	: Auto	Skewness	: 1.1576
Distribution Base	: Volume	Kurtosis	: 3.5244
Material	: sediments	Diameter on Cumulative %	: (2)10.00 (%)- 29.9723(µm)
Source	: lake caron		: (9)90.00 (%)- 682.8786(um)
Sample Number	:	•	(,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,
Test or Assay. Number	: 00002		
Refractive Index (R)	: soil[soil(1.230 - 0.000i),Water(1.333)]		
Refractive Index (B)	: soil[soil(1.230 - 0.000i),Water(1.333)]		



		Diar	meter			Dismete	4 .			Dia	neter			Diamete	er.
	Diameter	PH	MILS	Microns	Frequency	Frequency	CUMULATIVE		Diameter	PHi	MILS	Microns	Frequency	Frequency	CUMULATIVE
F PEBBLE	5	-2.00	157.48	4000.00	6.00	0.00	100.00	V FINE SILT		6.00	0.15	3.91	0.00	0.02	0.0
	6	-175	132.42	3363.59	C.00		100.00			8.25	0 13	3.28	0.00		0.0
	7	-1.50	111.36	2828.43	C.00		100.00			8.50	0.11	2.76	0.00		0.00
	8	-1.25	93,64	2378 41	0.00		100.00			8.75	8.09	2.32	0.00		0.00
FINE PEBBLE	10	-1.00	78.74	2000.00	C.00	0 00	100.00			9.00	0 0B	1.95	0.00		0.00
	12	-0.75	66.21	1681.79	C.00		100.00			9.25	0.06	1.64	0.00		0.00
	14	-0.50	55.68	1414.21	0.00		100,00			9.50	0.05	1.38	0.00		0.00
	16	-0.25	46.82	1189.21	6.39		99.61			9.75	0.05	1.16	0.00		0.00
V CRS SAND	18	C D0	39.37	1000.00	1,13	1,52	98 48	CLAY		10.00	0.04	0.98	9.00	0.00	0.00
••	20	0 25	33.11	840.90	2.74		95.74			10.25	0.03	0.82	0.00		0.00
	25	0.50	27.84	707.11	4.66		91.08			10.50	0.03	0.69	0.00		0.00
	30	0.75	23.41	594.60	6.08		85 00			10 75	C.02	0.58	0.00		0.00
CRS SAND	35	1 00	19.69	\$00.00	6.26	19.74	78 74			11.00	0.02	6.49	0.00		0.00
	40	1.25	16.55	420.45	5.57		73.17			11.25	0.02	0.41	0.00		0.00
	45	1.50	13.92	353,55	4.72		62 44			11.50	0.01	0.35	0.00		0.00
	50	1,75	11.70	297.30	3.95		64 50			11.75	0.01	0.29	0.00		0.00
MED SAND	60	2.00	9.64	250.00	3.53	17.78	60 96			12.00	0.01	0.24	0,00		0.00
	70	2.25	8.25	210.22	3.44		57.53			12.25	0.01	0 21	0.00		0.00
	80	2.50	6.95	175,78	3.38		54 15:			12.50	0.01	0.17	0.00		0.00
	100	2.75	5.85	145.65	3.24		50.91			12.75	0.01	0 15	0.00		0.00
FINE SAND	120	3 00	4.92	125.00	3.67	13 12	47.84			13.00	3.00	0 12	8 99		8.90
	14G	3.25	4 14	105.11	3.22		44.62			13.25	9.00	6,10	0.00		0.00
	170	3 50	3 48	58.39	4 42		40.20			13.50	0.00	G.09	0.08		0.00
	200	3,75	2.93	74.33	5.61		34,58			13.75	0.00	C 07	0 00		0.00
V FINE SAND	230	4 60	2.46	62.50	5.79	19.05	28.80			14.00	9,00	0.06	C 00		0.00
	270	4.25	2.07	52.56	5.60		23 20			14.25	0.00	C 05	0.00		0.00
	325	4.50	1,74	44 19	5.09		5.11°			14.50	0.00	C.04	C 00		0.00
	430	4,75	1.45	37.1E	4.21		13 90			14.75	0.00	0.04	C.00		0.00
CRS SILT	450	5.0C	1.23	31.25	3.22	18 11	10.68			15 00	0,00	0.03	0.00		6.00
	500	5.25	1.03	26.25	2,46		5.22			15.25	0.00	0.03	000		C.00
	635	5 50	0.87	22.10	2.10		5.12			15.50	0.00	0,02	0 00		G 00
		5,75	0.73	18.58	193		4.19			15 75	0.00	0.02	0 00		C.00
MED SILT		6.00	0.62	15,63	1.52	8 11	2 57			*6.00	0 09	0 02	C 00		0.00
		6.25	9.52	13.14	1 17		1.40.			16.25	0 05	0.01	0 00		0.00
		6 50	5.42	44.04	0.75		2 4 2	00000		16 62	0.00	5.01	6.00	0.00	C-02



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(Particle size distribution CS3)

Nai me ttar ttar itar itar itar Nui Nui Nui Nui Nui Nui Nui Nui Nui Nui	ne ce(R Spee beed tribut Base nber ay. N ndex ndex)) d ion (R) (B)	ber	121232520AVS12055	ake c 0081 akeca 90.0(38.5(0)FF oluto 'olum ake c 0002 oil[sc oil[sc	aron 10315 ironS3 %) %) ients aron pil(1.2 pil(1.2	341101 31 30 - 0. 30 - 0.	000i),V 000i),V	Vaten	(1.33 3 (1.33 3	9)] 9)]	M N V S M S C C S H E	Median Mean S /arianc Std. Dev Mode S Span Geo. Ma Geo. Va Skewne Curtosis Diamete	Size Size Size Size Size Size Size Size	ce Cumula	ative %	: 245.95 : 458.18 : 2.7016 : 519.7 : 831.8 : OFF : 205.5 : 2.6050 : 1.40 : 4.48 : (2)10.0 : (9)90.0	9821(µm 3140(µm 3E+5(µm 881(µm) 964(µm) 621(µm ²) 70 05 00 (%)-1 00 (%)-1))) ²)) 22.0 251.
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			Diame	36	1.0000		4000 XC	0.0		0.00	100 00	V FINE SILT		8 25	0.15	3.91	9 03 3 00	C.97	
	P≅BBi	.E	Diame	5 E	-2.00	132.42	3363.54							8 50	0.11	2.75	0 00		
	PEBBI	E	Diame	5 6 7 8	-2.00 -1.75 -1.50 -1.25	132.42 111.38 93.64	3363 59 2628 43 2378.41	0 O 0.4	3		100.00			8 75	0.09	2.32	0.00		
Fint	PEBBI	Е Е	Diame	5 E 7 8 10 12	-2.90 -1.75 -1.50 -1.25 -1.00 -0.75	132.42 111.38 93.64 78.74 66.21	3363 59 2828 43 2378.41 2000 00 1681.79	00 0.4 1.1 2.2) 	1.56	160.00 99.59 98.44 96.21			875 900 925	0.09 0.03 0.05	2.32 1 95 1.64	0.00		
FIN	PEBBI	LE	Diame	5 7 8 10 12 14	-2.90 -1.75 -1.50 -1.25 -1.90 -0.75 -0.50 -0.25	132.42 111.38 93.64 78.74 66.21 55.68 45.62	3363 59 2628 43 2378 41 2000 00 1681.79 1414 21 1189.21	00 0.4 1.1 22 3.3 4.1) 5 1 1	1.56	100.00 99.59 98.44 96.21 92.88 88.72			8 75 9 00 9 25 9 50 9 75	0.09 0.08 0.05 0.05 0.05	2.32 1.95 1.64 1.38 1.15	0.00 0.00 0.00 0.00		
FINI V Ç	PEBBI PESBI	LE	Diame	5 7 8 10 12 14 18 18 20	-2.00 -1.75 -1.50 -1.25 -1.00 -0.75 -0.50 -0.25 0.00 0.25	132.42 111.38 93.64 78.74 66.21 55.68 45.62 39.37 33.11	3363 59 2828 43 2378 41 2000 00 1681.79 1414 21 1189 21 1000 00 640 90	00 0.4 1.1 2.2 3.3 4.1 6.7 5.0		1.56 4.42	100.00 99.59 98.44 96.21 92.88 88.72 84.02 78.98	YAJO		8 75 9 00 9 25 9 50 9 75 10.00 10.25	0.09 0.08 0.05 0.05 0.05 0.05 0.05	2.32 1.95 1.64 1.38 1.15 0.98 0.62	0.00 0.00 0.00 0.00 0.00 0.00	6.00	
FINE V C	: PEBBI : PESBI RS S41	LE IC	Diame	5 7 8 10 12 14 18 20 25 30	-2.00 -1.75 -1.50 -1.25 -1.00 -0.75 -0.50 -0.25 0.00 0.25 0.50 0.50 0.75	132.42 111.38 93.64 78.74 66.21 55.68 45.82 39.37 33.11 27.84 23.41	3363 59 2628 43 2378 41 2000 00 1681.79 1414 21 1189 21 1000 00 840 90 707 11 594 50	00 04 1.1 22 3.3 4.1 4.7 5.0 5.0 5.0 4.8		1.56 4.42	100.00 99.59 98.44 96.21 92.88 88.72 84.62 73.95 69.15	CLAY		8 75 9 00 9 25 9 50 9 75 10.00 10.25 10 50 10.75	0.09 0.06 0.05 0.05 0.04 0.03 0.03 0.03 0.02	2.32 1 95 1.64 1.38 1.15 0.95 0.69 0.69 0.56	0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.0	6.00	
Fini V C	PEBBI PESBI RS SAN	LE IC ID	Diame	5 7 8 10 12 14 16 18 20 25 30 35 40	-2.00 -1.75 -1.50 -1.25 -1.25 -0.50 -0.25 0.00 0.25 0.50 0.75 1.00 1.25	137.48 132.42 111.38 93.64 78.74 65.21 55.68 45.82 39.37 33.11 27.84 23.41 19.69 18.55	3363 59 2628 43 2378 41 2900 00 1681.79 1414 21 1189 21 1000 00 640 90 707 11 554 50 506 00 420 45	00 0.4 1.1 2.2 3.3 4.1 4.1 5.0 5.0 5.0 4.8 4.3 4.3 3.9		1.56 4.42 9.18	100.00 99.59 98.44 96.21 92.88 88.72 84.62 73.95 69.15 64.84 60.90	CLAY		875 900 925 950 975 10.00 10.25 10.30 10.75 11.00 11.25	0.09 0.08 0.05 0.05 0.05 0.05 0.05 0.03 0.03 0.03	2.32 1 95 1.64 1.35 0.96 0.62 0.69 0.56 0.49 0.41	0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.00	6.00	
Fini VC C	PEBBI PESBI RS SAN	LE IC ID	Diame	5 7 8 10 12 14 18 20 25 30 35 40 45 50	-2.00 -1.75 -1.50 -1.25 -1.00 -0.75 -0.25 0.00 0.25 0.50 0.75 1.00 1.25 1.50 1.50 1.25 1.50 1.75 1.50 1.75 1.50 1.75	137.46 132.42 111.38 93.64 78.74 66.27 55.68 45.55.75.75.75.75.75.75.75.75.75.75.75.75	3363 59 2628 43 2378 41 2030 30 1681.79 1414 21 1189 21 1000 30 640 90 707 11 594 50 506 00 420 45 355 55 297 30	00 0.4 1.1 2.2 3.3 4.1 6.7 5.0 5.0 5.0 5.0 4.8 4.3 3.9 4.3 3.9 3.8 3.8 3.8 3.4		1.56 4.42 9.18	100.00 99.59 98.44 96.21 92.88 98.72 84.62 73.95 69.15 64.84 60.90 57.24 53.77	CLAY		8 75 9 00 9 25 9 50 9 75 10.00 10.25 10.75 11 00 11 25 11 30 11 75	0.09 0.08 0.05 0.05 0.04 0.03 0.02 0.02 0.02 0.02 0.02 0.02	2.32 1 95 1.64 1.38 1.15 0.96 0.56 0.49 0.49 0.49 0.49 0.49	000 000 000 000 000 000 000 0.00 0.00	6.00	
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FINE VC C M	PEBBI PEBBI RS SAN RS SAN ED SAN		Diame	5 7 8 10 12 14 18 18 20 23 30 40 45 50 60 20 20 40 40 40 40 40 40 40 40 40 4	$\begin{array}{c} -2.00\\ -1.75\\ -1.25\\ -1.00\\ 0.75\\ -0.50\\ 0.25\\ 0.50\\ 0.75\\ 1.20\\ 1.50\\ 2.25\\ 2.55\\ 2.55\\ 2.55\\ 3.25\\ \end{array}$	137.422 137.422 137.422 131.38 93.66.21 55.68 45.62 45.62 45.62 45.62 39.37 33.11 19.69 18.59 18.59 18.59 11.70 9.34 8.284 23.41 19.69 5.65 5.65 5.65 5.65 5.65 5.65 5.65	3363 55 2628 43 2628 43 2078 44 2000 00 1681 79 1681 79 1681 79 1681 79 1681 79 1681 79 1681 79 1681 79 1681 79 640 90 640 90 640 90 640 90 707 11 564 50 250 00 210 22 215 76 148 85 125 00 105 11	00 04 11 22 33 41 42 50 50 50 50 50 48 43 43 43 39 38 34 34 34 33 32 33 32 33 32 33 32		1.55 4.42 9.18 4.51	100.00 99.5e 98.44 96.21 92.88 88.72 84.62 73.95 69.15 64.84 60.50 57.24 53.77 50.32 46.83 73.95 50.32 46.83 73.95 50.32 46.83 73.95 50.32 73.95 50.32 73.95 50.32 73.95 50.32 73.95 50.32 73.95 50.32 74.53 75.24 75.25	CLAY		875 9005 9975 1005 10075 11120 11120 11120 11120 11120 1205 1205	0.69 0.08 0.05 0.65 0.65 0.64 0.63 0.63 0.63 0.62 0.62 0.62 0.62 0.61 0.61 0.61 0.61 0.61 0.61 0.61 0.61	2.32 1 95 1.64 1.38 1.15 0.95 0.69 0.56 0.49 0.56 0.49 0.41 0.29 0.24 0.24 0.24 0.21 0.15 0.15 0.15 0.15 0.15	0.00 0.00	6.00	
FINI VC C	F PEBBI F PEBBI RS SAH RS SAH ED SAN			5 F 7 8 10 12 14 18 20 25 30 35 40 20 20 20 20 20 20 20 20 20 2	-2.00 -1.75 -1.50 -1.25 -1.00 -0.75 -0.25 -0.	137.42 137.42 137.42 137.42 111.38 93.64 27.74 66.27 55.68 45.82 39.37 33.11 27.84 45.82 39.37 33.11 27.84 45.82 39.37 13.74 19.69 13.92 11.70 9.34 45.82 6.96 5.55 6.96 5.55 4.92 4.92 4.93 2.93 2.93	3363 55 2628 43 2628 43 2000 00 1681 79 1681 79 1682 79 100 20 640 90 546 56 500 00 640 45 594 56 500 00 640 45 594 56 500 00 250 0000000000	00 04 1:1 22 33 4:1 4:7 5:0 5:0 5:0 5:0 5:0 5:0 3:9 3:9 3:9 3:9 3:4 3:4 3:4 3:3 3:3 3:3 3:4 3:4 3:4		1.56 4.42 9.18 4.51 3.64	100.00 99.59. 98.44 96 21 84.62 78.98 73.96 73.96 73.96 73.96 73.96 73.96 73.96 73.96 73.96 73.96 73.96 73.96 73.96 75.74 50.32 75.74 50.32 57.74 50.32 50.55 50.5	CLAY		875 9005 950 950 1005 1005 1005 1005 1005	0.69 0.68 0.65 0.65 0.65 0.63 0.63 0.63 0.63 0.63 0.63 0.63 0.63	2.32 1 954 1.64 1.38 1.15 0.96 0.65 0.49 0.46 0.49 0.44 0.41 0.35 0.29 0.24 0.21 0.17 0.15 0.12 0.17 0.15 0.12 0.17 0.15 0.12 0.67	000 000 000 000 000 000 000 000	6 <u>.00</u>	
FINE VC C M FI	F PEBBI F PEBBI RS SAN RS SAN ED SAN VE SAN			5 6 7 8 10 12 14 18 18 20 230 35 40 50 60 70 80 60 70 80 80 70 80 80 80 80 80 80 80 80 80 8	$\begin{array}{c} -2.00\\ -1.75\\ -1.50\\ -1.25\\ -1.00\\ -0.75\\ -0.25\\ -0.25\\ 0.50\\ 0.5$	137.422 137.422 111.32 136.42 111.38 93.64 278.74 135.68 135.62 135.76 135.77 19.69 18.55 13.57 19.69 18.55 13.57 1.70 9.34 8.29 11.70 9.34 8.29 4.92 4.93 4.92	3363 55 2628 43 2628 43 2000 00 16581.79 1414 21 1189.21 1000 00 640 90 777 11 594 50 500 00 420 45 303 55 250 00 420 45 216 22 216 22 2175 76 145 65 125 00 105 11 88 39 74 35 85 250	00 04 1:: 22 33 4:: 4,7 50 50 50 50 4,8 4,3 34 34 34 34 33 34 33 34 33 34 33,3 3,4 3,3 3,4 3,2 2,8		1.56 9.18 4.51 3.64 3.45	100.00 99.50 98.44 96.21 92.88 98.72 94.62 73.965 69.15 7.24 57.24 57.24 50.32 46.33 39.68 39.68 39.58 39.68 39.58 20.32	CLAY		875 99250 99505 900250 900250 100250 111200 111200 1112050 112000 112050 110000 110000 11000000	0.69 0.68 0.65 0.65 0.64 0.63 0.62 0.62 0.62 0.62 0.62 0.62 0.61 0.61 0.61 0.61 0.61 0.61 0.61 0.61	2.32 1 955 1.64 1.38 1.15 0.96 0.69 0.69 0.41 0.35 0.29 0.24 0.24 0.21 0.17 0.15 0.12 0.17 0.15 0.12 0.17 0.15 0.12 0.17 0.15 0.24 0.24 0.24 0.24 0.24 0.24 0.24 0.24	200 200 200 200 200 200 200 200	6. <u>22</u>	
FINI VC C M FI	F PEBBI RS SAN RS SAN ED SAN VE SAN			5 E 7 8 10 12 14 16 18 20 30 35 60 20 20 30 70 30 70 30 77 5 20 3	$\begin{array}{c} -2.00\\ -2.00\\ -1.50\\ -1.1.25\\ -1.1.25\\ -0.0.75\\ -0.0.50\\ -0.250\\ -0.250\\ 0.0.25\\ 0.0.25\\ 0.0.25\\ -0.250\\ -0.25\\ -0$	137.42 137.42 111.38 137.42 111.38 136.44 136.4 136.47 136.47 136.47 136.47 136.47 136.47 137.44 139.55 119.69 13.92 11.70 9.34 1.82 9.55 4.92 1.70 9.34 2.78 4.348 2.93 2.97 1.74 1.44 2.97 1.74 1.44 2.97 1.74 1.44 2.97 1.74	3363 55 2628 43 2628 43 2000 00 1681.79 1414 21 1189.21 1000 00 640 50 707 11 1594 50 500,00 420 45 353 55 250 00 250 60 250 60 105,11 88,39 74 33 86 250 52 50 52 50 50 50 50 50 50 50 50 50 50 50 50 50 5	00 04 1:: 22 33 4: 50 4: 35 56 4: 35 36 34 34 33 34 33 34 33 34 33 34 33 34 32 32 32 32 32 32 32 32 32 32 32 32 32		1.56 9.18 4.51 3.64 3.45	100.050 99.562 98.441 962 11 922 88, 94.022 73 965 73 97 75 92 74 75 92 74 75 92 75 95 75 95	CLAY		8 75 0 0 5 0 0 10 0 10 0 0 11 11 20 25 0 5 10 0 10 0	0.69 0.68 0.65 0.65 0.64 0.63 0.62 0.62 0.62 0.62 0.61 0.61 0.61 0.61 0.61 0.65 0.65 0.65 0.65 0.65 0.65 0.65 0.65	2.32 1 955 1,64 1.15 0.96 0.659 0.56 0.49 0.41 0.35 0.29 0.24 0.24 0.21 0.17 0.17 0.17 0.17 0.17 0.17 0.12 0.12 0.12 0.12 0.12 0.12 0.12 0.12	5 05 5 05	6.05	
FINE VC C M FI	F PEBBI FEEBBI RS SAN RS SAN RS SAN <u>ED SAN</u> <u>NE SAN</u> <u>VE SAN</u>	LE IC ID ID		s = 7 s = 10 7 s = 10 12 14 18 20 225 33 5 40 45 50 70 80 60 20 20 20 20 20 20 20 20 20 20 20 20 20	$\begin{array}{c} -2.00\\ -2.00\\ -1.50\\ -1.50\\ -1.1.25\\ -0.050\\ -0.25\\ -0.250\\ -0.$	132.42 132.42 111.38 93.64 78.74 66.74 55.68 445.82 39.37 33.31 33.31 33.31 127.84 45.68 45.6	3363 55 2828 43 2978 41 2000 00 1681 79 1118 21 118 21 1000 00 840 50 504 50 505 00 207 07 11 554 50 505 00 207 07 215 25 250 00 255 00 255 00 255 00 105 11 88 39 74 33 82 56 85 55 125 00 105 11 88 39 74 33 82 56 85 55 125 00 105 11 15 76 125 00 105 11 15 76 125 00 105 11 15 76 125 00 105 11 15 76 125 00 15 76 125 00 125 000000000000000000000000000000000000	00 04 04 1:: 33 35 50 48 43 43 36 34 34 34 34 34 34 34 34 33 34 34 34 34		1.56 4.42 9.18 4.51 3.64 2.43 9.28	100.09 99.58 98.44 96.21 97.28 88.73 84.62 87.395 64.84 60.94 57.24 53.73 95 64.84 60.94 57.24 53.73 95 64.84 60.94 57.24 53.73 95 64.84 57.24 53.73 95 64.84 57.24 53.73 29.54 20.25 20.2	CLAY		8 750 9 9 250 9 9 9 750 10 10 10 10 10 10 10 10 10 10 10 10 10 1	0.69 0.65 0.65 0.65 0.65 0.65 0.63 0.63 0.63 0.63 0.63 0.63 0.63 0.63	2.32 1 955 1.64 1.38 0.69 0.56 0.49 0.56 0.49 0.24 0.21 0.21 0.21 0.15 0.24 0.24 0.21 0.21 0.15 0.24 0.24 0.21 0.15 0.24 0.24 0.21 0.15 0.55 0.24 0.24 0.21 0.15 0.55 0.24 0.24 0.21 0.55 0.24 0.55 0.55 0.24 0.55 0.55 0.24 0.55 0.55 0.55 0.24 0.55 0.55 0.55 0.55 0.55 0.55 0.55 0.5	0.00 0.00	6.05	
	F PEBBI F PEBBI RS SAN RS SAN ED SAN NE SAN NE SAN NE SAN	LE ID ID .T		5 E 7 8 10 12 14 18 20 5 33 40 45 5 60 70 80 60 22 14 0 77 8 30 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5	$\begin{array}{c} 2.00\\ -2.00\\ -1.50\\ -1.25\\ -1.25\\ -0.50\\ -0.50\\ -0.50\\ -0.50\\ -0.55\\ -0.$	132.42 132.42 111.38 93.64 78.74 66.74 55.68 45.55 68 45.32 33.31 33.31 33.31 33.31 127.84 45.56 83.33 13.32 13.57 13.56 8.55 13.59 14.55 13.59 14.55 13.59 14.55 13.59 14.55 14	3363 55 2828 43 2978 41 2000 00 1681 79 1182 21 1182 21 1000 00 640 90 707 11 594 50 506 00 250 00 250 00 250 00 250 00 250 00 250 00 250 00 255 00 255 00 255 00 105 11 88 39 74 33 82 56 33 125 00 105 11 125 00 105 11 125 00 125 000000000000000000000000000000000000	0 0 0 4 1:1 2 2 3 3 4 1 4 7 5 0 5 0 5 0 5 0 4 8 3 4 3 4 3 4 3 4 3 4 3 4 3 4 3 4 3 4 3 4		1 55 4 42 9 18 4 51 3 64 3 64 9 28	100.09.50 99.54 96.211 96.211 97.283 98.73 96.283 98.73 96.283 98.73 96.283 98.73 96.283 98.73 96.243 99.54 99.57 24.43 25.73 26.438 20.353 27.59 26.439 27.59 2	CLAY		8 750 9 9 9 9 700 3 9 9 9 700 3 00 10 10 10 10 10 10 10 10 10 10 10 10	0.69 0.65 0.65 0.65 0.65 0.65 0.65 0.65 0.65	2.32 1 95 1 64 1 38 1 15 0 95 0 49 0 56 0 49 0 44 0 24 0 55 0 49 0 55 0 49 0 49 0 49 0 55 0 55 0 55 0 49 0 55 0 55	000 000 000	6. <u>66</u>	
	F PEBBI E PEBBI RS SAN RS SAN ED SAN NE SAN NE SAN NE SAN NE SAN	LE IC IC ID ID .T		6 E 7 8 10 12 11 18 12 25 30 35 14 50 0 70 0 30 0 15 0 35 15 15 0 35 15 0 35 15 15 0 35 15 0 35 15 0 35 15 0 35 15 0 35 15 15	$\begin{array}{c} 2.00\\ -2.00\\ -1.50\\ -1.25\\ -1.50\\ -1.25\\ -0.$	137.42 137.42	3363 55 2528 43 2578 41 2000 00 1681 79 1681 79 1682 79 1682 79 1000 00 564 50 1000 00 564 50 565 50 500 00 210 22 250 00 105 11 188 39 74 33 56 250 105 12 125 00 52 56 44 19 37 16 31 25 26 26 21 0 25 65 26 26 21 0 25 65 26 26 21 0 25 56 21 0 25 56 25 56	0,4 0,4 1,1 2,2 3,3 4,1 4,7 5,0 5,0 5,0 5,0 5,0 5,0 5,0 5,0		1 55 4 42 5 12 4 51 3 64 2 43 9 28 6 18	100.00 99.56 98.44 99.243 99.243 99.243 99.243 99.243 73.945 73.945 57.24 50.32 57.24 53.77 50.32 50.32 53.73 50.32 53.73 50.32 53.73 50.32 53.73 50.32 53.73 50.32 53.73 50.32 53.73 50.32 53.73 50.32 53.73 50.32 53.73 50.32 50.55 50.5	CLAY		8 750 250 50 250 50 250 250 250 250 250 250	0.09 0.06 0.05 0.05 0.05 0.05 0.05 0.05 0.05	2.32 1.955 1.64 1.38 1.15 0.96 0.62 0.42 0.41 0.35 0.44 0.29 0.24 0.21 0.15 0.15 0.15 0.15 0.15 0.15 0.15 0.15 0.15 0.25 0.21 0.25 0.21 0.25 0.21 0.25 0.25 0.25 0.21 0.25	000 000 000 000 000 000 000 000 000 00	6. <u>22</u>	
	F PEBBI E PEBBI RS SAN RS SAN ED SAN NE SAN NE SAN NE SAN	LE ID ID .T		5 E 7 8 10 12 25 33 5 10 12 25 33 5 10 12 25 33 5 10 12 25 33 5 10 12 25 33 5 10 12 12 12 12 12 12 12 12 12 12 12 12 12	$\begin{array}{c} 2.00\\ -2.00\\ -2.01\\ -2.02\\ -2.$	137.60 137.42 111.38 152.42 111.38 156.44 157.62.44 157.62.44 155.64 157.62 145.22 145.22 145.22 147.00 15.92 117.00 15.92 15.9	3363 45 3363 45 2628 43 27628 43 2000 00 1681.79 1414 21 1185.21 1000 00 640 90 707 11 1185.21 1000 00 640 90 707 11 1185.21 1000 00 640 90 707 11 550 00 200 45 353 56 250 00 215 76 88 39 74 33 82 50 255 00 215 76 88 39 74 33 82 50 255 00 125 125 125 00 125 125 125 125 125 125 125 125 125 125	0 0 0 4 1 1 2 2 3 3 4 1 5 0 5 0 5 0 5 0 5 0 5 0 5 0 5 0 5 0 5 0		1.55 9.18 4.51 3.64 3.243 9.28 8.18	100.00 99.56 98.44 99.24 99.24 99.24 99.24 99.24 99.24 99.24 99.24 99.24 99.24 99.24 99.24 99.24 99.54 99.54 99.54 99.54 99.54 99.54 99.54 99.54 99.54 99.54 99.54 99.54 99.54 99.54 99.54 99.54 99.54 99.54 99.55	CCILOID		8 9 9 9 9 9 10 10 11 11 11 12 12 12 13 13 14 14 14 15 15 15 15 16 16 16 16 16 16 16 16 16 16 16 16 16	0.09 0.05 0.05 0.05 0.05 0.05 0.05 0.05	2.32 1.955 1.64 1.38 0.96 0.62 0.62 0.41 0.29 0.21 0.21 0.21 0.15 0.15 0.15 0.15 0.15 0.15 0.15 0.15 0.15 0.25	000 000 000 000 000 000 000 000 000 00	<u> </u>	
	F PEBBI F PEBBI RS SAM RS SAM RS SAM ED SAM NE SAM NE SAM JPS SII AED SAI	LE IC IC ID ID ID ID		5 7 8 10 12 14 18 18 12 20 20 20 20 20 20 20 20 20 2	$\begin{array}{c} 2.00\\ -2.$	$\begin{array}{c} 13, 22, 22\\ 131, 33, 42\\ 131, 35, 44\\ 52, 74, 135, 64\\ 56, 27\\ 155, 66, 27\\ 155, 66, 27\\ 155, 66, 27\\ 155, 66, 27\\ 155, 66, 27\\ 155, 66, 27\\ 155, 66, 27\\ 155, 66, 27\\ 155, 66, 27\\ 155, 66, 27\\ 155, 25\\ 155, 27\\ 110, 20\\ 100, 20\\ 1$	3463 59 2283 43 2378 44 2528 43 2378 44 2528 43 2378 44 2528 43 2378 44 14 22 12 2508 50 2528 50 50 50 50 50 50 50 50 50 50 50 50 50	0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0		1.55 4.42 9.18 3.64 3.64 9.28 8.18 8.18	100.00 96.50 96.21	CLAY		8 75 9 9 25 9 9 9 25 9 9 9 75 10 25 10 br>10 25 10 10 25 10 10 10 25 10 10 10 10 10 10 10 10 10 10 10 10 10	0.09 0.06 0.05 0.05 0.05 0.05 0.05 0.05 0.05	2.32 1.95 1.64 1.38 1.15 0.65 0.42 0.45 0.44 0.24 0.24 0.24 0.25 0.25 0.25 0.55 0.25 0.55 0.25 0.55	0 000 0 0000 0 0000 0 0000 0 0000 0 0000 0 0000 0 0000 0 00000	<u>. 20</u> 0 	

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(Particle size distribution CS4)



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(Particle size distribution CS5)



(Particle size distribution CS6)



HORIBA Laser Scattering Particle Size Distribution Analyzer LA-950

Sample Name : ID# : Data Name : Transmittance(R) : Transmittance(B) : Circulation Speed : Agitation Speed : Ultra Sonic : Form of Distribution : Distribution Base : Material : Source : Sample Number : Test or Assay. Number : Refractive Index (R) :

lake caron 200811031628110 lakecaronS72 91.2(%) 92.3(%) 5 2 OFF Auto Volume sediments lake caron 00002

- 00002 soil[soil(1.230 - 0.000i),Water(1.333)] soil[soil(1.230 - 0.000i),Water(1.333)]
- Median Size Mean Size Variance Std.Dev. Mode Size Span Geo.Mean Size Geo.Variance Skewness Kurtosis Diameter on Cumulative %

: 192.03979(µm) : 222.65384(µm) : 19412(µm²) : 139.3277(µm) : 139.3277(µm) : 0FF : 0FF : 180.2124(µm) : 1.2482(µm²) : 1.3282 : 5.2323 : (2)10.00 (%)- 79.2644(µm) : (9)90.00 (%)- 412.7701(µm)



(Particle size distribution HS1)





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(Particle size distribution HS6)

Laser Scattering Particle Size Distribution Analyzer LA-950 HORIB Sample Name ID# lake caron 200811031744128 Median Size 81.09304(µm) 135.38969(µm) 20738(µm²) Mean Size Variance Data Name huronsrivers62 Transmittance(R) 82.5(%) 144.0054(µm) Std.Dev. Transmittance(B) 75.9(%) Mode Size 214.7704(µm) OFF **Circulation Speed** 5 Span 62.3946(µm) Agitation Speed 2 Geo.Mean Size Ultra Sonic OFF Geo.Variance 2.5381(µm²) Form of Distribution Auto Skewness 1.4070 4.7106 (2)10.00 (%)- 7.0544(μm) (9)90.00 (%)- 342.8344(μm) Distribution Base Material Volume Kurtosis sediments Diameter on Cumulative % Source lake caron Sample Number Test or Assay. Number 00002 soil[soil(1.230 - 0.000i),Water(1.333)] soil[soil(1.230 - 0.000i),Water(1.333)] Refractive Index (R) Refractive Index (B) LA-950 Phi Scale Graph SAND SILT CLAY COLLOID med 100 6.7 -----6.0 90 **584** 5.4 80 4.7 70 × 60 4.0 ulative Frequency 50 3.4 50 40 2.7 30 2.0 **a2**8 20 1.3 018 10 0.7 ٥ 0.0 1000 100 0.1 0.01 4000 10 1 μm PARTICLE DIAMETER PHI -2 -1 0 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 Diameter Diameter Diameter Diameter requency CUMULATIVE TIVE Diameter MILS PHI PH Ciameter MILS Micro cuency Cl 4000.00 3363.59 2828.43 2378.41 2000.00 1681.79 1414.21 1189.21 0.00 100 00 100 00 100 00 100 00 8 00 8 25 8 50 8 75 9 00 9 25 9 50 9 75 FPEBBLE 157.48 152.42 111.35 93.64 76.74 55.68 46.82 39.37 33.11 27.84 23.41 19.69 16.55 13.52 11.76 54 8.28 V FINE SILT 5 13 5 13 5 13 5 13 5 09 5 08 6 205 5 08 6 205 6 0.04 0 0.03 0 0.02 6.61 3 11 3 276 2 762 2 7 6 8 10 12 14 15 18 20 50 35 45 50 60 70 FINE PEBBLE 100.00 100.00 100.00 100.00 100.00 0.00 0.00 V CRS SAND CLAY 4.21 100.00 99.72 55.89 97.10 94.41 90.73 35.08 80.65 74.95 CRS SAND 2.90 MED SAND 16.44 69.45 64.52 80 100 120 120 120 230 230 270 325 400 450 500 535 5.50 4 93 4.47 4 17 3.94 3.88 3.72 5 45 FINE SAND 20.60 60.05 55.64 60.05 51.64 64.38 67.72 31.56 7.72 31.56 7.72 25.75 44.38 67.72 25.75 44.57 31.56 14.57 32.55 598 53.25 598 53.25 598 53.25 598 53.25 598 54 50.55 51.54 51.55 51.54 51.54 51.54 51.55 51.54 51.55 51.54 51.54 51.55 51.54 51.55 51.54 51.55 51.54 51.55 51.54 51.55 51.54 51.55 51.54 51.55 51.55 51.54 51.55 51.55 51.54 51.55 515 V FINE SAND 15.72 3 15 2.95 2.95 3.16 3.21 2.99 2.57 2.15 1.96 1.84 1.74 1.69 12 47 CRS SILT MEDSILT 1231 COLLOID 0.01 0.21 FINE SILT § 52

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