PHOSPHORUS MOBILITY IN SEDIMENTS
UPON LAKE ACIDIFICATION

PHOSPHORUS MOBILITY IN LACUSTRINE SEDIMENTS UPON LAKE ACIDIFICATION

by

TATIANA MAYER, Dipl. Eng.

A Thesis
Submitted to the School of Graduate Studies
in Partial Fulfilment of the Requirements
for the Degree of
Master of Science

McMaster University
September 1984

MASTER OF SCIENCE
(Geology)

McMASTER UNIVERSITY
Hamilton, Ontario

TITLE: Phosphorus Mobility in Lacustrine Sediments Upon Lake Acidification

AUTHOR: Tatiana Mayer, Dipl. Eng.

SUPERVISOR: Professor James R. Kramer

NUMBER OF PAGES: xii, 136

ABSTRACT

The forms of phosphorus in sediments of acid and non-acid shield lakes were determined in order to assess the effects of lake acidification on the mobility of sediment phosphorus. Sediment phosphorus is conveniently classified into three categories: non-apatite inorganic phosphorus (NAI-P), apatite-P and organic P. The distribution of P between different categories was found to be dependent on the lithology of the lake basin, the pH in the water column, and the redox conditions.

More than 90% of inorganic P in shield lake sediments was in the NAI-P category, associated presumably with hydrated Fe and Al oxides. Organic P accounted for more than 40% of total P in sediments of acid lakes, which is proportionally higher than that found in sediments of neutral lakes. Bioavailable P, a measure of the fraction of sediment inorganic P readily available for biological utilization, amounted to ~70% of NAI-P, similar to that found in hard water lakes.

A series of experiments was designed to investigate the immobilization of P from solution. The uptake of P by solid phase was explained by an adsorption mechanism. The quantitative estimates of phosphate sorption parameters for sediments of acid and non-acid lakes show that mineralogical and chemical characteristics of sediments are more important than the pH of water in determining their efficiency of P removal. Therefore, acidification of lakes does not significantly influence the uptake of P by sediments.

ACKNOWLEDGEMENTS

My sincere appreciation and gratitude go to my research supervisor Dr. J.R. Kramer for his guidance and advice. With his broad understanding of the subject he provided me with the wealth of information and ideas which were very important in the preparation of this study.

Grateful thanks are extended to Drs. P.G. Manning and R.A. Bourbonniere for their numerous helpful suggestions and for their valuable criticisms.

Drs. D.S. Lean and B.K. Burnison are gratefully acknowledged for their help with ^{32}P analyses. Special appreciation is given to Mr. O. Murdoch for his help with X-ray fluorescence analyses. The advice and counsel of Dr. J.O. Nriagu is also deeply appreciated. Mr. W. Keller from OME provided morphometric maps and other necessary documentation concerning the studied lakes and Mr. P. Côté provided the B.E.T. surface analyser.

I am indebted to many members of CCIW staff for their aid during the study. Furthermore, I wish to thank Drs. G.K. Rodgers and J. Barica for allowing me to pursue my studies at McMaster University. Mrs. R. Vollick, Cheryl Minnie and Dianne Crabtree are acknowledged for their patient typing of the manuscript and Mr. J. Van Nynatten for preparing the final illustrations.

The financial support of the Department of the Environment is also acknowledged.

Last, but not least my thanks go to my husband and family for their patience and support.

TABLE OF CONTENTS

TABLE OF CONTENTS (cont'd) **Page**

LIST OF FIGURES

LIST OF FIGURES (cont'd)

LIST OF TABLES

LIST OF TABLES (cont'd)

CHAPTER 1

INTRODUCTION

1.1 STATEMENT OF THE PROBLEM

The deleterious role of phosphorus in nutrient enriched streams and lakes has been extensively studied and well documented (Ohle, 1953; American Water Works Association, 1966; Vollenweider, 1968; American Chemical Society, 1969; Allen and Kramer, 1972; Burns and Ross, 1972). The large amount of this nutrient in natural waters stimulates an excessive growth of algae and macrophytes. Besides the excessive growth of aquatic plants, other undesirable effects of eutrophication such as fish kills, filter clogging, undesirable taste and odour of potable water are well documented.

The concept of sediment functioning as "phosphate buffer" in regulating dissolved inorganic P concentration has been recognized by many investigators (Einsele, 1938; Mortimer, 1941; 1970; Olsen, 1964; Bostrom _et al_, 1982). Hence, sediments are important components of the whole-lake mass balances of phosphorus and as such their diagenetic chemical reactions received considerable attention (Berner, 1971; 1980; Lerman, 1979).

Although P mobility has been studied in detail, the results relate mostly to hard water lakes with large fluxes of P. Consequently, little information is available on the mobility of P in acid lakes, determined largely by its forms in sediments. The present work therefore concerns itself with the state of P in sediments of acid lakes and with the immobilization of this element by adsorption onto sediments.

Specific goals of this research are to:

1. define operationally the forms of P in sediments of acid and non-acid lakes in order to assess the effect of lake acidification on sediment P distribution,
2. relate the forms of sediment P to availability of P, and
3. investigate the effect of pH on the sorption of P by lacustrine sediments.

1.2 FORMS OF PHOSPHORUS IN WATER COLUMN

Considerable evidence exists that the primary productivity in most inland waters is primarily determined by their phosphorus concentration (Vollenweider, 1968; Schindler, 1974). The ecological importance of phosphorus in the aquatic system stems from the role it plays in biological metabolism of aquatic plants. Because of this the distribution of phosphorus in the water column has been studied extensively.

It is generally considered that phosphorus is present in the water column in two forms (Wetzel, 1975): dissolved phosphorus and suspended particulate phosphorus. A complete list of forms of phosphorus in the water column is found in Table 1.2.1.

Although inorganic soluble phosphorus, "Dissolved P_i," constitutes only a few percent of the total phosphorus, it has a major importance in the P-cycle of the lakes, because of its rapid cycling in the zone of utilization (Lean, 1973; Wetzel, 1975). It is generally agreed that this fraction of P is readily available to the aquatic plants.

The amounts and the forms of P in the lacustrine system are dependent on the input to and output from the lake and on the interchange among the various sediment and water P compartments. The interchange among the compartments is controlled by various processes such as precipitation and/or dissolution, biological utilization, respiration and physical agitation (Syers _et al_, 1973). Under constant environmental conditions the changes of the P levels in different compartments are small and rather slow. Thus, the system can be considered approximately as a dynamic steady-state system (Syers, 1973). Figure 1.2.1 shows a schematic representation of different P compartments in the lake and their interaction.

Table 1.2.1 Forms of phosphorus in water column.

Dissolved Forms of P	Dissolved Species	Suspended Particulate Forms of P	Solid Representative
Dissolved inorganic P "Dissolved P_i"	Orthophosphates ($H_2PO_4^-$, HPO_4^{2-}, PO_4^{3-}, $FeHPO_4^+$) Hydrolyzable polyphosphates ($H_2P_2O_7^{2-}$, $CaP_2O_7^{2-}$, $P_3O_{10}^{5-}$, $P_3O_9^{3-}$)	Particulate inorganic P "Particulate P_i"	Mineral phases of rock and soil (hydroxyapatite) Phosphorus adsorbed on clays and other inorganic complexes
Soluble organic P "Dissolved P_o"	Low molecular organic compounds (glucose 1-phosphate, inositol hexaphosphate) Macromolecular colloidal phosphorus	Particulate organic P "Particulate P_o"	Phosphorus in organisms Phosphorus adsorbed on dead particulate matter Pin macro-organic aggregations

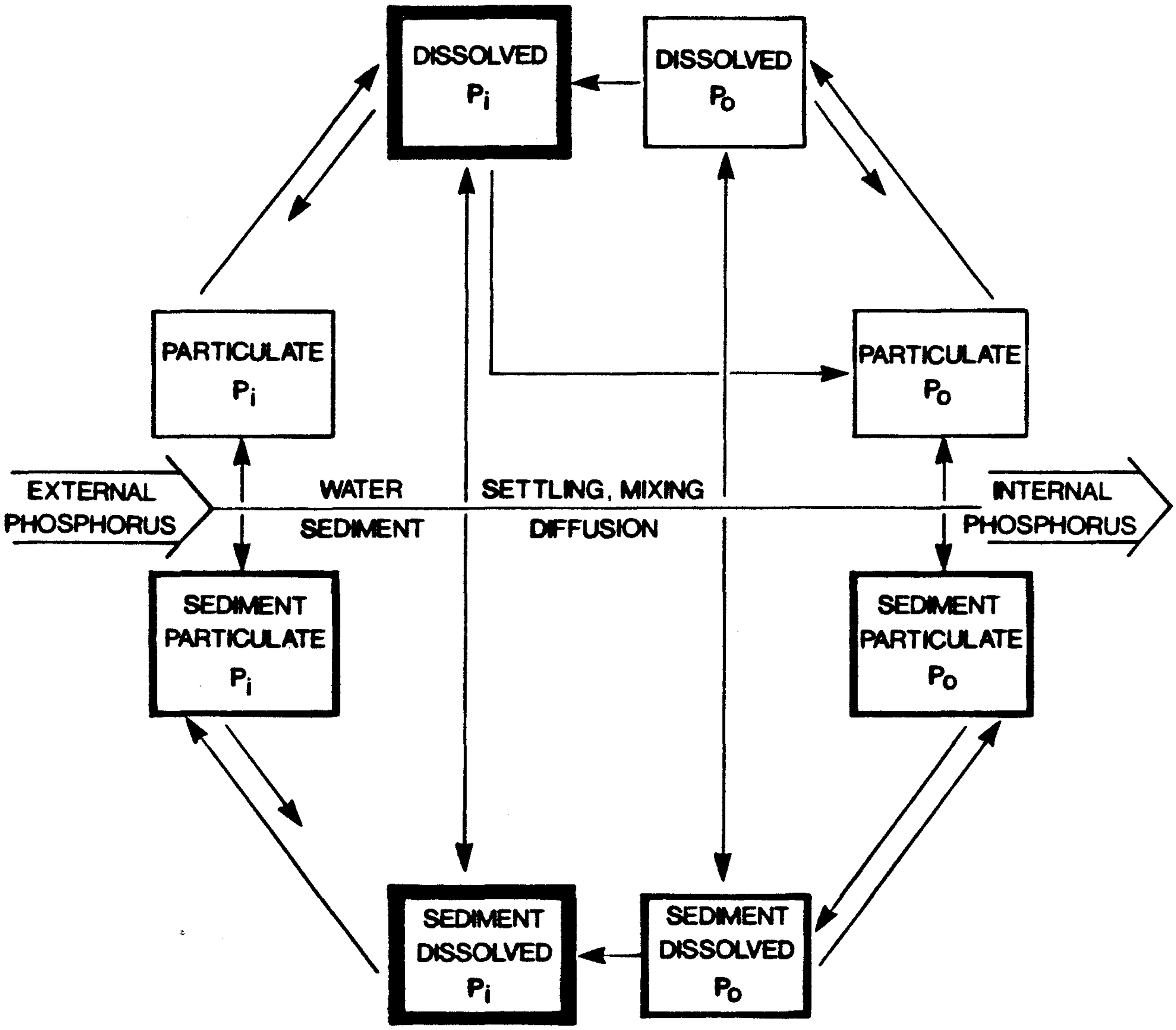


Fig. 1.2.1 - Interchange between water and sediment P compartments (from Syers *et al* 1973).

1.3 FORMS OF PHOSPHORUS IN SEDIMENTS

Our knowledge of the different forms of phosphorus and their amount in sediments is derived mainly from various operational methods. It needs to be kept in mind that there may not always be a simple correspondence between chemical species of phosphorus and these operationally defined forms.

The total content of phosphorus in sediments vary in wide range and depends on the levels of inorganic and organic P.

Inorganic phosphorus

The inorganic P usually constitutes the major fraction of total sediment P (Rittenberg et al, 1955; Williams et al, 1971c). It is present in sediments as discrete mineral phases (apatite, vivianite) and as phosphate adsorbed on clays, oxides, and hydrated oxides of iron and aluminum.

The existence of discrete solid phases of Fe, Mn, Al, and Ca phosphates in sediments is determined by heterogenous equilibria, characterized by the solubility products of the appropriate phosphate minerals. At fixed Ca concentration the variables of principal importance in the sediment phosphate chemistry are Eh and pH. Table 1.3.1 lists the environmental conditions along with the corresponding

Table 1.3.1 Conditions for precipitation of various phosphate mineral phases in sediments.

Redox Conditions	3>pH	pH 3-6	pH >7	Reference
oxic ($p\varepsilon>0$)	strengite	variscite	apatite	Stumm and Morgan, 1980
	lipscombite	lipscombite	beraunite & rockbrigite	Nriagu and Dell, 1974
anoxic ($p\varepsilon<0$)			vivianite, anapatite, reddingite	Nriagu and Dell, 1974

thermodynamically stable mineral phases derived from Figure 1.3.1 and Figure 1.3.2.

Examination of the Figure 1.3.1 shows that under oxic conditions $FePO_{4(s)}$ (strengite) is the stable mineral form at pH < 3, in pH 3 - 6 $AlPO_{4(s)}$ (variscite) is the stable solid phase while metastable hydroxophosphate Al (III) of Fe(III) precipitate at pH > 6 (Stumm and Morgan, 1981). Although the formation of strengite and variscite may be thermodynamically favoured, neither has been found to be a major constituent of lacustrine sediments (Nriagu and Dell, 1974; Warry and Kramer, 1976. Thus, beraunite and rockbrigite would be the common form of phosphate minerals in oxic waters at pH > 7, whereas lipscombite would be stable in oxic waters at low pH (< 7) (Figure 1.3.2). Vivianite ($Fe_3(PO_4)_2 \cdot 3H_2O$) and anapatite would be common phosphate minerals occurring in anoxic waters with pH > 7 (hard waters). If the concentration of Mn is high enough reddingite ($Mn_3(PO_4)_2$) can coprecipitate with the vivianite.

The formation of vivianite in reduced sediments by direct precipitation from interstitial water has been reported (Mackereth, 1966; Rosenquist, 1972; Emerson and Widmer, 1978) and its presence has been confirmed using petrographic microscope and Mössbauer spectroscopy (Dell, 1973; Nembrini _et al_, 1983).

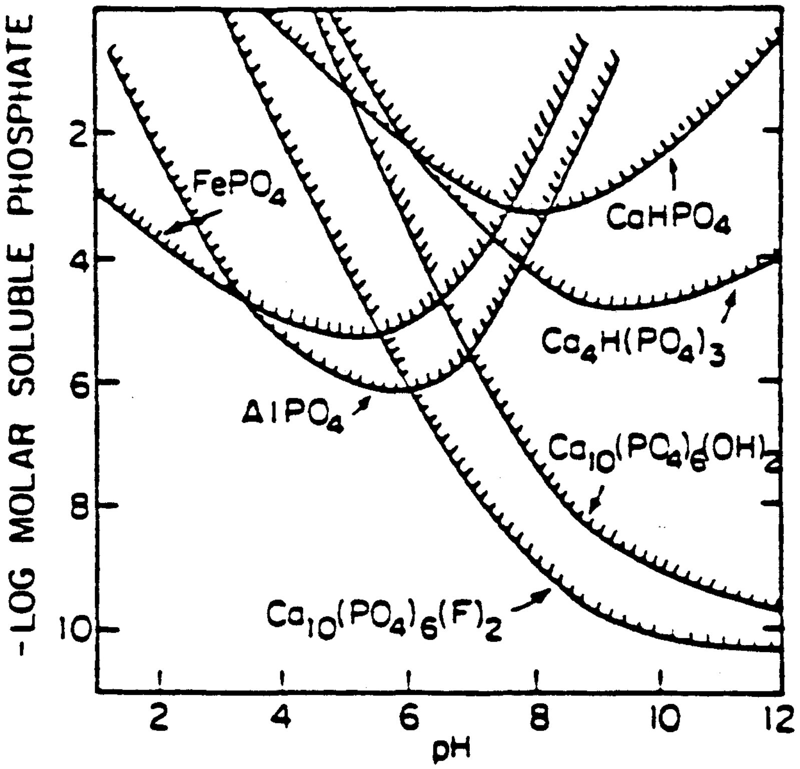


Fig. 1.3.1 Solubility of metal phosphates at $[Ca^{2+}] = 10^{-3}M$. F^- is regulated by the solubility of CaF_2 (from Stumm and Morgan, 1980).

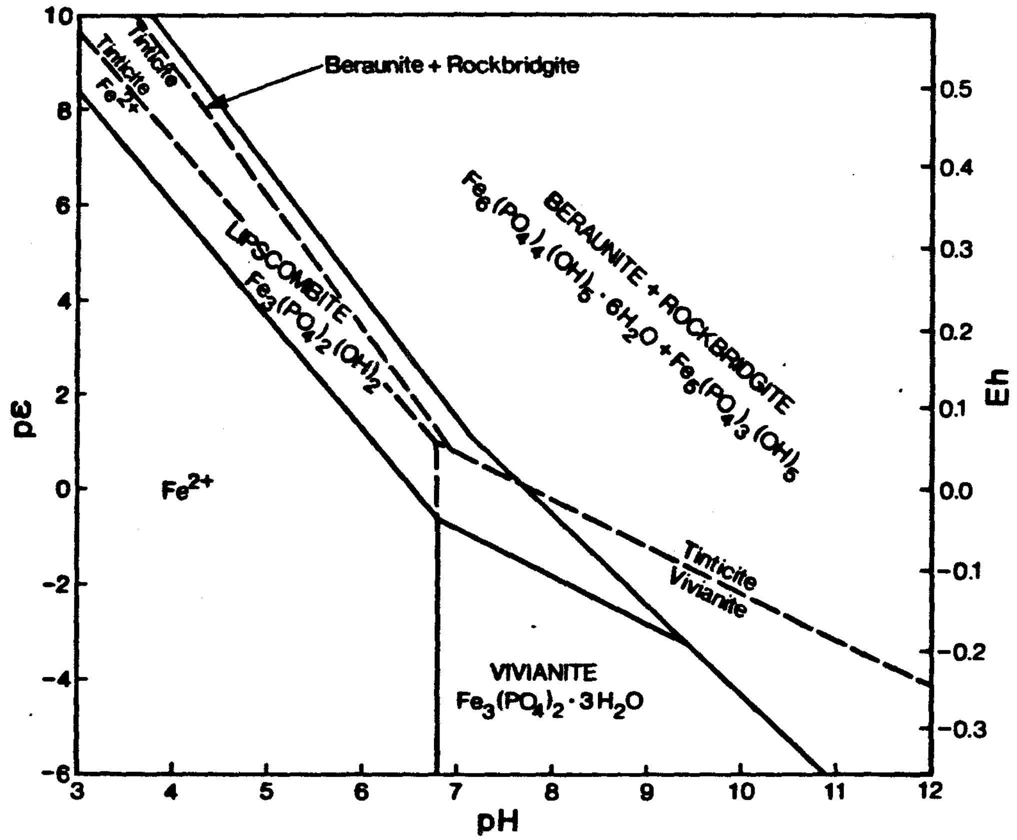


Fig. 1.3.2 Stability of ferrosoferric hydroxyphosphates at dissolved phosphate activities of 10^{-6} (dotted lines) and 10^{-4} (solid lines) (from Nriagu and Dell, 1974).

In hard waters ($pH > 7$), the concentration of soluble phosphate is apparently influenced by the calcium content. Under oxic conditions precipitation of hydroxylapatite takes place in sediments. Kramer (1967) and Sutherland et al (1966) used the equilibrium model involving hydroxylapatite to explain the concentration of dissolved inorganic P in the Great Lakes.

Although the details of mineralogy may vary, one may generalize that Ca-phosphates may be common in hard waters (and $pH > 7$), whereas Fe(II, III) and Al-phosphates may be stable in soft waters and $pH < 7$.

Various extraction methods have been used to determine forms of P associated with clays and hydrated Fe and Al oxides. It is known that these components of the solid phase have a strong tendency to adsorb phosphate; thus they can efficiently immobilize the dissolved P in a form of amorphous complex (Jackson and Schindler, 1975).

Organic phosphorus

Little information is available on the forms of organic P in sediments. Furthermore, the accurate estimation of the amount of sediment organic P is complicated by lack of direct methods for its determination.

Organic compounds of phosphorus originate in lake sediments partly from plant and animal remains and partly from microbial synthesis of inorganic phosphorus compounds (Hesse, 1973). Once deposited, the organic compounds undergo the slow process of mineralization that results in the increase of phosphate concentration in interstitial waters (Rittenberg _et_ _al_, 1955; Williams and Mayer, 1972; Nissebaum _et_ _al_, 1972; Krom and Berner, 1981). The rate and extent of degradation is increased by the presence of benthic bacteria and microfauna.

Specific organic P compounds which have been found in lake sediments include small amounts of adenosine triphosphate (ATP) (Lee _et_ _al_, 1971) and inositol hexa- and pentaphosphates (Sommers _et_ _al_, 1972).

1.4 ADSORPTION OF PHOSPHATE BY SOLIDS

There is considerable controversy in the literature about the mechanism of P immobilization in the aquatic environment. Three proposed mechanisms of phosphate removal from water are commonly cited:

1. Inorganic precipitation mechanisms (Einsele, 1938; Mackareth, 1966; Stumm and Leckie, 1970; Golterman, 1973; Emerson and Widmer, 1978).
2. Bacterial conversion of PO_4 to soluble organic forms (Hayes and Philips, 1958; Hayes, 1964).

3.- Adsorption onto the solid particles (Carrit and Goodgal, 1954; Olsen, 1958; 1964; Williams et al, 1971; Syers et al, 1973; Krom and Berner, 1980).

Most investigators believe that under constant redox conditions biotic mechanisms of P removal are unimportant relative to abiotic mechanisms. Experiments, using biological inhibitors such as antibiotics (Kimmel and Lind, 1970; Fillos and Swanson, 1975) under uniform redox conditions confirmed the importance of abiotic processes in the uptake of phosphorus.

A general assumption is that hydrated surfaces of Fe and Al oxides and clays are responsible for the adsorption processes. In natural aquatic systems the metal oxides and clays develop a pH-dependent surface charge (Parks, 1975) by:

a) amphoteric dissociation (equivalent to desorption of H^+)

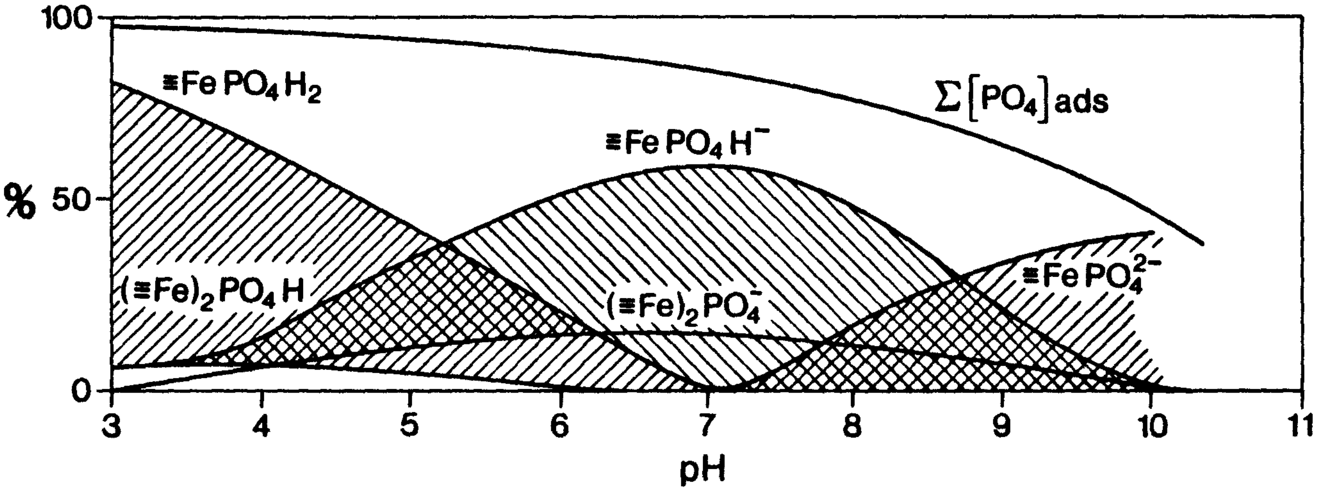
$$\equiv MeOH \rightleftharpoons MeO^- + H^+ \qquad (1)$$

or by b) hydrolysis (equivalent to adsorption of H^+)

$$\equiv MeOH + H^+ \rightleftharpoons MeOH_2^+ \qquad (2)$$

The retention of phosphate on the surfaces of metal oxides occurs by specific adsorption (Hingston et al, 1967; 1972). Such reaction involves a ligand exchange between $-OH_2^+$ or $-OH$ groups, bound directly to the structural metal coordinating ion (Stumm et al, 1980), and the P sorbing species (Parfitt, 1977; Huang, 1975; Lijklema, 1980). The proportion of $-OH_2^+$ to $-OH$ is determined by the pH_{zpc} (pH of zero point of charge) of the surface and by ionic strength and pH of matrix solution (McLaughlin et al, 1977; Ryden et al, 1977). Similarly, pH controls the proportion of $H_2PO_4^-$ to HPO_4^{2-} in solution. At lower pH, protonation of oxides and hydroxides creates more positive sites and concentration of competing hydroxyls is lower. Thus, lower pH favours the adsorption of phosphates onto solids (Balistieri and Murray, 1982). Maximum adsorption of $H_2PO_4^-$ species occurs around $pH = pK_1$, HPO_4^{2-} species around $pH = pK_2$, etc, where K_1 and K_2 denote the first and second dissociation constants of phosphoric acid, respectively. At any given pH the magnitude of phosphate adsorption, $\sum PO_4$ is then given by the sum of the individual surface species (Stumm et al, 1980). Figure 1.4.1 shows that the magnitude of the phosphate adsorption increases with decreasing pH. The highest adsorption of phosphate on metal oxides and clays was observed at pH values between 3-4.5 (Hingston et al, 1967; 1972; Huang, 1975; Edzwald et al, 1976; Stumm et al, 1980).

Various functions have been used to relate the concentration of material adsorbed (C_A) to the concentration of the material in the solution (C). The simplest of



α-FeOOH 6 g/L

Fig. 1.4.1 Adsorption of phosphate on α-FeOOH
(from Stumm <u>et al</u>, 1980).

all is the linear adsorption isotherm (Trais and Etnier, 1981):

$$C_A = K_d\ C \tag{3}$$

where the distribution coefficient, K_d, is the measure of solute retention by the solid phase. This isotherm is often valid for low values of C.

The Freundlich equation:

$$C_A = K\ C^b \tag{4}$$

is empirical. In this equation K and b are constants related to the bonding energy (Castellan, 1983). This equation, similarly as the linear adsorption isotherm, does not imply a maximum quantity of adsorption. Thus, it frequently does not satisfactorily explain adsorption when most adsorption sites are saturated, e.g., high concentration values.

The Langmuir function is derived for a constant surface charge non-interactive model. Two standard forms of the Langmuir isotherm are (Stumm and Morgan, 1981; Trais and Etnier, 1981):

$$\Gamma = \frac{\Gamma_M\ C}{K + C} \tag{5}$$

and

$$\frac{1}{\Gamma} = \frac{1}{\Gamma_M} + \frac{K}{\Gamma_M\ C} \tag{6}$$

where Γ = adsorption density, K = equilibrium constant of adsorption, Γ_M = adsorption capacity, which is a measure of maximum amount of solute that can be adsorbed by the surface of the solid. K is related to the free energy of adsorption (ΔG) (Stumm and Morgan, 1981) through the relation $K = \exp [\Delta G°/RT]$, where R = gas constant (8.314 $\mathrm{Jmol^{-1}K^{-1}}$) and T = absolute temperature in °K. The distribution coefficient K_d, is defined by:

$$\Gamma = K_d\ C \qquad (7)$$

where $K_d = \frac{\Gamma_M}{C}$. Equation (7) can be shown to be an approximate form of the Langmuir equation when C is small ($C \ll K$). Γ is related to C_A (the concentration of adsorbed material) through specific surface area, and they would be approximately proportional for a given surface area (grain size) and constant substrate (Stumm and Morgan, 1981; Castellan, 1983).

1.5 CHEMICAL MOBILITY OF SEDIMENT INORGANIC P

As previously mentioned, benthic sediments are very important to the mobility of phosphorus in the aquatic ecosystem. Extensive literature (Einsele, 1938; Mortimer, 1941; 1942; 1971; Rittenberg, 1955; Pomeroy et al, 1965; Vollenweider, 1968; Fillos and Swanson, 1975; Theis and McCabe, 1978) provides ample evidence that, depending upon limnological conditions, sediment may act as either sink or source of nutrients. The role that sediment plays in regeneration of phosphorus depends largely on various environmental factors. Besides the forms of phosphorus in sediment, two closely related factors play an important role in controlling the mobility of P in sediments. These factors are:

1. oxidation - reduction potential of the surficial layer, largely related to the amount of oxygen in the over-laying water;
2. transport of P between sediment interstitial water and the overlying water.

Under aerobic conditions, the P-equilibria between water and sediment are largely unidirectional towards the sediment (Fitzgerald, 1970; Scheider, 1978; Reckhow, 1979; Bostrom _et al_, 1982) and depend on factors such as mineral-water equilibria, adsorption-desorption processes and bioturbation. Though retention of phosphate is favoured in aerobic sediments, release of phosphate from oxic sediments of primarily eutrophic lakes has also been reported (Ryding and Forsberg, 1976; Ullen, 1978; Gallepp, 1979; Graneli, 1979; Bates and Neafus, 1981; Bostrom and Pettersson, 1982). Available information indicates that between 25-80% of phosphorus loaded into the lakes from external sources can be removed and retained by surficial sediments if oxygenated conditions are maintained (Burns and Ross, 1972; Stumm and Morgan, 1981). The retention mechanism is believed to be adsorption predominantly by highly active ferrioxyhydroxides and/or precipitation of ferric phosphate compounds. Under aerobic conditions, pH range between 4 and 7 is optimal for removal of phosphate from solution (Warry and Kramer, 1976).

Under anaerobic conditions, an appreciable amount of dissolved phosphate from sediment interstitial water emanates into the overlying water (Holdren and Armstrong, 1980; Krom and Berner, 1980; Mayer *et al*, 1982). The release of sediment P is attributed to the disappearance of the aerobic layer, resulting in reduction of the ferric complexes, and consequently in a lower sorption capacity of the surficial sediment (Olsen, 1958; 1964; Froehlich *et al*, 1979; Krom and Berner, 1980).

1.6 LIMNOLOGY OF ACID LAKES

Many lakes in the Precambrian Shield are susceptible to acidification (Dillon *et al*, 1978). The large scale impact on water quality associated with airborne emissions from the Sudbury smelting complex is already apparent. Of over 200 lakes studied within 200 km radius from Sudbury, 30% have pH 5.5 (Keller *et al*, 1980). The zone of acidified lakes exhibits a distinct northeast-southwest bias from Sudbury, reflecting prevailing winds. The low buffering capacity of the lakes reflects the local geology.

In most low pH lakes in the Sudbury area sulphate has apparently replaced bicarbonate as the major anion in solution (Ellis and Golomb, 1981; Yan and Miller, 1982) probably due to large additions of sulfuric acid.

Although the primary productivity of large number of acid lakes is low, dense growth of benthic filamentous algae, apparently a direct response to low pH, has been observed in some low pH lakes (Keller _et_ _al_, 1980). A recent study of several Sudbury lakes (Yan and Miller, 1982) reveals that the diversity of phytoplankton community is reduced in acid lakes, whereas phytoplankton biomass and productivity is not.

In acid lakes increased clarity of water possibly due to the coagulation of organic matter by aluminum (Almer _et_ _al_, 1978; Harvey _et_ _al_, 1981) has a profound effect on vertical distribution of phytoplankton. For example, in Clearwater Lake phytoplankton grew at greater depth than normally possible in Precambrian Shield lakes (Yan and Miller, 1982) due to increased transparency.

A good inverse correlation between the growth rate of attached filamentous algae and pH suggests that decreasing pH promotes the proliferation of this type of phytoplankton (Hendrey, 1976; Stokes, 1980). However, the results of some studies (Yan, 1979) suggest that nutrients, in particular phosphorus, might be more important for algal growth than H^+ concentration. Phosphorus is frequently very low in concentration and thus is probably a limiting nutrient in acid lakes (Yan, 1979). Phosphorus concentrations in some acid and non-acid lakes are shown in Table 2.2.1. This table also lists selected water chemistry parameters for the lakes studied.

Low concentrations of nutrients in the water column of acid and non-acid lakes however, does not necessarily imply low concentrations in sediments or low cycling of P.

Recently, dated sediment cores from acid, neutralized, and fertilized lakes were investigated by Dillon and Smith (1982). The results of the investigations reflect the drastic increase in sedimentation rates, that began 40-50 years ago. Approximately at the same time concentration of total phospohrus (TP) and total nitrogen (TN) began to drop. A possible explanation for decrease in sediment TP concentration put forward by Dillon and Smith (1982) involves an increase in sedimentation of eroded material of non-biologic origin (e.g., sand, clay, etc) and reduction in biological uptake and settling.

Although a large number of acid lakes are oligotrophic, symptoms of eutrophication can develop if concentration of nutrients (nitrogen and phosphorus) is increased (Yan and Lafrance, 1982). Thus, it is clear that acidification of the lakes will not prevent the development of the symptoms of eutrophication.

1.7 PREVIOUS WORK

Forms of P in sediments

Numerous attempts have been made to identify and characterize the forms of P in sediments. To achieve this objective various selective and sequential extraction procedures were carried out. The major problem of this kind of analysis is that insoluble sediment phosphorus is rendered soluble during the analysis and it is no longer in its original form (Golterman, 1973).

The close relation between Fe and P in lake sediments has been well established (Wentz and Lee, 1969; Bortleson and Lee, 1974). Frink (1967) and Williams et al (1971c) found a high correlation between the levels of inorganic P in sediments and amount of Fe extracted by acid-ammonium oxalate or by neutral citrate-dithionite-bicarbonate (CDB). Similarly, Serruya (1971) observed a high linear correlation between P and Fe in the subsurface sediment samples from the deeper parts of Lake Kinneret in Israel. In addition to the strong correlation between sediment Fe and P, an inverse relationship between Ca and P was reported by all the above investigators. Based on the close relationship between Ca and the sand size fraction of the sediments, it was concluded that a natural grading process is responsible for finer iron-phosphate particles to be carried to the deeper parts of the lake, while coarser particles, that incorporate phosphorus associated with calcium, presumably settle in nearshore areas (Serruya, 1971). The work of Williams et al (1976a) supports the preferential deposition of coarser sediments containing phosphorus in association with Ca in nearshore zones. Krom and Berner (1980) estimated "labile inorganic P" in marine sediments by treatment with H_2S. They suggested that the H_2S-extractable P to be the direct measure of that fraction of inorganic P, which is closely associated with Fe and which is rapidly released upon burial of sediment.

Although a close correlation of manganese and phosphorus in sediments has been reported (Delfino et al, 1969; Bortleson and Lee, 1974; Williams et al, 1976a) it is generally believed that the concentration of P in sediments is related more to Fe than to Mn. Williams et al (1971c; 1976a) concluded that the relation between P and Mn is an indirect one, attributed mainly to a strong correlation between Fe and Mn. The strong positive correlation between Fe and Mn results from the common association of Fe and Mn in mineral species. Mackereth (1966) and Wentz and Lee (1969) proposed six modes of P association in sediments. These include detrital phosphate minerals (derived from watershed), phosphate coprecipitated with Fe and Mn, phosphate sorbed on clays and metaloxyhydroxides, phosphate associated with carbonates and P in combination with autochtonous or allochtonous organic matter.

Several workers (Petersen and Corey, 1966; Williams et al, 1967) used the modified extraction procedure of Chang and Jackson (1957) designed for soils, to determine forms of sediment inorganic P. The sequence of extraction steps and corresponding forms of extracted inorganic P are listed in Table 1.7.1.

It was initially assumed (Chang and Jackson, 1957) that the extraction with NH_4F and NaOH reagent in the fractionation procedure presented in Table 1.7.1 would selectively remove Al phosphate and Fe phosphate. However, subsequent investigations (Fife, 1962; Bronfield, 1967; Williams et al, 1971b) showed that between 50 and 75% of the inorganic P associated with iron oxide was removed with NH_4F. Furthermore, problems arose when Chang and Jackson's scheme or its modification (Williams et al, 1967) (Table 1.7.1) were used on calcareous lake sediments. In the course of extraction the phosphates released during NH_4F and following NaOH treatment were readsorbed onto calcareous materials, presumably due to formation of CaF_2 - orthophosphate complex. Phosphorus resorbed by this mechanism

Table 1.7.1 Procedure for the Fractionation of Soil and Sediment Phosphorus (after Williams *et al*, 1967)

Step No	Extraction Step	Name of Fraction	Form of Inorganic P Extracted
1	0.5 M NH_4Cl for 30 min	easily-soluble P	(1) inorganic P dissolved interstitial water and weakly sorbed phosphate
2	0.5 M NH_4F, pH 8.2, for 24 hr, with correction for resorption of phosphate from solution during extraction	NH_4F-P	
3	0.1 N NaOH + 1 M NaCl for 17 hr	1st NaOH-P	(2) + (3) Al + Fe bound phosphorus
4	extraction with dithionite-citrate bicarbonate	reductant-soluble P	(4) occluded phosphorus
5	1 M NaOH for 17 hr	2nd NaOH-P	
6	0.5 N HCl for 1 hr, followed by 1 N HCl for 4 hr if 1st HCl-P >20 ppm	1st HCl-P 2nd HCl-P sum = acid extractable Ca-P	
	ignition at 550C for 1 hr, followed by 1 N HCl for 16 hr	residual org P	
7	Na_2CO_3 fusion	residual inorg P	

was then released during subsequent citrate-dithionite-bicarbonate (CDB) and acid extraction (Williams _et al_, 1971a; Syers _et al_, 1972). As a result, the fractionation data obtained for calcareous sediments, using NH_4F were meaningless because of underestimation of NH_4F-P and NaOH-P and overestimation of remaining inorganic P.

In terrestrial soils and benthic sediments reductant soluble P (CDB-extractable P) is thought to originate in matrices of crystalline oxides and hydrous oxides of Fe (Bauwin and Tyner, 1957) and is considered to be "occluded phosphate." The acid-extractable P (Table 1.7.1) is believed to be Ca-bound, presumably apatite (Williams _et al_, 1976a; 1976b). The amount of inorganic P in the acid-extractable fraction was found to be low for noncalcareous sediments and considerably higher for calcareous sediments (Shofield, 1968; Williams _et al_, 1971a; 1971b).

After a few modifications, Williams _et al_ (1980a) tested the fractionation scheme outlined in Figure 1.7.1 on a large suite of phosphate minerals that are commonly found in soils and sediments. The scheme results in two inorganic sediment phosphorus fractions: (1) non-apatite inorganic phosphorus (NAI-P), that is extracted with the CDB and NaOH reagent and (2) apatite phosphorus, that is extracted with HCl.

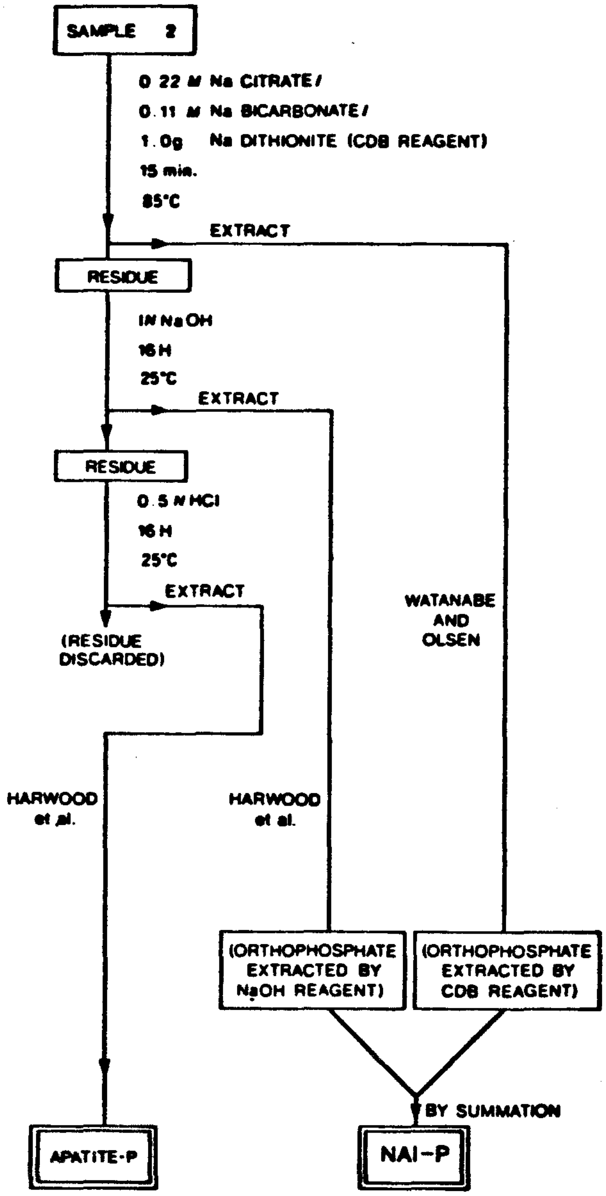


Fig. 1.7.1 Extraction procedure used to determine the forms of inorganic P in sediments (after Williams et al, 1976a).

The above investigators reported that most of the P in iron and aluminum phosphates was extracted by CDB + NaOH treatment as NAI-P, while a major portion of apatitic P was extracted by the HCl treatment. However, one interesting exception was found. A large portion of the P from fish bones was extracted by the CDB reagent although the fish bone was identified as poorly crystallized hydroxyapatite by X-ray diffraction analysis. The results of Williams et al (1980a) emphasize the influence of the degree of crystallinity on the dissolution of mineral phases.

The need for a rapid method for measuring bioavailable P in sediments led to development of new extraction techniques. Golterman (1977), using NTA and Sagher (1976), using NaOH/NaCl extractants, reported good correlation between algal P uptake and P extracted by their respective methods. Recently Schroeder (1976) used an anion exchange resin to estimate the amount of "readily extractable inorganic P" in sediments. Williams et al (1980b) evaluated the above methods and concluded that NAI-P was most closely correlated with NaOH-P, the latter averaging about 70% of the former. Further, they concluded that apatite-P can be considered, for all practical purposes, unavailable for biological utilization. This conclusion is consistent with earlier findings (Logan, 1978; Logan et al, 1979; Verthoff and Heffner, 1979).

Immobilization of phosphate by adsorption mechanism

Laboratory studies have shown that inorganic P, added at concentrations considerably greater than those present in the interstitial waters of sediments is retained. Adsorption of P rather than precipitation is favoured by several investigators (Gastuche et al, 1963; Cole et al, 1953; Olsen, 1964; Shukla et al, 1971; Krom and Berner, 1980), although often the two processes may be experimentally indistinguishable. Research concerned with adsorption of P by solid phases is extensive and it includes studies carried out on sediments, soils and well defined solid phases (e.g., clay minerals and Fe and Al oxides), commonly present in natural environments.

The study on the estuarine sediment (Carrit and Goodgal, 1954) indicated that rapid initial adsorption of P followed by a much slower diffusion-controlled reaction governed the retention of P. Li et al (1972), using radioactive phosphorus (^{32}P), observed extensive and rapid exchange of inorganic P. In their opinion the rapid equilibration indicated that the adsorption was the mechanism responsible for removal of P from the aqueous phase. Olsen (1958; 1964), using radioactive P, estimated the net adsorbed quantity of phosphate in sediments (a) as the difference between the gross adsorption (A) and the exchange of phosphate from sediment to water and vice versa

(b) $a = A - b$. Gross adsorption A follows the Freundlich adsorption isotherm: $A = K \cdot c^v$ and b is a hyperbola-like function, mathematically described by the equation $b = K_b \cdot c^{-v_b}$. In both expressions c represents the concentration of P in solution and K_b, K, v, v_b are constants. From his experiments Olsen concluded that phosphate adsorption depends on a number of different factors: temperature, oxidation-reduction potential and iron and calcium content of sediment. Hayes (1964) found that organic matter depressed phosphate adsorption, whereas iron increased it and that adsorption capacity of the sediment is directly related to the ratio of iron to organic carbon. Davis (1982) attributed the reduced phosphate adsorption by alumina in the presence of organic matter to the competition for adsorption sites and possible electrostatic repulsion. Williams _et_ _al_ (1970) and Shukla _et_ _al_ (1971) have studied both the adsorption of inorganic P and the desorption of sorbed-added inorganic P. They compared the adsorption and desorption properties of calcareous and noncalcareous sediments and showed that calcareous sediments adsorbed less P, but desorbed a higher proportion of added P than noncalcareous sediments. The amount of added P sorbed was largely determined by the amount of amorphous Fe oxides (as determined by oxalate extraction). The levels of native inorganic P in the sediments were closely related to the ability of the sediments to sorb added inorganic P in the laboratory.

Ku _et_ _al_ (1978), investigating lake sediments, observed an increase in adsorption arising from a decrease in pH. The same investigators found the adsorption process much more exothermic at higher pH than at lower pH. Adsorption of P by sediment was reduced after oxalate extraction and at low redox potential.

Krom and Berner (1980; 1981) observed that anoxic marine sediments adsorbed 25 times less phosphorus than oxic sediments. They attributed the lower adsorption capacity of anoxic sediments to the presence of ferrous iron phases such as siderite, FeS and FeS_2. All these phases are much less efficient at adsorbing phosphates than ferric oxyhydroxides, present in oxic sediments. Another explanation of reduced adsorbance proposed by these authors might be the presence of organic coating on clays in sediments, which would inhibit the adsorption of phosphates. Hwang _et_ _al_ (1976) evaluated the effect of the sediment particle size on the adsorption properties of sediment. They observed that both colloidal and noncolloidal fractions are significant in phosphate adsorption. These investigators found the best adsorption efficiency for size 5-2 μm. The kinetic experiments of the same investigators indicated that, similar to other studies (Muljadi _et_ _al_, 1966; Chen _et_ _al_, 1973;

Kuo and Lotse, 1974; Edzwald et al, 1976; Krom and Berner, 1980) the adsorption equilibrium was attained within 24 hrs. Chen et al (1973) and Edzwald et al (1976) explained the slow step of the phosphate-clay adsorption reaction that followed an initial rapid stage as a probable nucleation and growth of an $AlPO_4$ phase. The slow process is apparently significant only under acid pH conditions.

Hingston et al (1967; 1972) proposed three steps for phosphate metal oxide reaction: (1) neutralization of positive charge at pH values below pH of zero point charge (pH_{zpc}), (2) ionization of the proton of the adsorbed acid anion, and (3) enhancement of the tendency of the surface itself to acquire a more negative charge. Breeuwsma and Lyklema (1973) proposed two processes for the adsorption of phosphate on hematite. Reaction commences with exchange of phosphate against -OH or $-OH_2^+$ groups, followed by subsequent adjustment of phosphate equilibria in the aqueous phase.

Stumm et al (1980) calculated surface speciation and surface charge of goethite equilibrated with inorganic components of hard water lake, using surface equilibrium constants. Their results are presented in Table 1.8.1.

The high affinity of phosphate for the surface of hydrated metal oxide is evident from the high percentage of surface sites covered by phosphate, despite the low concentration of this species in the lakewater.

Table 1.8.1 Speciation of the Goethite Surface in a Natural Lakewater (from Stumm *et al*, 1980)

X	C_T mol dm^{-3}	Surface Species	log $K_{intr.}$	[≡FeX] mol dm^{-3}	% [≡FeOOH)$_T$
-	-	=FeOH	-	$2.5 \cdot 10^{-7}$	25
H^+	$3.2.10^{-8}$	$=FeOH_2^+$	-6.4	$1.6 \cdot 10^{-7}$	16
OH^-	$4.9.10^{-7}$	$=FeO^-$	-9.25	$5.5 \cdot 10^{-10}$	0.05
SO_4^-	1.10^{-4}	$=FeSO_4^-$	-5.8	$1.0 \cdot 10^{-11}$	$1 \cdot 10^{-3}$
$H_2PO_4^-$	1.10^{-6}	$=FeHPO_4^-$	7.2	$3.5 \cdot 10^{-7}$	35
H_4SiO_4	5.10^{-}	$=FeH_3SiO_4$	4.1	$1.5 \cdot 10^{-7}$	15
		$=FeH_2SiO_4^-$	-3.3	$2.4 \cdot 10^{-8}$	2.4
HCO_3^-	5.10^{-3}	$=FeCO_3^-$	2.5	$4.9 \cdot 10^{-8}$	4.9
Mg^{2+}	2.10^{-4}	=FeOMg	-6.2	$7.8 \cdot 10^{-9}$	0.8
Ca^{2+}	1.10^{-3}	$=FeOCa^-$	-8	$4.9 \cdot 10^{-10}$	0.05
Pb^{2+}	1.10^{-8}	$=FeOPb^-$	-3	$4.9 \cdot 10^{-10}$	0.05

C_T = assumed total concentration of inorganic component

pH = 7.5

total number of surface sites [≡$FeOH_T$] = 1.10^{-6} mol/dm^3

Several researchers (Bache, 1964; Hingston, 1968a; 1968b; Ryden et al, 1974; McLaughlin et al, 1977) investigating the adsorption of P on soils, interpreted the poor fit of Langmuir isotherm to the adsorption data as evidence for the presence of different types of sites on adsorption surface. The same investigators resolved this problem by applying three distinct Langmuir equations to describe the overall adsorption isotherm. Posner and Bowden (1980) however, argued that good à priori reasons must be present for splitting the isotherm into series of Langmuir isotherms. Using Bowden's model (Bowden et al, 1974; 1977), that takes some account of the electrostatic interactions, they showed that the driving force for the phosphate adsorption is a ligand exchange reaction.

1.8 SUMMARY

The forms of P in sediments, adsorption of P by solids and the chemical mobility of sediment P, relative to soft and hard water lakes can be summarized as follows:

1. Phosphorus in sediments occurs as organic P and inorganic P. The presence and the abundance of different forms of sediment P is determined by the pH and Eh conditions in the lake and by the concentration of calcium in the water.

2. The Fe(II,III) and Al phosphates are the thermodynamically stable phases in sediments of soft water lakes (pH $<$ 7), whereas Ca-phosphates may be common in hard water lakes (pH $>$ 7).
3. The uptake and the release of P from sediment into the overlying water is dependent largely on the redox conditions at the sediment-water interface and on the transport of P between sediment interstitial water and the overlying water.
4. The uptake of phosphorus by sediments is most frequently explained by adsorption of P onto surfaces of hydrated metal oxides and hydroxides. The process is enhanced by the lower pH values.

CHAPTER 2

EXPERIMENTS ON THE PHOSPHORUS ADSORPTION AND ITS SPECIATION

2.1 INTRODUCTION

Knowledge about the forms of P in acid lake sediments and the effect of lake acidification on the adsorption of P by solids is limited. To increase our understanding of the P mobility and the role of sediments in P cycling in acid lakes, two series of experiments were undertaken:

1. The first series of experiments was designed to determine the forms of P in sediments and relate them to other experimentally determined physical and chemical sediment parameters.
2. The second series of experiments was designed to evaluate the adsorption properties of sediments and to investigate the effect of pH, ionic strength and chemistry and mineralogy of sediments on their adsorption behaviour.

Experiments and analyses carried out to achieve the first objective were:

- elemental analyses,
- selective extractions, using respective methods of McKeaugue and Sagher (Section 2.4), and

- sequential extractions, using Williams' method (Sections 1.6; 2.4).

Adsorption and desorption experiments with different types of sediments were carried out to meet the second objective. The effect of pH and ionic strength was investigated by employing a matrix solution of different pHs and different ionic strengths.

2.2 LOCATION OF THE STUDY AREA AND GEOLOGY OF THE LAKE BASINS

Surficial sediments from five Ontario lakes were chosen for this study. The sediment samples were selected to allow comparison of sediments from lakes of different geology, pH and different trophic status. Availability of water quality data and other related information was also taken into consideration. Table 2.2.1 provides a compilation of selected water chemistry data obtained by other investigators which were considered for selection of the lakes.

Shield lake sediments used in this study were from oligotrophic acid-stressed lakes (Wavy, Clearwater), oligotrophic neutral lake (Windy L.) and acid-stressed productive lake (Swan L.). All the shield lakes are situated within the Sudbury area. The information concerning the location of the study sites and some morphometric data are summarized in Table 2.2.2. Geology of the study area can be found in Figure 2.2.1 which shows that three provinces of the Precambrian shield are representd in the area, where the study lakes are located. These are: felsic plutonic rocks of Superior Province, meta-sediments and meta-volcanics of Southern Province and the younger clastic siliceous metasediments and felsic igneous rocks of the Grenville Province. A separate grouping known as Sudbury Nickel Irruptive, consisting of unique rock types (layered intrusive rocks) invades both the Superior and Southern Provinces.

The main rock types present in the area of the studied lakes are: norite, granophyre, tuff and breccia quartzite, gneiss (migmatite), granite and gabbro (Ontario Ministry of the Environment, 1982).

Two sediments (WB and E-30) were from depositional basins of Lake Ontario (Figure 2.2.2, Table 2.2.3), which is a mesotrophic hardwater lake (Dobson, 1980), underlain by Ordovician limestone, shale and sandstone (Sly and Lewis, 1972). The Lake Ontario sediments were included for comparison.

2.3 SAMPLE COLLECTION AND PREPARATION

Surface sediments from Precambrian lakes were obtained in the summer of 1981 using an Ekman dredge

Table 2.2.1 Water chemistry data of selected lakes (Ontario Ministry of Environment 1978; 1982; Dobson 1981; 1984)

Lake	pH	Alkalinity (mg/L $CaCO_3$)	Total Kjeldahl Nitrogen µg N/L	Nitrite & Nitrate µg N/L	Total P µg/L	Chlorophyl µg/L
Wavy	4.5	1.2	164	25	5	0.2
Clearwater	4.4	0.1	85	52	4	0.3
Swan	4.0	<0	232	78	11	1.9
Windy	6.4	4.3	177	14	4	1.2
L. Ontario (1975)	8.5	85		287	21	5.3

Table 2.2.2 Location and morphometric data for studied Precambrian Shield Lakes.

Lake	Township	Latitude	Longitude	Surface Area (ha)	Maximum Depth (m)
Windy	Dowling	46°36'	81°27'	1111.6	54.9
Wavy	Eden	46°18'	81°06'	255.1	33.5
Clearwater	Broder & Tilton	46°22'	81°03'	76.9	21.5
Swan	Broder	46°22'	81°04'	5.78	8.8

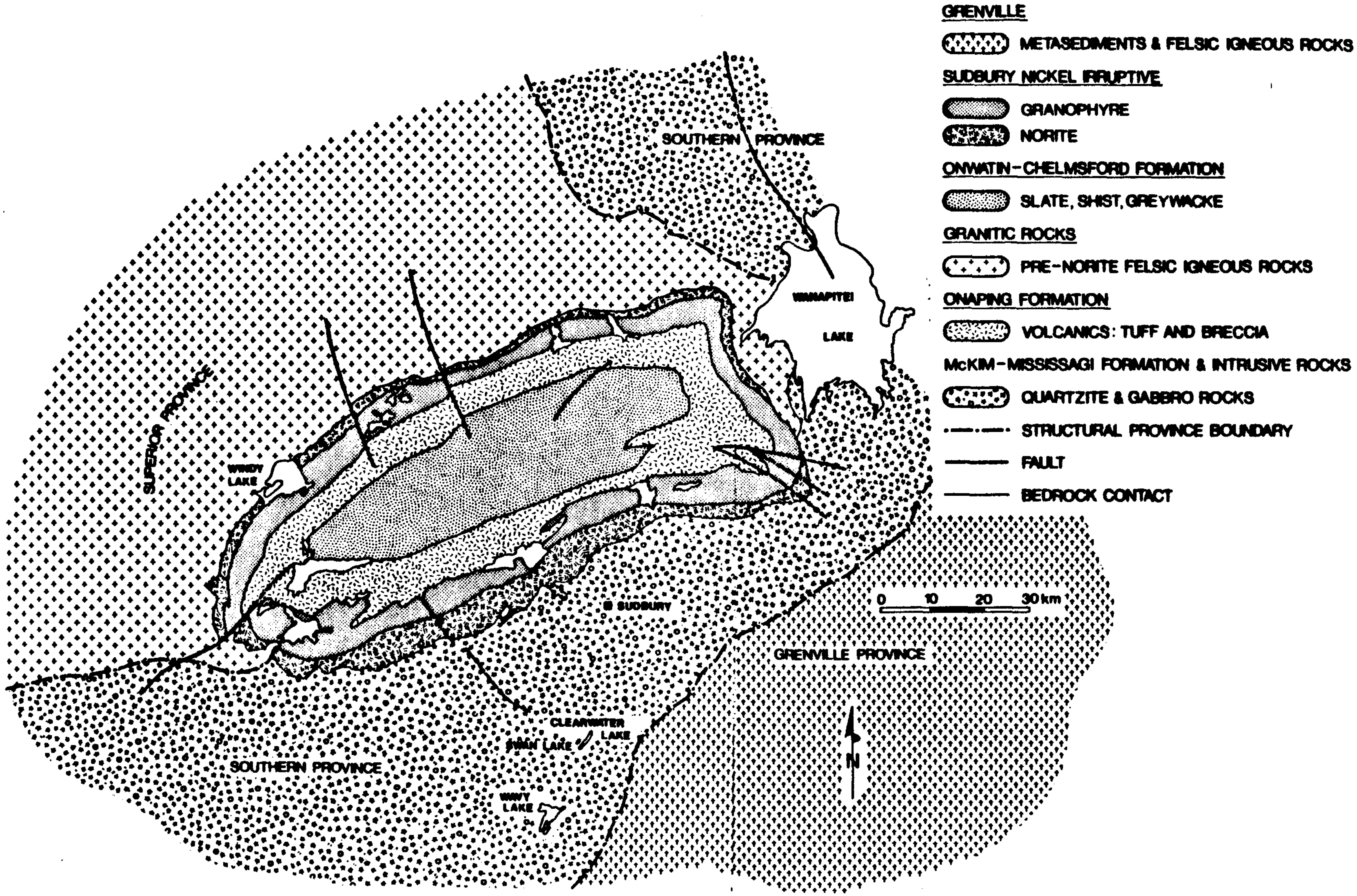


Fig. 2.2.1 Location of the sampling sites and geology of the study area.

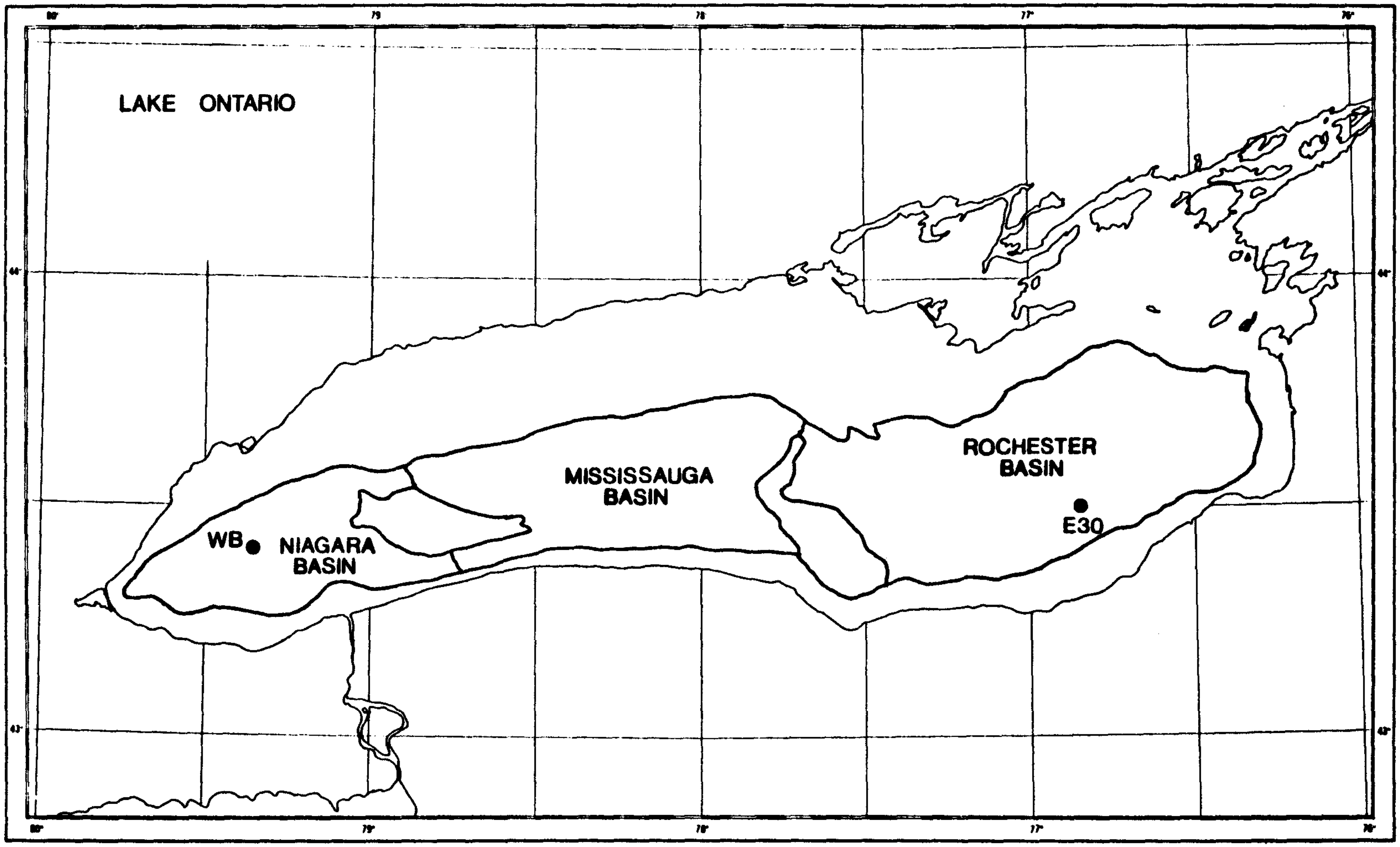


Fig. 2.2.2 Lake Ontario sample locations.

Table 2.2.3 Location and morphometric data from L. Ontario sample sites.

L. Ontario Sample Location	Latitude	Longitude	Water Depth (m)	Sedimentation* Rate (mm yr^{-1})
WB	43°24.1'	79°43.6'	101	1.3
E-30	43°30.7'	76°54.0'	225	1.6

*Sedimentation rate from Kemp *et al* (1977).

sampler. The sampling sites were typically in the middle of the deep basins of the lakes. The samples were transferred into pre-washed glass jars, quickly frozen and subsequently freeze-dried.

Surface sediments from Lake Ontario were collected in May of 1975 with a double-Shipek from two locations.

The samples were stored at 4°C and subsequently freeze-dried. Dry sediments were ground with a procelain mortar and pestle and passed through the U.S. standard sieve. Sediment particles less than 250 μm were used for all the experiments.

Amorphous hydrous ferric oxide gel used for adsorption study was prepared by dissolution of 3.3642 g of analytical grade $Fe(NO_3)_2 \cdot 9H_2O$ in approximately 200 mL doubly distilled water. The pH of suspension was adjusted to 7 with 1 M NaOH. The suspension was filtered and washed several times with doubly distilled water. The washed precipitate was then diluted up to 200 mL to yield a final suspension concentration of 4.45 g $L^{-1} Fe(OH)_3$. The suspension was readily soluble in acid-ammonium oxalate (pH 3) and 1 M HCl, indicating that there had been little or no crystallization. This was confirmed by X-ray diffraction.

2.4 ELEMENTAL AND FRACTIONATION ANALYSES

The following section describes a variety of experimental methods used for evaluation of physical and chemical characteristics of sediments and forms of sediment P.

Analysis of the major elements (Si, Al, Fe, Mn, Ca, Mg, K, Mn) was carried out by X-ray fluorescence on samples fused with lithium metaborate ($LiBO_2$).

Loss on ignition was determined after overnight heating of dry sediments to 475°C.

Inorganic and organic carbon were determined on replicate samples by Leco furnace. Organic carbon was measured after removal of the carbonate carbon with sulfurous acid (H_2SO_3) (Kemp, 1971).

Qualitative estimation of minerals was done by powder X-ray diffraction method, using CuK_α radiation.

The amorphous Fe and Al in sediments was estimated by oxalate extraction. The analytical procedure used in this study is similar to that described by McKeague (1978). One gram of dry sediment was extracted with 40 mL of acid oxalate solution (1.3:1 mixture of 0.2 M ammonium oxalate/ 0.2 M oxalic acid) in the dark for 4 hrs. The extract was recovered by centrifugation and decantation. Fe and Al concentration in the extracts was determined by atomic absorption spectrophotometry upon further dilution of the extracts. Inorganic P was also determined in these extracts by the method of Watanabe and Olsen (1962).

Total and organic sediment P were determined on replicate samples according to the scheme outlined in Figure 2.4.1.

Forms of inorganic phosphorus were determined on replicate samples following the fractionation scheme shown in Figure 1.7.1. Both of the procedures used in this work to evaluate the forms of phosphorus in sediments are described in detail in Mayer and Williams (1981). The analytical estimate of bioavailable phosphorus was obtained by using the procedure of Sagher (1976). In this procedure 25 mg of sample was extracted with 50 mL of 0.1 N NaOH/1.0 N NaCl solution for 16 hrs at room temperature. The inorganic P in the extract was determined by the method of Harwood _et al_ (1969).

Native exchangeable P was determined by ^{32}P exchange following the procedure outlined by Li _et_ _al_ (1972). Carrier-free ^{32}P (2.2 μCi) was added in 0.5 mL aliquot to 100 mL polypropylene centrifuge tubes containing 1 g of sediment and 40 mL of 0.1 N NaCl. Samples were shaken for 142 hrs. After this time the suspensions were centrifuged and passed through a 0.45 μm Millipore filter. Solution ^{31}P concentration was determined by the method of Harwood _et_ _al_ (1969). To determine solution ^{32}P concentration 1 mL aliquot was added to 10 mL of PCS-xylene scintillation cocktail in a vial, for counting on a Searle Mark III

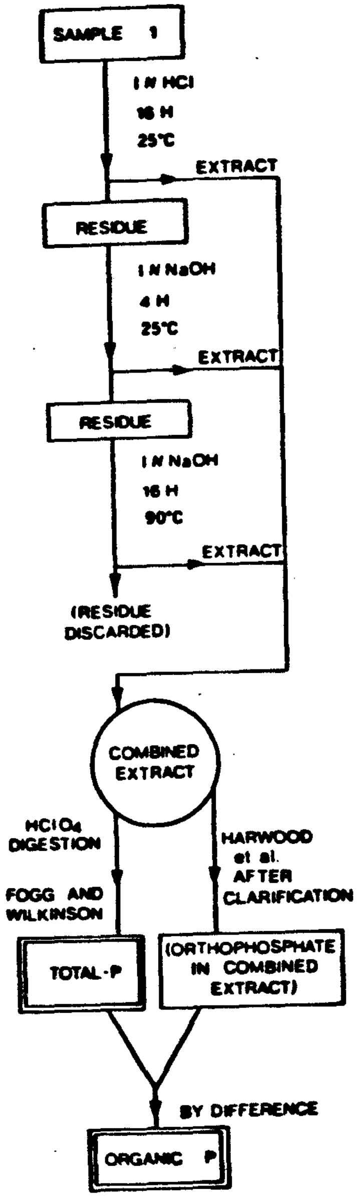


Fig. 2.4.1 Analytical procedure used to determine organic and total phosphorus in sediments (from Williams *et al*, 1976a).

liquid-scintillation spectrometer. Blank aqueous extract of each sediment was used for quench correction.

2.5 ADSORPTION AND DESORPTION EXPERIMENTS

The sorption of inorganic P was evaluated by equilibrating the sediment suspensions with various levels of phosphorus. The appropriate amount of P was added in 5 mL aliquots to 1.0 g of freeze-dried sediment, placed in a pre-weight 100 mL polypropylene centrifuge tube. Thirty-five (35) mL of 0.1 N NaCl was added to obtain the sediment-solution ratio of 1:40.

NaCl was used to facilitate particle settling during centrifugation. This salt solution, referred to as "matrix solution", contains nonspecifically adsorbable cation and anion, hence it is very suitable for the adsorption experiments. Bacterial uptake of P was eliminated by addition of $HgCl_2$. Each system contained 147 μmole $HgCl_2L^{-1}$. The samples were equilibrated by shaking for 72 hrs at 21°C. After the equilibrium had been established the aqueous and solid phase were separated by centrifugation followed by filtration through a Millipore filter apparatus with a 0.45 μm membrane filter. The filtrate was analyzed for phosphate, using the colorimetric method of Harwood et al (1969). The solid residue was retained for subsequent desorption analysis. The tubes with sediment residue were weighed to determine the volume of solution entrapped in the residue. Measurement of P desorption from the sediment involved addition to the residue of 40 mL 0.1 N NaCl; the 72-hr extraction, recovery and removal of the supernatant followed by subsequent P determination, carried out as above.

Sorption of P from 10^{-4} N NaCl was evaluated essentially by the same method as sorption of P from 0.1 N NaCl, with change in the ionic strength of the electrolyte being the only difference.

If the initial pH of matrix solution used for adsorption was different than that of sediment, equilibration prior to the adsorption experiment was carried out with the electrolyte of the desired pH and ionic strength. During this procedure no significant release of P was observed.

The sorption of P by Fe-gel from 0.1 N $NaClO_4$ was determined by the same method as that described for sediments, except that 1 mL of gel suspension containing 1 mg Fe was used.

Controls containing desired P concentration in 40 mL 0.1 N NaCl (or 10^{-4} N NaCl) but no sediment were run to check for possible adsorption on the surfaces of the container.

The surface area of amorphous hydrous ferric oxide gel was measured by the classical, low temperature gas adsorption (B.E.T.) technique. Nitrogen gas was used as adsorbate at 77°K.

CHAPTER 3

RESULTS

3.1 INTRODUCTION

A detailed investigation of the state of P in sediments of acid and non-acid lakes and P immobilization by adsorption onto sediments is described. The results obtained from the various experimental and analytical tests described in the previous chapter are presented in the form of diagrams and tables. Their interpretation provides further information on the subject of P cycling in acid lakes.

3.2 CHARACTERISTICS OF SEDIMENTS

The surficial sediment of the acid lakes (Wavy, Clearwater and Swan) appeared to be quite flocculent and without any well defined interface. Both of the sediment samples from Lake Ontario were similar in their physical characteristics. In the first few mm of sediment, the solids consisted of a reddish-brown floc, which overlaid a soft gray to dark gray ooze. The fine grained sediments used in this study contained different proportion of silt and clay, reflecting the energy conditions in the zone of deposition.

Water content of shield sediments was exceedingly high (Table 3.2.1). Loss-on-ignition (LOI), a measure of the organic content of sediments and bound water was considerably higher in sediments from acid lakes than from the bottom deposits of neutral lakes (Table 3.2.1).

An exceptionally high content of organic matter in sediment from Swan Lake appears to be the result of both high biomass productivity in this lake and suppression of organic degradative processes in sediment (Rao and Dutka, 1983).

The Lake Ontario sediments consisted of quartz feldspars, carbonates and the following clay minerals: illite, chlorite, and kaolinite. No carbonates were identified in shield lake sediments and crystalline clay minerals were also absent, except for small amounts in Windy Lake sediment.

3.3 ELEMENTAL COMPOSITION AND FORMS OF PHOSPHORUS IN SEDIMENTS

The results of elemental analysis and different extraction techniques enable us to relate the sediment phosphorus to the other chemical parameters. This approach

Table 3.2.1 Water content* and LOI

Sediment Sample	Water Content %	LOI %
Wavy	92	36.51
Clearwater	91	26.99
Swan	96	53.70
Windy	93	15.66
L.O. WB	87	11.86
L.O. E-30	88	11.43

*Water content data from Bourbonniere (1984, Personal communication) and Kemp _et_ _al_ (1977).

is particularly useful in explaining the association of P with metal oxides and sediment organic matter.

The results of X-ray fluorescence analysis showing the concentration of major elements (Si, Al, Fe, Mg, Ca, Na, K, Ti, Mn) in sediments are sumamrized in Table 3.3.1.

Higher values of Ca and Mg in Lake Ontario sediments than those of shield sediments are attributed to the presence of calcite and dolomite in Lake Ontario sediments. Lower values of Al, Mn, and K in sediments of acid-stressed shield lakes suggest leaching of the above cations from sediments (Ellis and Golomb, 1981). Deposition of solids, impoverished in major cations as a result of leaching in the catchment basin, may also account for lower values of Al, Mn, and K in acid lake sediments (Torrenueva, 1981; Ellis and Golomb, 1981).

The results of selective oxalate extraction used to estimate Al and Fe associated with amorphous oxides and hydroxides (Al_{OX}, Fe_{OX}) are presented in Table 3.3.2.

The values of Fe_{CDB} (citrate-dithionite-bicarbonate extractable Fe) (Table 3.3.2) estimate the amount of iron present in both amorphous Fe-complexes and in fine grained crystalline iron oxides (e.g., goethite, hematite) and are in average 7% higher than values of Fe_{OX}.

In shield lake sediments the amorphous Al as estimated by the oxalate extraction comprised between 16-47% of

Table 3.3.1 Major elements, as determined by XRF-Analysis

Sediment Sample	Si %	Al %	Fe %	Mg %	Ca %	Na %	K %	Ti %	Mn %
Wavy	23.20	3.43	2.67	0.70	0.59	0.185	0.58	0.14	0.04
Clearwater	26.15	3.62	4.17	0.83	0.88	0.21	0.68	0.15	0.03
Swan	15.83	2.13	4.01	0.45	0.63	0.13	0.17	0.01	0.34
Windy	27.71	4.83	7.17	0.53	0.67	0.84	0.95	0.21	0.64
L.O. E-30	26.05	7.64	4.92	1.83	1.77	0.24	2.42	0.37	0.22
L.O. WB	26.38	7.89	4.85	1.98	1.40	0.29	2.76	0.43	0.26

Table 3.3.2 Concentration of Fe and Al as determined by different extractions.

Sediment Sample	Fe_T* mg g^{-1}	Fe_{OX} mg g^{-1}	Fe_{OX} as % Fe_T	Fe_{CDB} mg g^{-1}	Fe_{CDB} as % Fe_T	Al_T* mg g^{-1}	Al_{OX} mg g^{-1}	Al_{OX} as % Al_T
Wavy	26.7	4.69	17.6	7.08	26.5	34.3	16.0	46.6
Clearwater	41.7	6.96	16.7	12.62	30.3	36.2	8.8	24.2
Swan	40.1	11.67	29.1	14.04	35.0	21.3	5.5	25.8
Windy	71.7	44.37	61.9	47.43	66.1	48.3	7.7	16.0
L.O. E-30	49.2	12.19	24.8	15.68	31.9	76.4	1.1	1.5
L.O. WB	48.5	13.76	28.4	14.99	30.9	78.9	2.3	2.9

*Fe_T and Al_T values are results of elemental analysis as determined by X-ray fluroescence spectrometry (Table 3.3.1) and represent the total quantities of respective elements.

Al_T. In contrast, only 1.5-3% of Al_T is present as amorphous Al in Lake Ontario sediments. The low values of Al_{OX} in Lake Ontario sediments (E-30, WB) suggest that the clay minerals account for most of the Al in these sediments. This finding is in accordance with the conclusion of Kemp and Thomas (1976).

The amount of sediment inorganic phosphorus associated with amorphous Al and Fe complexes (P_{OX}) and the amount of bioavilable-P as determined by NaOH extraction is indicated in Table 3.3.3. The same table contains the values of CDB-P used later for calculation of NAI-P. As seen from Table 3.3.3, the CDB-P values are in close agreement with the oxalate-P values corrected for apatite phosphorus (from Table 3.3.4). The similarity of the two sets of values (P_{OX} and P_{CDB}) can also be seen in the plot of molar concentrations of P_{CDB} versus P_{OX} (Figure 3.3.1). The plot shows the linear relationship between the two parameters with a slope of about 1.

Based on the results of sequential extractions, the phosphorus in the investigated surficial sediments can be divided into three major categories: phosphorus associated with apatite, non-apatite inorganic phosphorus (NAI-P), and organic phosphorus.

The amount of apatite-P, NAI-P, organic P, and total P estimated by sequential extraction (Figure 1.7.1;

Table 3.3.3 Bioavailable, oxalate and CDB phosphorus values.

Sediment Sample	P_{OX} µg g^{-1}	P_{CDB} µg g^{-1}	P-bioavailable µg g^{-1}	Bioavailable-P as % NAI-P
Wavy	1061	1073	1049	85.6
Clearwater	479	460	560	99.3
Swan	179	244	238	79.1
Windy	1285	1221	950	68.5
L.O. E-30	590	621	656	98.2
L.O. WB	532	523	472	80.0

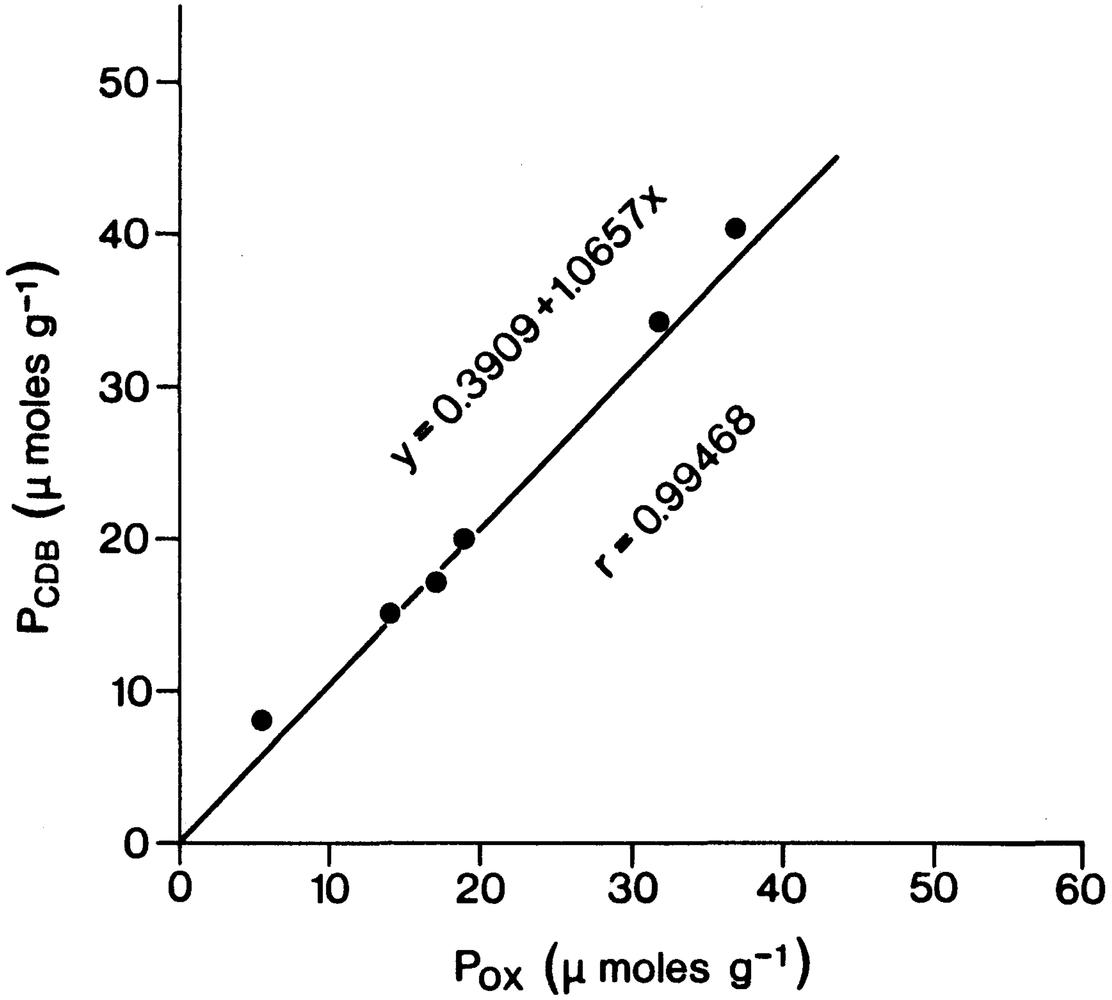


Fig. 3.3.1 Relation between oxalate and CDB extractable phosphorus.

Figure 2.4.1) is presented in Table 3.3.4. Here, the distribution of inorganic P among different categories is briefly reviewed in order to assess the P distribution in investigated sediments.

The apatite-P fraction is comprised of orthophosphate present in the crystal lattices of apatite grains. The NAI-P fraction includes orthophosphate adsorbed on Fe- and Al-oxides and hydrous oxides, Fe- and Al-P minerals and Ca-P minerals other than apatites. In addition this fraction includes soluble orthophosphate ions from sediment pore water (Logan et al, 1979). The values of NAI-P are generally higher than observed values of oxalate P or CDB-P. Table 3.3.4 shows that the NAI-P category comprises on average 97% of inorganic phosphorus in sediments from shield lakes, while inorgnaic P from Lake Ontario is more evenly distributed between the two categories: apatite-P and NAI-P.

The NAI-P is linearly correlated (r = 0.9562) with bioavailable P as determined by NaOH extraction (Sagher, 1976). Based on the slope of regression line from Figure 3.3.2, the bioavailable P amounts to 70% of the NAI-P, which is in accordance with results obtained by other investigators (Williams et al, 1980).

The last category of sediment phosphorus, "organic phosphorus", embraces all phosphorus associated with carbon

Table 3.3.4 Values of individual forms of phosphorus as determined by sequential extractions.

Sediment Sample	NAI-P $\mu g\ g^{-1}$	Apatite P $\mu g\ g^{-1}$	Organic P $\mu g\ g^{-1}$	Inorganic* P $\mu g\ g^{-1}$	Total P $\mu g\ g^{-1}$	Organic P as % total P
Wavy	1225	77	742	1103	1845	40.2
Windy	1378	138	460	1420	1863	24.7
Clearwater	564	49	535	607	1142	46.8
Swan	301	14	785	303	1088	72.1
L.O. E-30	668	316	155	953	1108	14.0
L.O. WB	590	358	200	991	1191	16.8

*Inorganic P as determined from the scheme outlined in Figure 2.4.1.

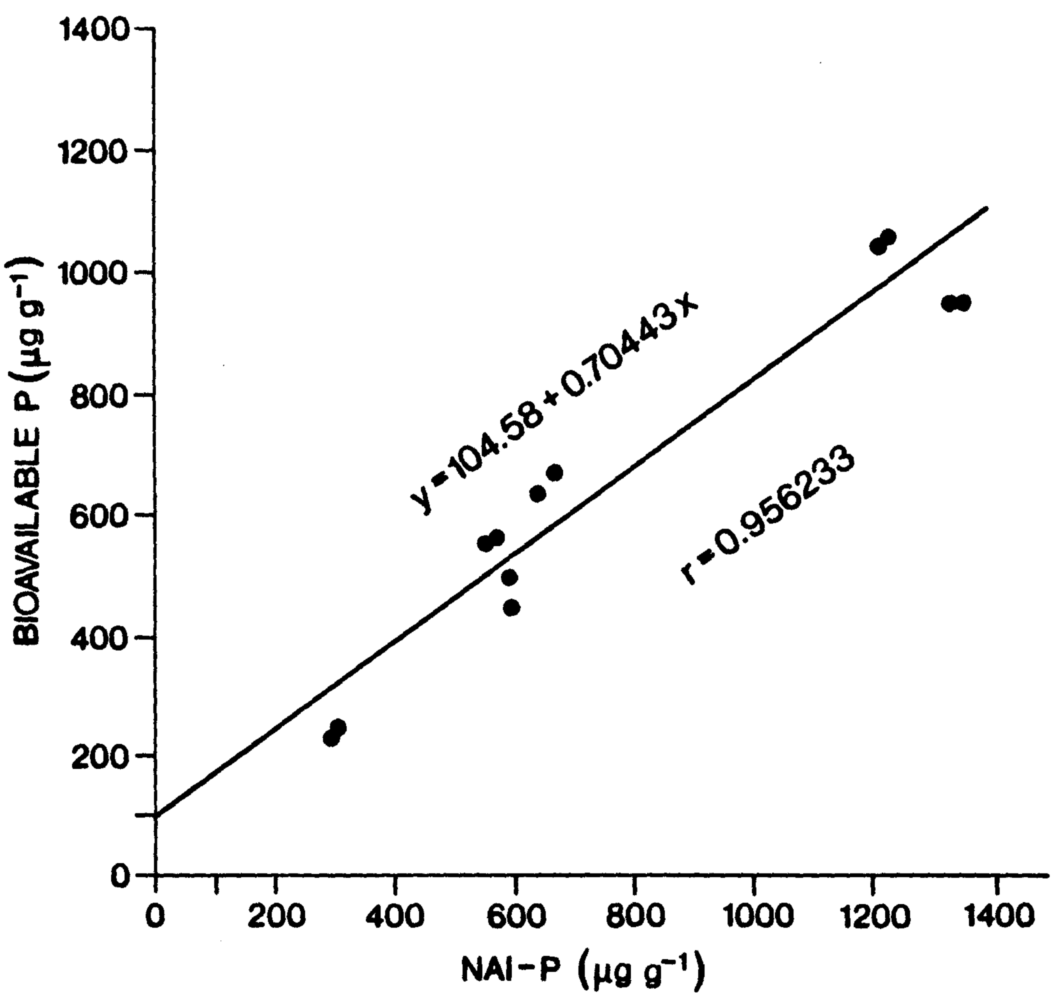


Fig. 3.3.2 Concentration of bioavailable phosphorus as a function of NAI-P concentration.

atoms via C-O-P or C-P bonds (Williams *et al*, 1976a) and includes also organic phosphorus compounds present in sediment interstitial water (Logan *et al*, 1979). The organic P values in samples from acid lakes varied between 40-70% of total P and were considerably higher than those observed in samples from the neutral lakes (14-25% of total P).

The sum of apatite-P, NAI-P and organic-P values is essentially equal to the total amount of phosphorus extracted from the sediment sample by the procedure used to determine organic-P (Figure 2.4.1). This value is slightly less than the true value of the total phosphorus content of the sediments, the difference being due to phosphorus present within the lattices of silicate minerals, which is not extracted during the organic-P procedure.

Organic carbon and organic phosphorus data (Table 3.3.5) are consistent with the LOI values (Table 3.2.1). As can be seen from Table 3.3.5, somewhat higher values of organic carbon and organic phosphorus were measured in sediments from acid lakes than in sediments from the neutral lakes. The molar org C/org P ratio appears to be relatively constant, 419±54, except for Swan Lake sediment, which is characterized by a very high org C/org P ratio (707).

Table 3.3.5 Total and organic carbon content of investigated sediments and the molar org C:org P ratios.

Sediment Sample	Total C %	org C %	org P µmoles g^{-1}	Molar org C/org P
Wavy	13.09	12.84	23.93	442
Windy	6.62	6.53	14.84	366
Clearwater	10.15	9.68	17.26	461
Swan	21.58	21.04	25.32	707
L.O. E-30	2.94	2.48	5.00	408
L.O. WB	3.02		6.45	

The mean value of molar org C/org P ratio (Swan Lake excluded), 419, compares favourably with 426, the mean value of org C/org P ratio obtained by Williams et al (1976a) for the 46 surficial Lake Erie sediments.

3.4 ADSORPTION AND DESORPTION

The findings of the adsorption and desorption experiments are presented in this section. The main advantage of a laboratory scale study is that the experiments are carried out under controlled conditions. Hence, the effect of desired physical and chemical parameters (e.g., pH of aqueous phase, particle size, etc) on adsorption process can be assessed with greater certainty. However, it has to be kept in mind that because of the complexity of natural environment, the results of such laboratory studies should be applied with caution.

Equilibrium sorption of inorganic P by five sediments is presented graphically in Figures 3.4.1 to 3.4.5. The amount of adsorbed P was obtained by adding the value of native surface P (Table 3.4.1) to all values of added P sorbed (Table 3.4.2 and Table 3.4.3). The value of native exchangeable P (Sed Exch $^{31}P_i$) (Table 3.4.1) converted into molar concentrations was used as an estimate of native surface P.

Table 3.4.1 Levels of exchangeable sediment phosphorus.

Lake	Sed Exch $^{31}P_i$ µg g^{-1}	Sed Exch $^{31}P_i$ as % of inorganic P
Wavy	1053	81
Clearwater	445	72
Windy	560	37
E-30	176	18
WB	209	22

Table 3.4.2 Adsorption of added inorganic phosphorus by Shield lake sediments.

Sediment Sample	pH of Matrix Solution	Ionic Strength of Matrix Solution (M)	Added P sorbed in μmoles g^{-1} for added P levels (μmoles P g^{-1})											
			10	20	30	40	60	80	100	120	140	150	160	170
Wavy	5.5	10^{-1}	9.94	19.89	29.80	39.61	58.98	77.14	93.72	108.56	120.32	126.47	131.38	133.82
Wavy	7	10^{-1}	9.92	19.80	29.50	39.30	57.34	74.61	89.66	102.26	113.92	118.56	121.77	128.26
Wavy	7	10^{-4}	9.69	19.32	28.53	36.93	51.32	62.21	72.39	81.77	87.29	90.93	93.71	94.80
Clearwater	4.5	10^{-1}	9.89	19.92	29.85	39.70	58.93	76.83	91.11	103.40	110.55	116.30	120.09	125.06
Clearwater	7	10^{-1}	9.41	19.88	29.65	39.15	56.13	68.10	79.53	87.60	91.36	95.08	99.52	102.98
Windy	7	10^{-1}	9.95	19.91	29.81	39.66	58.79	76.42	92.86	107.78	117.03	121.87	124.90	126.99

Table 3.4.3 Adsorption of added P by Lake Ontario sediments

Sediment Sample	pH of Matrix Solution	Ionic Strength of Matrix Solution (M)	Added P sorbed in µmoles g^{-1} for added P levels (µmoles P g^{-1})												
			2	4	6	8	10	15	20	25	30	40	50	60	70
L.O. E-30	7	10^{-1}	1.81	3.66	5.49	7.17	8.78	12.21	15.42	17.22	19.18	22.31	24.78	27.61	28.88
L.O. E-30	7	10^{-4}	1.91	3.83	5.70	7.48	9.07	12.94	15.51	18.30	19.51	23.51	24.58	25.72	27.71
L.O. WB	7	10^{-1}	1.79	3.63	5.43	7.19	8.89	12.67	15.65	17.86	19.99	23.25	26.32	29.66	31.01

Native exchangeable P at equilibrium was determined from isotope dilution by:

$$\text{Sed Exch } {}^{31}P_i = {}^{31}P_{soln} \frac{\text{Sed Exch } {}^{32}P}{{}^{32}P_{soln}} \qquad (8)$$

where Sed Exch ${}^{31}P_i$ = exchangeable sediment inorganic P, expressed as μg/g sediment;

${}^{31}P_{soln}$ = inorganic P in solution expressed as μg/g sediment;

${}^{32}P_{soln}$ = the ${}^{32}P$ in solution expressed as % of added ${}^{32}P$;

Sed Exch ${}^{32}P$ = the ${}^{32}P$ in the sediment expressed as % of added ${}^{32}P$.

The precision of estimation of exchangeable P was low in the case of Shield Lake sediments. The major source of error in exchangeable P determination was the large value of the second term in equation (8). Similar problems were also encountered by other investigators (Li et al, 1972).

Langmuir adsorption isotherms (Figure 3.4.1 to Figure 3.4.6) for given experimental data sets were obtained by least squares fit to the standard form (equation 5). The overall shape of isotherms was similar despite the great differences in the amount of P sorbed at a particular solution P concentration. Each isotherm was characterized by a

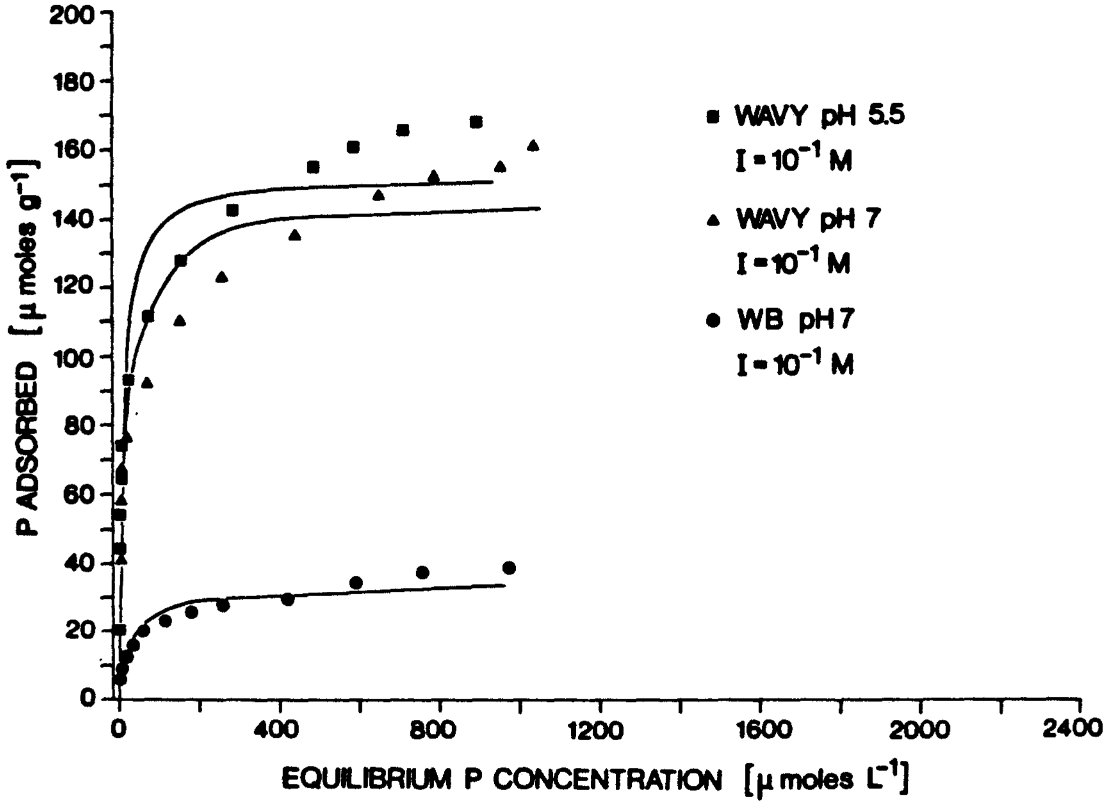


Fig. 3.4.1 Adsorption isotherms for Wavy Lake and Lake Ontario WB sediments. The lines were obtained by least squares fit to the Langmuir equation. Matrix solution 10^{-1} M NaCl.

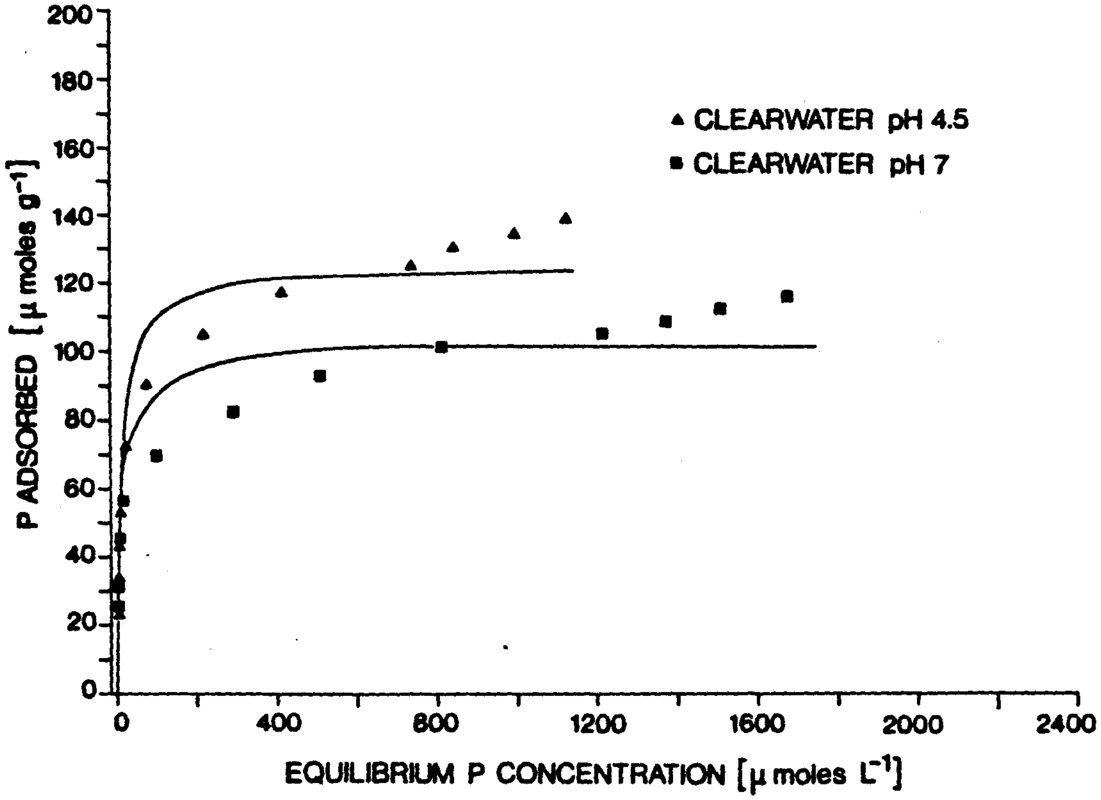


Fig. 3.4.2 Adsorption isotherms for Clearwater Lake sediments. The lines were obtained by least squares fit to the Langmuir equation. Matrix solution 10^{-1} M NaCl.

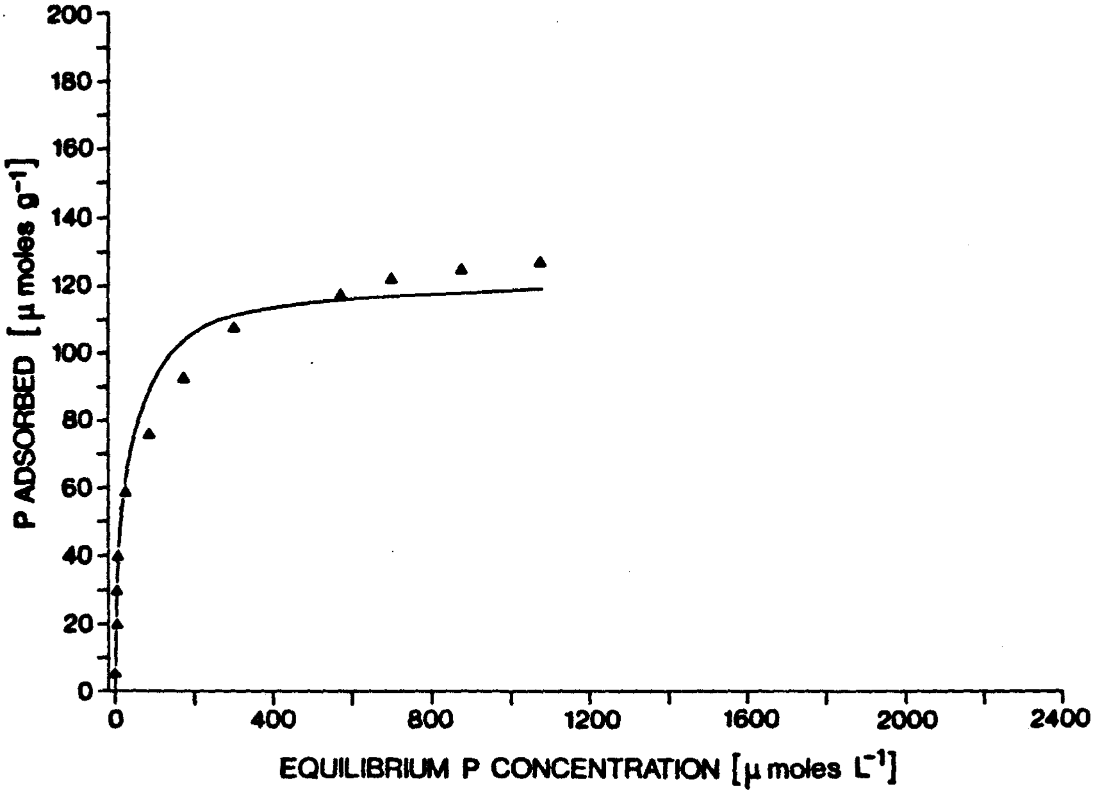


Fig. 3.4.3 Adsorption isotherm for Windy Lake sediment. The line was obtained by least squares fit to the Langmuir equation. Matrix solution 10^{-1} M NaCl.

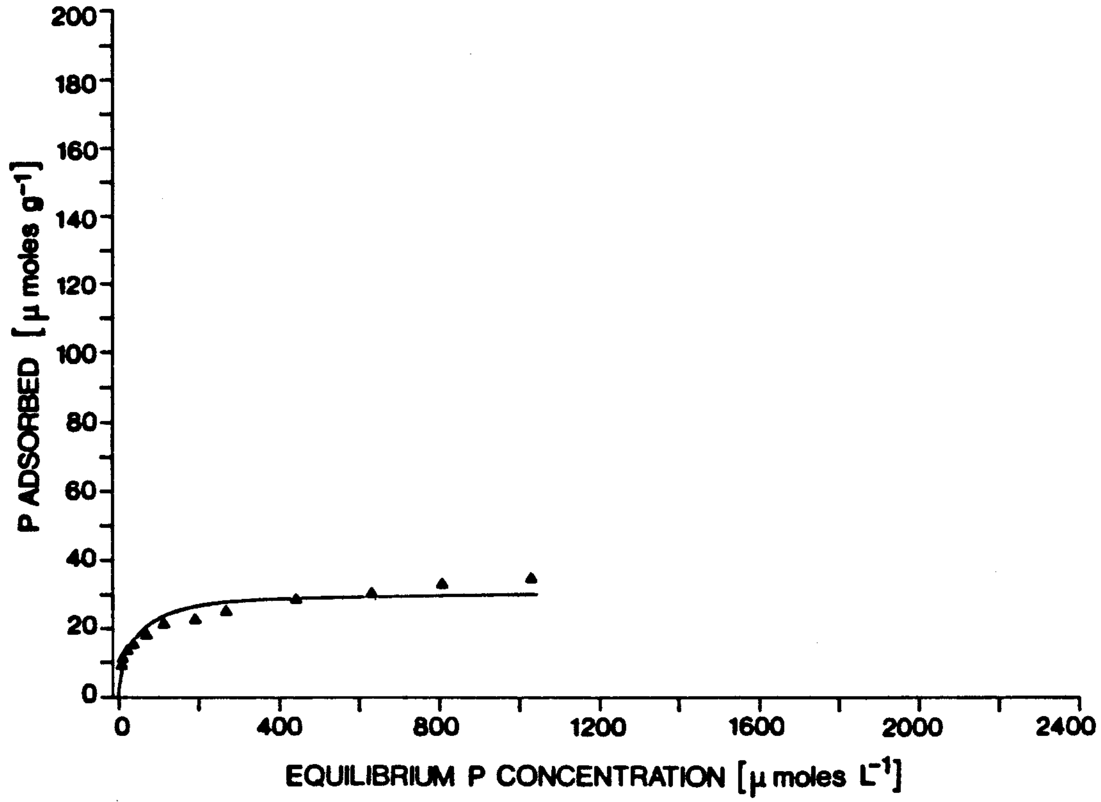


Fig. 3.4.4 Adsorption isotherm for Lake Ontario E-30 sediment. The line was obtained by least squares fit to the Langmuir equation. Matrix solution 10^{-1} M NaCl.

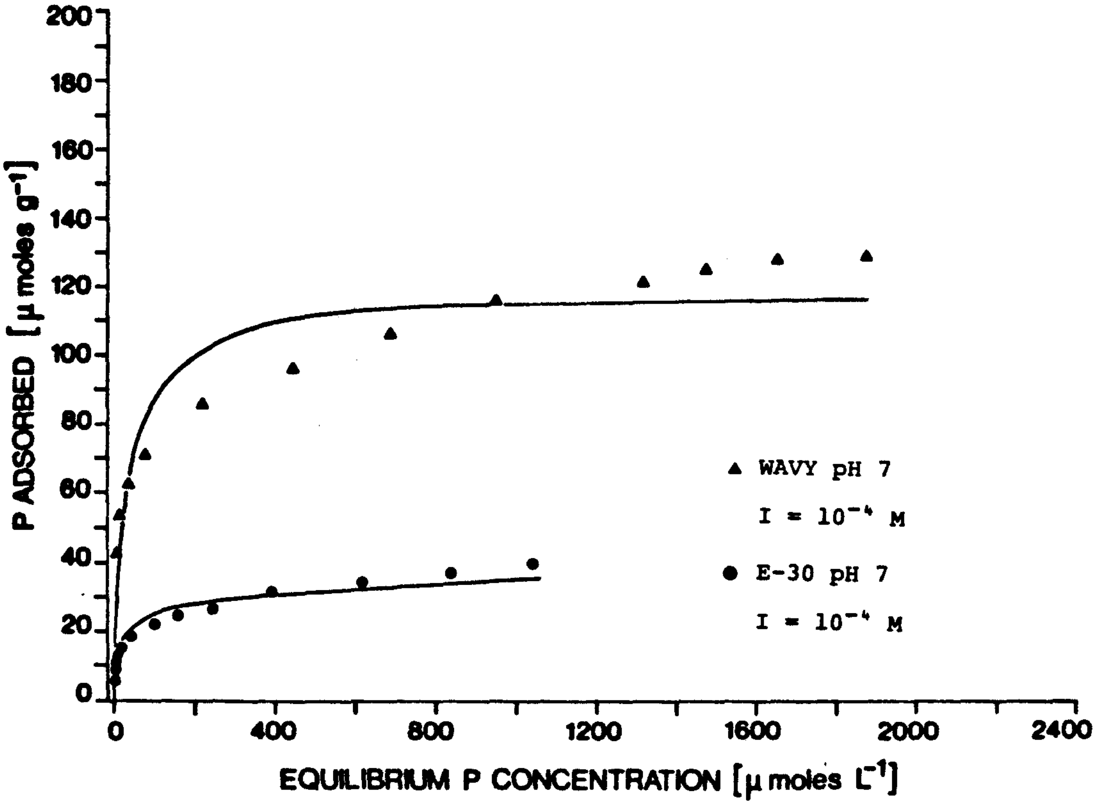


Fig. 3.4.5 Adsorption isotherms for Wavy Lake and Lake Ontario E-30 sediments. The line was obtained by least squares fit to the Langmuir equation. Matrix solution 10^{-4} M NaCl.

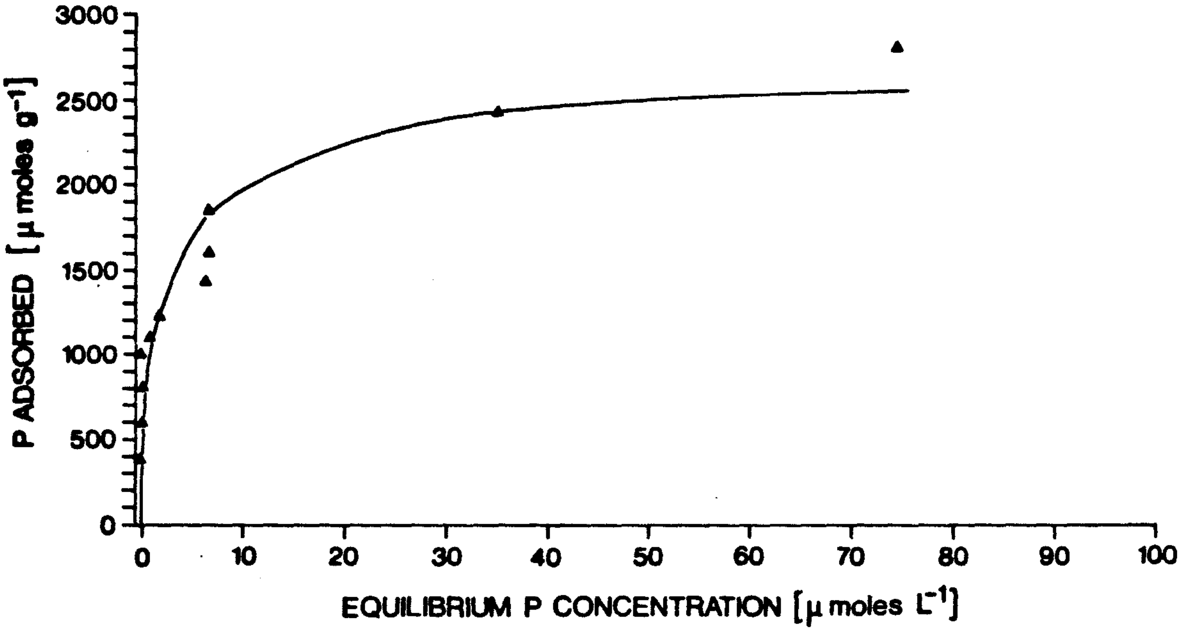


Fig. 3.4.6 Adsorption isotherm for Fe-gel. The line was obtained by least squares fit to the Langmuir equation. Matrix solution 10^{-1} M $NaClO_4$.

large change in the amount of P adsorbed at lower solution P concentration. This was followed by a more gradual change in the amount of P sorbed with increasing solution P concentration. At higher solution P concentrations the isotherms showed deviation from the Langmuir function.

Adsorption isotherm similar to those obtained for sediments was also obtained for hydrous ferric oxide gel (Fe-gel) (Figure 3.4.6), which had a B.E.T. area of 165 m^2g^{-1}. Comparison of the sediment isotherms with that of the Fe-gel suggests the presence of more than one type of adsorption site, possibly on the surfaces of Al oxide.

The values of Langmuir parameters (K, Γ_M) and R^2 values shown in Table 3.4.4 were estimated from equilibrium solution P concentration and the amount of adsorbed P using the non-linear least squares iteration Gauss-Newton method. For comparison, Table 3.4.4 contains data obtained in other adsorption studies.

To facilitate comparison with other physical and chemical processes, the free energies of adsorption ΔG were determined using the relationship $\Delta G = -RT \ln K$ (Graham, 1953; Aveyard and Haydon, 1973; Stumm and Morgan, 1981). This relationship which equates K with the equilibrium constant assumes that the activity coefficients of occupied and unoccupied sites are the same (Ryden et al, 1977). The values of ΔG calculated by the above equation are given in

Table 3.4.4 Langmuir parameters and the values of free energy of adsorption.

Sediment Sample	pH^a	I^b (M)	K L µmol^{-1}	Γ_M µmoles g^{-1}	R^2	ΔG kJmol^{-1}	
Wavy	5.5	10^{-1}	0.1137	151.8	0.8735	-28.5	
Wavy	7	10^{-1}	0.0612	145.2	0.8460	-26.9	
Wavy	7	10^{-4}	0.0329	118.2	0.8365	-25.4	
Clearwater	4.5	10^{-1}	0.0895	124.5	0.9189	-27.9	
Clearwater	7	10^{-1}	0.0690	102.9	0.8622	-26.9	
Windy	7	10^{-1}	0.0842	132.7	0.9004	-27.7	
L.O. E-30	7	10^{-1}	0.0308	31.3	0.8941	-25.3	
L.O. E-30	7	10^{-4}	0.0578	29.7	0.8838	-26.8	
L.O. WB	7	10^{-1}	0.0311	33.9	0.8952	-25.3	
Hydrous ferric oxide gel (Fe-gel)	7	10^{-1c}	0.3530	2632	0.8827	-31.2	
Fe-gel	7	10^{-1c}		1020		-30.7	Ryden <u>et</u> <u>al</u> (1977)
New Zealand soils	7	10^{-1}		10-104		-28.5 to -30.1	Ryden <u>et</u> <u>al</u> (1977)
Lake sediments	4.8-7.0	dist. water	0.033-1.036				Ku <u>et</u> <u>al</u> (1978)

a pH of matrix solution.

b I = Ionic strength of matrix solution (10^{-1} M NaCl)

c matrix solution 10^{-1} M $NaClO_4$

Table 3.4.4. The values appear to be remarkably similar and compare favourably with those obtained for soils by Ryden et al (1977).

The relatively large discrepancy in the values of Γ_M for Fe-gel obtained in this study and that obtained by Ryden et al (1977) could have resulted from difference in age of the suspensions. Ryden et al did not mention how fresh the suspension was in their study. Lijklema (1980) demonstrated that the binding capacity of the fresh precipitate was about 1.7 times greater than that of one-day-old precipitate. The P binding capacity of the Fe-gel used in this study, 2632 μmoles g^{-1}, is in reasonably good agreement with the value of 3210 μmoles g^{-1} obtained by Lijklema for fresh hydrous ferric oxide gel.

The experiments with different lake sediments show a close relationship between the capacity of the sediment to adsorb and retain added inorganic phosphorus. The retention properties of sediments are indicated by the proportion of added inorganic P adsorbed and the proportion of P desorbed in subsequent extraction (Table 3.4.5 to Table 3.4.8).

3.5 SUMMARY

The results of the experimental studies provide an assessment of the effect of pH and related factors (sediment chemistry and mineralogy) on sediment P distribution and on

Table 3.4.5 Adsorbed inorganic phosphorus expressed as percentage of total added P.

Sediment Sample	pH of Matrix Solution	Ionic Strength of Matrix Solution (M)	For added P level (μmoles P g^{-1})											
			10	20	30	40	60	80	100	120	140	150	160	170
			Added P adsorbed as % total added P											
Wavy*	5.5	10^{-1}	99.5	99.4	99.3	99.0	98.3	96.4	93.7	90.5	85.9	84.3	82.1	78.7
Wavy*	7	10^{-1}	99.2	99.0	98.3	98.2	95.6	93.3	89.7	85.2	81.4	79.0	76.1	75.4
Wavy	7	10^{-4}	96.9	96.6	95.1	92.3	85.5	77.8	72.4	68.1	62.3	60.6	58.6	55.8
Clearwater	4.5	10^{-1}	98.9	99.6	99.5	99.2	98.2	96.0	91.1	86.2	79.0	77.5	75.1	73.6
Clearwater	7	10^{-1}	94.08	99.4	98.8	97.9	93.5	85.1	79.5	73.0	65.3	63.4	62.2	60.6
Windy	7	10^{-1}	99.5	99.5	99.4	99.1	98.0	95.5	92.9	89.8	83.6	81.2	78.1	74.7
Wavy after oxalate	7	10^{-1}	-	-	-	2.3	2.3	n.d.	7.0	8.0	6.0	7.7	8.4	7.3

*Samples used to evaluate desorption of sorbed added inorganic P.

n.d. - not determined.

Table 3.4.6 Desorption of added inorganic P.

Sediment Sample	pH of Matrix Solution	Ionic Strength of Matrix Solution (M)	For added P level (μmoles P g^{-1})											
			10	20	30	40	60	80	100	120	140	150	160	170
			Added P desorbed as % added P adsorbed											
Wavy	5.5	10^{-1}	0.3	0.3	0.3	0.4	0.8	1.2	1.9	2.2	2.9	3.1	3.31	3.4
Wavy	7	10^{-1}	0.5	0.5	0.6	0.8	1.4	2.1	2.5	3.4	4.1	4.2	4.2	4.5
Windy	7	10^{-1}	0.3	0.2	0.2	0.3	0.4	0.6	0.9	0.9	1.2	1.1	1.2	0.9

Table 3.4.7 Adsorbed inorganic phosphorus expressed as percentage of total added P.

Sediment Sample	pH of Matrix Solution	Ionic Strength of Matrix Solution (M)	For added P level (μmoles P g^{-1})												
			2	4	6	8	10	15	20	25	30	40	50	60	70
			Added P adsorbed as % total added P												
L.O. E-30*	7	10^{-1}	90.7	91.6	91.5	89.6	87.8	81.4	77.1	68.9	63.9	55.8	49.6	46.0	41.3
L.O. E-30	7	10^{-4}	95.6	95.9	95.0	93.5	90.7	86.2	77.5	73.2	65.0	58.8	49.2	42.9	39.6
L.O. WB*	7	10^{-1}	89.5	90.9	90.4	89.8	88.9	84.5	78.3	71.4	66.6	58.1	52.6	49.4	44.3
L.O. E-30 after oxalate	7	10^{-1}	-	-	-	3.7	4.1	6.1	6.7	7.8	6.1	7.6	8.5	8.3	n.d.

*Samples used to evaluate desorption of sorbed added inorganic P.

n.d. - not determined.

Table 3.4.8 Desorption of added inorganic P.

Sediment Sample	pH of Matrix Solution	Ionic Strength of Matrix Solution (M)	For added P level (μmoles P g^{-1})												
			2	4	6	8	10	15	20	25	30	40	50	60	70
			Added P desorbed as % added P adsorbed												
L.O. E-30	7	10^{-1}	30.0	19.9	16.4	15.1	14.2	14.0	-	11.2	11.4	12.4	11.7	11.1	12.2
L.O. WB	7	10^{-1}	25.6	15.0	13.6	13.1	12.1	10.8	10.2	10.6	10.4	11.4	11.3	11.4	10.4

the immobilization of P by adsorption. The results reveal that:

1. Inorganic P is associated predominantly (~97%) with Fe/Al oxides in soft water lakes. In hard water lakes a significant proportion of inorganic P (~34%) is associated with apatite.
2. Organic P is high in sediments of acid lakes.
3. There is a remarkable similarity in free energy of adsorption (ΔG), -26.7 ± 1.8 $kJmol^{-1}$, for various sediments. However, ΔG of adsorption for Fe-gel, equal to -31.2 $kJmol^{-1}$ is slightly higher than that of the sediments.
4. Shield sediments have high P-binding capacity (118-152 μmoles g^{-1}) when compared with calcareous Lake Ontario sediments (30-34 μmoles g^{-1}).

CHAPTER 4

INTERPRETATION AND DISCUSSION

4.1 INTRODUCTION

In this chapter the effect of pH and other physical and chemical parameters on the state of P in sediments is discussed. The discussion is based on the results presented in the previous chapter which allow comparison of P distribution in sediments of acid and neutral Shield lakes and a hardwater lake.

A simple model is proposed to distinguish phosphate associated with amorphous Al-oxides from that associated with amorphous Fe-oxides.

Furthermore, the results of the adsorption study are analyzed in order to establish the effect of pH versus mineralogy and chemistry of substrate on adsorption and desorption equilibria.

4.2 DISTRIBUTION OF PHOSPHORUS IN SEDIMENTS

The results of analyses revealed that despite a relatively small variation in sediment total P concentration, the distribution of phosphorus among different categories was quite different.

The unusually high values of organic P in sediments of acid lakes (Table 3.3.4), concomitant with high LOI and organic C (Table 3.2.1 and Table 3.3.5) suggest that these sediments contain more organic matter than usually found in sediments of similar neutral lakes (Rao and Dutka, 1983).

The organic matter enrichment in acid lake sediments reflects the inhibition of processes of mineralization. This in turn is caused by decreased microbial population and reduction of microbial activity (Rao et al, 1984) in acid-stressed benthic environment.

The data presented in Table 3.3.5 show that the sediment org C:org P molar ratio, 419:1, is much higher than 106:1. This ratio is considered to represent an average composition of live plankton (Redfield, 1963) and is similar to composition of higher aquatic and terrestrial plants.

As already mentioned in the previous chapter, the org C:org P ratios of investigated sediments (419) (Swan Lake excluded) is similar to that previously found in surficial sediments from Lake Erie (Williams et al, 1976a) and is somewhat higher than that reported for marine sediments, 318±60 by Krom and Berner (1981).

From the measured C/P ratio of sediment organic matter it is concluded that in surficial sediments most of the reactive organic P fraction has been preferentially lost (relative to carbon) due to differential decomposition of org P relative to more refractory org C. The rate of organic C decomposition relative to organic P decomposition does not vary appreciably among the lakes. However, the rate of org P decomposition appears to be faster in lake sediments than that reported for marine sediments.

The extremely high org C/org P ratio in Swan Lake sediment suggests that the preferential loss of org P to org C is greater in this lake than in the other lakes studied. This anomaly is probably due to combination of both a higher amount of organic matter from terrestrial sources, containing more refractory org C and very low pH of water (Table 2.2.1). The low pH enhances the hydrolysis of labile organic phosphorus from the seston to soluble orthophosphate which is assimilated rapidly by the biota. The rapid loss of organic phosphorus from particulate matter before the deposition could significantly increase the org C/org P ratio of surficial sediment.

The distribution of inorganic phosphorus between the apatite-P and NAI-P category in shield sediments differs considerably from that of Lake Ontario sediments. Lake Ontario sediments contain an appreciable amount of apatite phosphorus which suggests that apatite is the stable phase in these sediments (Williams and Mayer, 1972; Williams et al, 1976a; 1976b). It is believed that some of the apatite found in the fine-grained sediments of the depositional basins would be of authigenic or diagenetic origin and some of detrital origin. Although the water of Lake Ontario is undersaturated with respect to hydroxyapatite, the concentration of phosphorus in interstitial water may rise due to the diagenetic processes to the point where precipitation of apatite commences (Williams and Mayer, 1972). Once crystalline apatite is formed it is unlikely that the release of phosphorus from this mineral to overlying water would be rapid. The detrital apatite entering Lake Ontario is thought to be derived from rocks, soils and unconsolidated deposits from the lake's watershed.

In contrast, shield sediments exhibit a very low proportion of apatitic P. This reflects the influence of geological setting on the water chemistry and sediment chemistry of studied lakes.

As discussed in Chapter 2, the Shield lakes are situated in the area which is underlain by noncalcareous bedrock of low solubility. Consequently, low concentrations of Ca are present in water and sediments of these lakes. Both the overlying and the interstitial water are undersaturated with respect to apatite (Carignan, personal communication), hence no precipitation of this mineral takes place. It is therefore not surprising that nearly all the inorganic P in these sediments is present in the form of

NAI-P. These findings also agree with the conclusions from stability diagrams discussed earlier which show that Ca-phosphates are stable at pH > 7, whereas Al- and Fe-phosphates are stable at pH < 7.

Based on the results of the extraction procedures, the NAI-P is on average about 12% higher (Swan Lake excluded) than oxalate-P or CDB-P.

The difference between the NAI-P values and CDB-P or oxalate-P values is probably due to the small amount of inorganic P present in the form of discrete phosphate mineral, which is not removed during the CDB or oxalate extraction, but is solubilized by the subsequent NaOH extraction. The study of extractability of P from different minerals (Williams et al, 1980a) revealed that only 6.2% of total P in variscite ($AlPO_4 \cdot 2H_2O$) was removed during the CDB extraction. The bulk of the P appeared in the NaOH fraction, suggesting that this mineral is readily hydrolyzed in the presence of NaOH to aluminum oxyhydroxide (Bache, 1963; Williams et al, 1980a). It is assumed here that minerals such as strengite ($FePO_4 \cdot 2H_2O$) and barrandite ($(Al,Fe)PO_4$ $2H_2O$) would behave similarly.

Although the above mentioned discrete phosphate minerals have not been observed in lacustrine sediments, one can speculate that they might occur in sediment in the amount which would be below their detection limit.

Since association of NAI-P with amorphous Fe compounds has been well documented (Williams et al, 1971b; 1971c; 1976a; 1976b; Manning et al, 1981; 1982) the amount of Fe associated with amorphous and crystalline oxides and oxyhydroxides was evaluated employing oxalate and CDB extraction procedures. The results (Table 3.3.2) revealed that in the sediments, crystalline Fe minerals such as goethite and hematite are of only minor importance. The amorphous nature of Fe-oxides in lake sediments is probably due to the fact that ions such as phosphate, silica and organic anions inhibit the conversion of amorphous Fe-oxides to crystalline forms (Shukla et al, 1971). In addition, there appears to be continuous seasonal alteration between aerobic and anaerobic conditions which would be unfavourable for the formation of crystalline forms. Since crystalline Fe minerals are of minor importance, only the association of amorphous Fe (Fe_{OX}) with phosphate requires further attention.

The similarity of CDB-P and oxalate-P values (Table 3.3.3 and Figure 3.3.1) suggests that most of the inorganic P other than apatite-P is associated with amorphous hydrated Fe-oxides rather than with crystalline materials.

It is conceivable that orthophosphate ions are contained in a complex of gel-like nature, composed of hydrated ferric oxide, phyllosilicate minerals and organic matter. The existence of such a complex in terrestrial soils and lake sediments was postulated by several investigators (Mattson et al, 1950; Williams et al, 1976a; Jackson and Schindler, 1975). Furthermore, results of adsorption on actual sediments and amorphous ferric oxide-gel confirm the importance of amorphous substrate, containing iron, in binding of inorganic phosphorus.

The association of sediment inorganic P with amorphous hydrated Al-oxides as determined by oxalate extraction (Table 3.3.2) is also plausible (Parfitt, 1977; Ku et al, 1978), though poor correlation between inorganic P and Al was observed (Williams, 1971c; Bortleson and Lee, 1974).

4.3 THE MODEL OF P UPTAKE ON AMORPHOUS Al/Fe OXIDES

Models are useful in interpreting the experimental data. In this study a simplified model is developed using the results of the selective extractions in order to assess the importance of Fe and Al oxides and hydrated oxides in binding of inorganic P.

The model is developed by assuming that a simple relationship exists between adsorbed phosphorus $[P_{SUBST}]$ and extractable phosphorus $[P_{EXTR}]$. Two types of adsorption sites are considered: $[P_{SUBST\ Al}]$, $[P_{SUBST\ Fe}]$, corresponding to the adsorption sites on aluminum and iron oxides, respectively.

The following mass balance equation can be written for phosphorus extracted from the oxide surfaces:

$$[P_{EXTR}] = P_{OX} = [P_{Al}] + [P_{Fe}] \tag{9}$$

where $[P_{Al}]$, $[P_{Fe}]$ represent phosphorus extracted from Al and Fe oxides, respectively. For low surface coverage, it is assumed that $[P_{Al}]$ and $[P_{Fe}]$ are related to the adsorbed phosphorus through linear relationships:

$$[P_{Al}] = K_{Al}\ [P_{SUBST\ Al}] \tag{10}$$

$$[P_{Fe}] = K_{Fe}\ [P_{SUBST\ Fe}] \tag{11}$$

If $[P_{Al}]$ and $[P_{Fe}]$ are proportional to the extractable aluminum $[Al_{OX}]$ and extractable iron $[Fe_{OX}]$, then the following expression can be written:

$$\frac{[P_{Al}]}{[P_{Fe}]} = K' \frac{[Al_{OX}]}{[Fe_{OX}]} \tag{12}$$

where $K' = \frac{\log K_{Al}}{\log K_{Fe}} \simeq 0.83$ (McMaster University, 1981).

Substitution of the equation (12) into the equation (9) results in a solution of P_{Fe} :

$$[P_{Fe}] = \frac{[P_{EXTR}]}{1 + K' \frac{[Al_{OX}]}{[Fe_{OX}]}} \tag{13}$$

Substituting for $[P_{Fe}]$ value in equation (9), the value of $[P_{Al}]$ can be calculated.

The results obtained by this calculation are tabulated in Table 4.3.1 and are graphically presented along with the experimental data from Table 3.3.2 in Figure 4.3.1 and Figure 4.3.2.

As seen in Figure 4.3.1 and Figure 4.3.2, better correlation exists between P_{OX} versus $[Fe_{OX}]$ ($r = 0.8916$) than between P_{OX} versus $[Al_{OX}]$ ($r = 0.4478$).

The comparison of calculated $[P_{Al}]$ and $[P_{Fe}]$ values with the experimental data P_{OX} reveals a close agreement between $[P_{Al}]$ and P_{OX} in acid lakes, suggesting an association of larger part of NAI-P in sediments of these lakes with Al-oxides. On the other hand, the reasonably close agreement between $[P_{Fe}]$ and P_{OX} in sediments from the neutral lakes suggests an association of major part of inorganic P with Fe-oxides.

The exception is the value of P_{OX} in sediment of Swan Lake which agrees well with calculated values of $[P_{Fe}]$ and $[P_{Al}]$, but is lower than the value predicted from the regression function.

The low P_{OX} value and consequently the NAI-P value in Swan Lake sediment could be explained by the fact that at the time of sampling anoxic conditions prevailed above the sediment-water interface (Bourbonniere, personal communication). Such conditions would result in release of both iron

Table 4.3.1 The calculated distribution of inorganic phosphorus between Fe and Al oxides and hydrated oxides.

Sediment Sample	$[P_{Fe}]$ µmoles g^{-1}	$[P_{Al}]$ µmoles g^{-1}
Wavy	4.99	29.21
Clearwater	4.90	10.60
Swan	3.19	2.58
Windy	31.89	9.51
L.O. E-30	25.21	3.99
L.O. WB	22.52	6.38

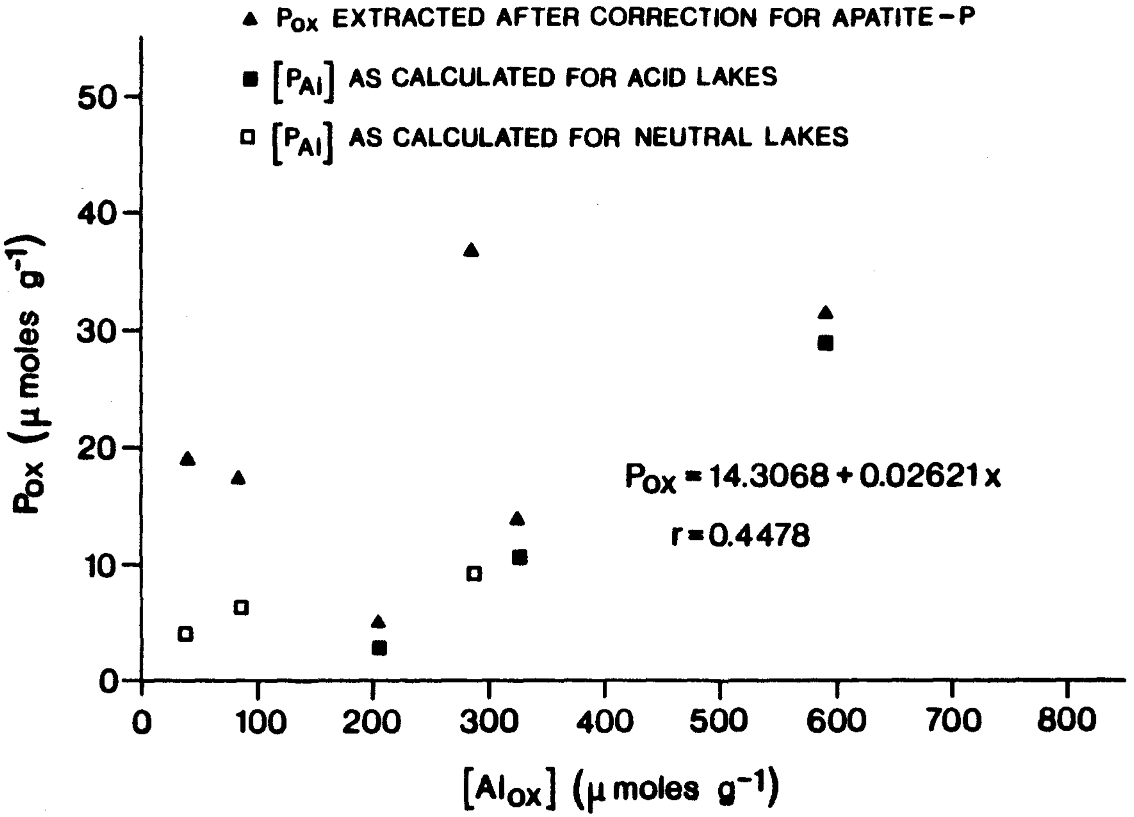


Fig. 4.3.1 Relation between oxalate extractable Al and P.

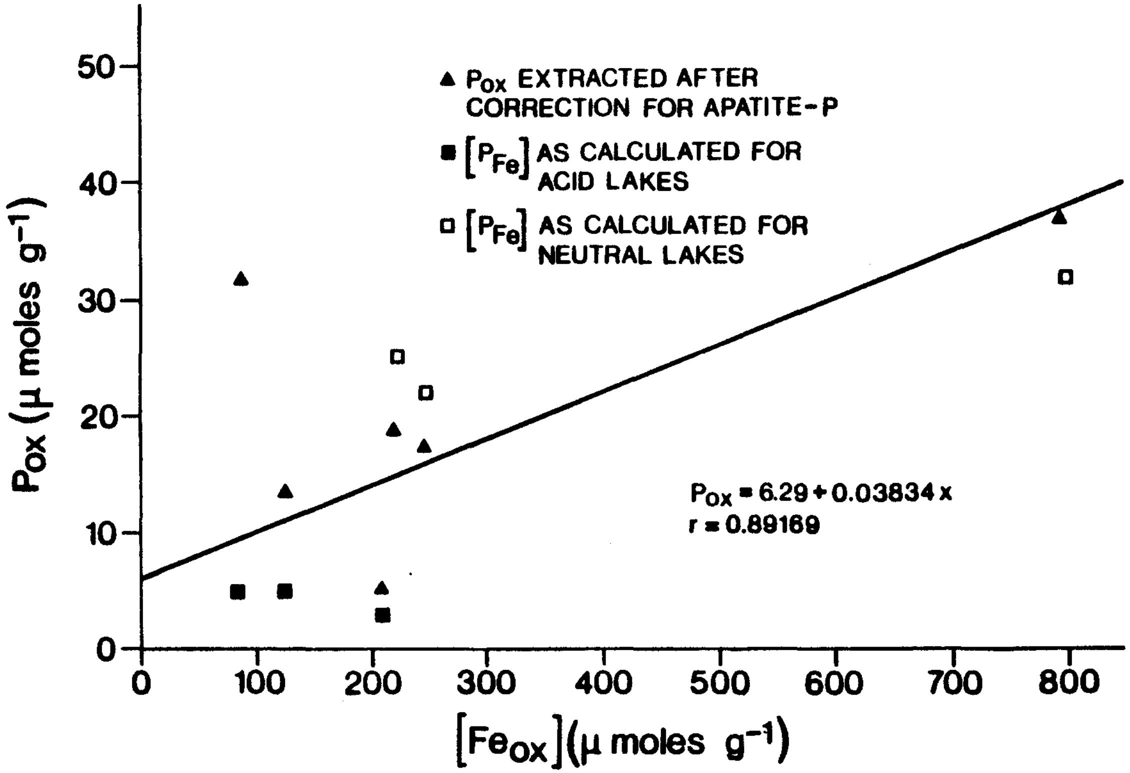


Fig. 4.3.2 Relation between oxalate extractable Fe and P.

and phosphate from sediments into overlying water, causing increased biological production in this lake.

If, however, phosphate was not released into the overlying water, the sediment P_{OX} would be higher and the discrepancy between P_{OX} and $[P_{Fe}]$ would probably be similar to those observed for the other acid lake sediments.

The sum of $[P_{Fe}]$ + $[P_{Al}]$ agrees well with the experimentally determined values of P_{OX} for Shield sediments. However, discrepancy appears when the Lake Ontario sediments are compared. For these sediments the sum of calculated values is higher than analytically obtained P_{OX}. One may speculate that the difference results from the extraction of some structural Fe from the chlorite lattice. This would result in overestimation of amorphous Fe, thus, in higher values of calculated $[P_{Fe}]$. Preliminary analysis by Mössbauer spectroscopy confirms this speculation.

The model developed here, based on the results of selective removal of certain forms of Fe, Al and P provides useful information on the association of inorganic P with Fe and Al complexes in lake sediments. It also suggests some limitation in using the empirical procedures for evaluation of forms of P in sediments.

4.4 FACTORS AFFECTING PHOSPHATE ADSORPTION EQUILIBRIA

The results of the laboratory scale adsorption study are assessed here for the purpose of explaining the behaviour of phosphate in systems with various types of sediments and hydrous ferric oxide gel under different conditions. Such an approach is very useful for better understanding of the effect of lake acidification on the retention properties of sediments.

The Langmuir equation was used to describe the adsorption mechanism. From numerous phosphate adsorption studies it is clear that the Langmuir model is a reasonable approximation; however, it takes no account of surface charges (Parfitt, 1977; Barrow, 1978; Posner and Bowden, 1980). Despite this limitation, the model can be used to give approximate empirical description of the curves and so summarize them with two parameters which then allow ready comparison of adsorption characteristics between the sediments (Posner and Bowden, 1980). The concept of the upper limit of adsorption implied from saturation of adsorption sites is a definite advantage of this model.

The discrepancy between the experimental data and the best fit curve calculated from the Langmuir model can be attributed to the fact that this rather simple model only approximately describes the adsorption process over relatively wide concentration range. It is conceivable that a better fit would be obtained using a more complicated model of Bowden et al (1974; 1977). However, this model requires the use of laborious procedures to generate the adsorption curves (Barrow, 1978), thus it is less suitable for comparative purposes.

The results of adsorption experiments indicate that the type and properties of sediments were only reflected in the magnitude of the sorption maxima Γ_M (Table 3.4.4). The noncalcareous sediments exhibited significantly higher adsorption capacity than did the calcareous Lake Ontario sediments. This suggests that more surface sites are available for adsorption in the former than in the latter. This in turn may reflect the difference in the chemistry and mineralogy between the investigated sediments. At the phosphate concentration typical of that found in the lake, the shield sediments adsorbed nearly 100% of added P. This is consistent with the field observations of Yan and Lafrance (1982), who reported between 72-86% loss of added P to the sediments. At higher phosphate solution concentration the shield sediments exhibited a continued linear adsorption, which is thought to indicate the presence of more than one type of adsorption site (Parfitt et al, 1975; 1977).

Results with model systems containing Al and Fe oxides suggest that the phosphate is adsorbed very strongly at low solution concentration and therefore it is difficult to distinguish between two types of sites (Parfitt, 1977). At higher phosphate solution concentration the isotherms on aluminum containing surfaces often show continued linear adsorption in contrast to the well defined plateau on iron oxide surfaces (Muljadi et al, 1966; Parfitt et al, 1975). Thus, it is reasonable to assume that continued linear adsorption observed at higher P concentration on the shield sediments is due to the presence of aluminum containing surfaces. The results of oxalate extraction (Table 3.3.2) support this conclusion.

Sorption in excess of that predicted from the Langmuir model in this study may involve dissolution and precipitation reactions involving primarily aluminum-containing surfaces (Chen et al, 1973; Parfitt, 1977). However, the phosphate concentration at which the deviation from the Langmuir model occurs is far beyond that encountered in water column or in interstitial water of sediments, therefore it is of no consequence to actual sediments.

The values of free energy of adsorption (ΔG) are remarkably similar for all the investigated sediments (Table 3.4.4). Such similarity strongly suggests that the nature and the properties of sediments do not affect the nature of the adsorption process. Neither the experimental conditions (e.g., variation of pH and ionic strength I) affect the nature of the adsorption reaction. The relatively large negative values of ΔG suggest that the nature of the P uptake is a strong chemisorption. A strong tendency towards chemical bonding between phosphate groups and metal ions in solid lattice has been reported (Stumm and Morgan, 1970; Ryden et al, 1977). Apparently, the forces involved in precipitation of Al or Fe phosphates are similar to those involved in adsorption of phosphates on the surface of Al or Fe oxides or hydroxides (Stumm and Morgan, 1970). In this view, adsorption is a special case of precipitation, with the formation of electrical double layer (EDL) being the significant difference.

The mechanism of phosphate adsorption on the surfaces of metal oxides is illustrated in this study by the example of amorphous hydrous ferric oxide gel (Fe-gel). The synthetic Fe-gel was chosen for the model surface for two reasons. Firstly, appreciable amount of amorphous Fe-oxide is present in lake sediments. Secondly, good correlation between extractable iron and inorganic phosphorus has been reported in a large number of environmental studies.

The close association between iron and phosphate results presumably from the high efficiency of phosphate removal by amorphous hydrous ferric oxide. This gel-like substance has an isoelectric point (IEP) of 8.5 (Parks, 1967) and at pH values below the IEP can remove as much as

5% of its own weight of phosphorus in orthophosphate form from solution (Stamm and Kohlschutter, 1965)

The proposed mechanism of P adsorption on the Fe-gel is represented in equation (14) below, which shows that the exchange reaction is accompanied by deprotonation of the ligand at the surface (Stumm and Morgan, 1981).

$$\left.\begin{array}{l}\mathrm{Fe-OH}\\ \mathrm{Fe-OH}\end{array}\right|^{\circ} + H_2PO_4^- \rightleftharpoons \begin{array}{l}\left.\begin{array}{l}\mathrm{Fe-OH}\\ \mathrm{Fe-H_2PO_4}\end{array}\right|^{0} + OH^- \\[1em] \left.\begin{array}{l}\mathrm{Fe-OH}\\ \mathrm{Fe-HPO_4}\end{array}\right|^{1-} + H_2O\end{array} \qquad (14)$$

Since phosphate ions confer a negative charge to the surface of hydrous oxide, the surface charge decreases (becomes more negative) and the isoelectric point is shifted to the lower pH values.

The results obtained (Table 3.4.4) confirm the high adsorption capacity of Fe-gel. The similarity of ΔG values of Fe-gel and those of sediments substantiates the importance of hydrous amorphous ferric oxide being an important adsorbing constituent in sediments.

To assess the importance of pH on the overall adsorption characteristics of sediments, the Langmuir parameters and the free energy of adsorption ΔG at various pH were evaluated for selected sediments. Comparison of Γ_M values (Table 3.4.4) reveals the stronger binding power of the same sediment at lower pH. For example, in case of Wavy sediment the decrease in pH by 1.5 units represents an increase in adsorption by 4%. For Clearwater sediment the decrease in pH by 2.5 units enhances the adsorption by ~17%.

The observed increase in magnitude of phosphate binding with decreasing pH is consistent with the adsorption model discussed earlier.

The effect of ionic strength on adsorption was also examined, since the experiments were conducted at ionic strength higher than that common to the environment of investigated sediments. Such high ionic strength was chosen in order to attain the equilibrium faster and to improve and speed up the separation of solid and aqueous phase at the end of experiments.

The results show that magnitude of the phosphate adsorption increased with the higher ionic strength. The increase was insignificant for Lake Ontario E-30 sediment; however, 18% increase in adsorption was observed with Wavy sediment when the ionic strength of matrix solution was increased by three orders of magnitude. The increase in adsorption resulting from the increase in ionic strength can be explained on the basis of the electric double layer (EDL) theory (Parks, 1975; Stumm and Morgan, 1981). According to this theory the thickness of the EDL (χ^{-1}) which controls the magnitude of adsorption is inversely related to the concentration of the electrolyte (I) by the relation

$$\chi^{-1} \sim \frac{2.8 \times 10^{-8}}{I} \qquad (15)$$

The reversibility of adsorption evaluated from the amount of added P desorbed indicates lower retention capacity of calcareous Lake Ontario sediments than that of noncalcareous shield sediments. Between 10-30% of added P sorbed was desorbed from Lake Ontario sediments, whereas only 0.5-4% of added P was released from the Shield lake sediments. The sediments which retained the most added P during adsorption tended to release the least during the subsequent desorption (Tables 3.4.6 to 3.4.8). Similar findings were reported on sediments from Wisconsin lakes by Williams _et al_, (1971c).

In general, the relatively low desorption of added inorganic P suggests that the adsorption process is not readily reversible. This is to be expected if removal of phosphate from solution takes place by specific adsorption.

The results of adsorption experiments have shown that the binding capacity of two sediments (Wavy and L.O. E-30) was drastically reduced (Table 3.4.5 and Table 3.4.7) after the sediments were extracted with oxalate reagent, confirming the importance of amorphous Al and Fe phase in adsorption properties of sediments.

The important conclusion which follows from the adsorption study, provides evidence for considerably higher adsorption capacity and better retention ability of Shield sediments than that of Lake Ontario sediments. The difference in the magnitude of adsorption caused by the shift of pH or ionic strength is relatively small when compared with the difference in adsorption due to the nature and properties of sediments. Thus, it is plausible that chemistry and mineralogy of sediments are of far greater importance in determining adsorption capacity of sediments than the pH of the lakes.

The effect of factors controlling adsorption and desorption of phosphates on the solids discussed in this chapter has significant implications in controlling the phosphate level in the water columns of studied lakes.

4.5 RELATION OF BIOLOGICAL AVAILABILITY TO SEDIMENT P DISTRIBUTION

Previous discussion shows that phosphorus in sediments is present in various forms which differ among each other in their solubility. Consequently, the availability of P is then dependent on the form in which this element occurs in sediment and on the factors that control the rate of P release from different sediment P categories.

In the present study the portion of sediment P which would be potentially available for biological utilization (bioavailable P) amounts to about 70% of NAI-P (Figure 3.3.2, Table 3.3.3). This fraction of sediment P probably represents the upper limit of sediment bioavailable P (Sonzogni _et al_, 1982). Using this finding one implies that the sediments with high NAI-P (Shield sediments with the exception of Swan sediment) contain high bioavailable P, whereas sediments containing some apatitic P (Lake Ontario sediments) contain less bioavailable P. The difference in bioavailable P concentration reflects the fact that phosphate bioavailability is a function of many variables (Logan _et al_, 1979; De Pinto, 1981): sediment geochemistry, sediment particle size, microfloral density and anthropogenic factors. The sediment geochemistry is determined by its mineral composition and degree of crystallinity of minerals in which phosphorus is contained. Amorphous phases are more easily dissolved and the P is more readily available to algae than crystalline phases.

Whether potentially available sediment P actually becomes available in the lake depends on the factors such as Eh, pH and physical agitation. Direct utilization of sediment phosphorus by nutrient deficient algae and higher aquatic plants may also occur (Golterman, 1973; 1977). This mechanism, however, would require resuspension of the sediment particles into the euphotic zone.

The low concentration of NAI-P, thus also the bioavailable P in Swan Lake sediment may be attributed to suppressed mineralization of the organic matter and to release of the significant amount of inorganic P from sediment into the overlying water. Anoxic conditions that prevailed in this small and shallow lake at the time of sampling and probably during the entire summer season would favour the release of the NAI-P. Net release of phosphrus during the summer months is apparently common in ponds and shallow eutrophic lakes (Lean and Charlton, 1976).

The mechanism of internal phosphorus loading just described may be responsible for elevated P level in the water and for dense mats of benthic algae observed in this lake (Stokes, 1980; Ontario Ministry of the Environment, 1982).

Obviously, the phosphorus capacity of the sediments from different lakes does not, as a single factor, condition the trophic state of the lakes. Factors other than chemical and physical characteristics of sediments such as redox conditions, pH and temperature may influence the movement of phosphorus between the water and the sediments.

4.6 SUMMARY AND CONCLUSIONS

On the basis of experimental evidence the following conclusions were derived:

1. Sediments from different types of lakes show a different distribution of P among the various categories. The concentration of apatite-P is considerably lower in Shield lake sediments than in Lake Ontario sediments, reflecting differences in local geology. This observation is also consistent with the prediction based on the thermodynamic criteria.
2. Most of NAI-P in sediments is associated with amorphous Fe and Al oxyhydroxides.
3. Bioavailable P, as determined by 0.1 N NaOH, constitutes about 70% NAI-P and accounts for a larger portion of inorganic P in Shield sediments than in calcareous Lake Ontario sediments. This again is attributed to the presence of biologically unavailable apatite-P in Lake Ontario sediments. The proportion of sediment bioavailable P determined in this study compares favourably with the results obtained by Williams et al (1980b) concerning sediments of neutral lakes.
4. The concentration of organic P observed in acid lakes is proportional to organic C and LOI and is significantly higher than in the sediments from neutral lakes. The enrichment in organic matter thus also in organic P

reflects inhibition of mineralization in acid lakes due to the reduction of microbial activity. These results support the conclusions of Rao and Dutka (1983) and Rao *et al* (1984).

5. The ratio of org C:org P (419) suggests preferential mineralization of phosphorus relative to carbon which is in accord with conclusion of Krom and Berner (1981).
6. Phosphorus uptake is a ligand exchange process in which the ligands from the surface of the solid oxyhydroxides exchange with phosphate ions in solution. The adsorption process, as indicated by ΔG values, is independent of the nature and properties of sediments which are largely determined by their physical and chemical characteristics.
7. The nature and properties of the sediments, however, effect the magnitude of adsorption. The noncalcareous Shield sediments adsorb considerably more phosphorus than calcareous Lake Ontario sediments. The difference in magnitude of adsorption may be due to more adsorption sites on hydrated Al oxides in Shield sediments.
8. The Shield sediments having higher adsorption capacities released less added P adsorbed in subsequent desorption reaction than did the calcareous Lake Ontario sediments with the lower adsorption capacity.

9. The effect of pH and ionic strength on the magnitude of adsorption is relatively small when compared with the effect of the properties of the sediment.

4.7 RECOMMENDED FUTURE WORK

The following course of action could be undertaken to gain a better understanding of the status of phosphorus in lake sediments:

1. A non-destructive method using Mössbauer spectroscopy would complement current extraction techniques. This method would help to verify the utility of the existing extraction procedures for evaluation of forms of P in sediments.
2. Phosphorus concentration and P retention capacity of suspended particulate matter in acid lakes should be determined. It is proposed to devote more attention to productive acid lakes, in particular to the mechanism of the internal P loading. In this regard, seasonal variation in dissolved Fe and P concentration in the water should be related to the quantity and the composition of the suspended particulate matter.
3. Finally, the role of aluminum versus iron in binding of inorganic phosphorus in sediments of acid lakes should be investigated. More data are necessary to support or to disprove conclusions of the model presented in this study.

REFERENCES

Allen, H.E., and J.R. Kramer (eds.). 1972. Nutrients in natural waters. Wiley-Interscience, New York. 457 p.

Almer, B., W. Dickson, C. Ekstrom, and E. Hornstrom. 1978. Sulfur pollution and the aquatic ecosystem. pp. 271-311 in J.O. Nriagu (ed.). Sulfur in the Environment: Part II Ecological Impacts. Wiley-Interscience, New York. 482 p.

Aveyard, R., and D.A. Haydon. 1973. An introduction to the principles of surface chemistry. pp. 214-215. London: Cambridge Univ. Press.

American Chemical Society, Subcommittee on Environmental Improvement Report. 1969. Cleaning our environment, the chemical basis for action. pp. 95-162.

American Water Works Association Task Group 2610-P Report. 1966. Sources of nitrogen and phosphorus in water supplies. 40 p.

Bache, B.W. 1963. Aluminum and iron phosphate studies relating to soils: 1. Solution and hydrolysis of variscite and strengite. J. Soil Sci. V. 14: 113-123.

Bache, B.W. 1964. Aluminum and iron phosphate studies relating to soils. II. Reactions between phosphate and hydrous oxide. J. Soil Sci. 15: 110-116.

Barrow, N.J. 1978. The description of phosphate adsorption curves. J. Soil Sci. 29: 447-462. ✓

Bates, M.H., and N.J.E. Neafus. 1980. Phosphorus release from sediments from Lake Carl Blackwell, Oklahoma. Water Res. 14: 1477-1481.

Bauwin, G.R., and E.H. Tyner. 1957. The nature of reductant-soluble phosphorus in soils and soil concretions. Soil Sci. Soc. Amer. Proc. 21: 250-257.

Berner, R.A. 1971. Principles of chemical sedimentology, McGraw-Hill, New York, 240 p.

Berner, R.A. 1980. Early diagenesis. Princeton Univ. 241 p.

Bortleson, G.C., and G.F. Lee. 1974. Phosphorus, iron, and manganese distribution in sediment cores of six Wisconsin lakes. Limnology and Oceanography, 1974 V. 19(5): 794-801.

Bostrom, B., M. Janson, and C. Forsberg. 1982. Phosphorus release from lake sediments. Arch. Hydrobiol. 18: 5-59.

Bostrom, B., and K. Pettersson. 1982. Different patterns of phosphorus release from lake sediments in laboratory experiments. Hydrobiologia. 92: 415-429.

Bourbonniere, R.A. 1984. Personal communication.

Bowden, J.W., A.M. Posner, and J.P. Quirk. 1974. Generalised model for anion and cation adsorption at oxide surfaces. Nature. 245: 81-84.

Bowden, J.W., A.M. Posner, and J.P. Quirk. 1977. Ionic adsorption on variable charge mineral surfaces. Theoretical charge development and titration curves. Aust. J. Soil Res. 15: 121-136.

Breeuwsma, A., and J. Lyklema. 1973. Physical and chemical adsorption of ions in electrical double layer on hematite (α-Fe_2O_3). J. Coll. Interface Sci. 43: 437-448.

Bromfield, S.M. 1967. Phosphate sorbing sites in acid soils. I. An examination of the use of ammonium fluoride as a selective extractant for aluminum-bound phosphate soils. Aust. J. Soil Res. 5: 93-102.

Burns, N.M., and C. Ross. 1972. Project HYPO. Canada Centre for Inland Waters, Paper No. 6. United States Environmental Protection Agency, Technical Report, TS-05-71-208-24.

Carignan, R. 1984. Personal communication.

Carritt, D.E., and S. Goodgal. 1954. Sorption reactions and some ecological implications. Deep-Sea Res. 1: 224-243.

Castellan, G.W. 1983. Physical Chemistry, Addison-Wesley Publishing Co.

Chang, S.C., and M.L. Jackson. 1957. Fractionation of soil phosphorus. Soil Sci. 84: 133-144.

Chen, Y.S., J.N. Butler, and W. Stumm. 1973. Kinetics study of phosphate reaction in aluminum oxide and kaolinite. Environ. Sci. Technol. 7: 327-332.

Colé, C.V., S.R. Olsen, and C.O. Scott. 1953. The nature of phosphate sorption by calcium carbonate. Soil Sci. Soc. Amer. Proc. 17: 352-356.

Davis, J.A. 1982. Adsorption of natural dissolved organic matter at the oxide/water interface. Geochimica et Cosmochimica Acta Vol. 46: 2381-2393.

Delfino, J.J., G.C. Bortleson, and G.F. Lee. 1969. Distribution of Mn, Fe, P, Mg, K, Na, and Ca in the surface sediments of Lake Mendota, Wisconsin. Environ. Sci. Technol. 3: 1189-1192.

Dell, C.I. 1973. Vivianite: an authigenic phosphate mineral in Great Lakes sediments. Proc. 16th Conf. Great Lakes Res., Internat. Assoc. Great Lakes Res. 1027-1028.

Dillon, P.J., D.S. Jeffries, W. Snyder, R. Reid, N.D. Yan, D. Evans, J. Moss, and W.A. Schneider. 1978. Acidic precipitations in South-Central Ontario: Recent observations. J. Fish Res. Board Can. 35: 809-815.

Dillon, P.J., and P.J. Smith. 1982. Sediment chemistry and rates of sedimentation in lakes near Sudbury, Ontario. In Studies of Lakes and Watersheds near Sudbury, Ontario: Final limnological report, SES009/82, Ontario Ministry of the Environment.

Dobson, H.F.H. 1984. Lake Ontario Water Chemistry Atlas. NWRI Contribution No. 84-15, Submitted to IWD, Scientific Series.

Dobson, H.F.H. 1981. Trophic conditions and trends in the Laurentian Great Lakes. W.H.O. Water Quality Bulletin, 6(4): 146-151, 158 & 160.

Dobson, H.F.H. 1980. Observed Phosphorus in Lake Ontario. Great Lakes Focus in Water Quality, 6(1), International Joint Commission, Windsor, Ontario.

Edzwald, J.D., D.C. Toensing, and M.C.Y. Leung. 1976. Phosphate adsorption reactions with clay minerals. Environ. Sci. Technol. 10: 485-490.

Einsele, W. 1938. Über chemische und kolloidchemische Vorgänge in Eisen-Phosphat Systemen unter limnochemischen und limnogeologischen Gesichtspunkten. Arch. Hydrobiol. 33: 361-387.

Ellis, J.D., and A. Golomb. 1981. Lake acidification and its neutralization. Ontario Hydro Research Review, Number 2.

Emerson, S., and G. Widmer. 1978. Early diagenesis in anaerobic lake sediments II. Thermodynamic and kinetic factors controlling the formation of iron phosphate, Geochim. et Cosmochim. Acta. V. 42: 1307-1316.

Fife, C.V. 1962. An evaluation of ammonium fluoride as a selective extractant for aluminum-bound soil phosphate. II. Soil Sci. 93: 118-123.

Fillos, J., and H. Biswas. 1976. Phosphate release and sorption by Lake Mohegan sediments. Jour. Environmental. Engr. Div. ASCE. 102: 239-249.

Fillos, J., and W.R. Swanson. 1975. The release of nutrients from river and lake sediments. J. Water Pollut. Control Fed. 47: 1032-1042.

Fitzgerald, G.P. 1970. Aerobic lake muds for the removal of phosphorus from lake waters. Limnol. Oceanogr. 15: 550-555.

Frink, C.R. 1967. Nutrient budget: Rational analysis of eutrophication in a Connecticut lake. Environ. Sci. Technol. 1: 425-428.

Froelich, P.N., G.P. Klinkhammer, M.L. Bender, N.A. Luedtke, G.R. Heath, D. Cullen, P. Dauphin, D. Hammond, B. Hartman, and V. Maynard. 1979. Early oxidation of organic matter in pelagic sediments of the eastern equatorial Atlantic suboxic diagenesis. Geochim Cosmochim Acta. 43: 1075-1091.

Gallepp, G.W. 1979. Chironomid influence on phosphorus release in sediment-water microcosms. Ecology. 60: 547-556.

Gastuche, M.C., J.J. Fripiat, and S. Sokolski. 1963. Fixation du phosphore par les hydroxydes de fer et d'aluminum amorphes et cristallisés. Pedologie 13: 155-180.

Golterman, H.L. 1977. Sediments as a source of phosphate for algal growth, p. 286-293. In H.L. Golterman (ed.), Interactions between sediments and fresh water. Junk.

Golterman, H.L. 1973. Vertical movement of phosphate in freshwater. In E.J. Griffith, A. Beeton, J. Spencer, and D. Mitchell (eds.). Environmental phosphorus handbook. Wiley-Interscience, New York.

Graham, D. 1953. The characterisation of physical adsorption systems. I. The equilibrium function and the standard free energy of adsorption. J. Phys. Chem. 57: 665-689.

Graneli, W. 1979. The influence of Chironomus plumosus larvae on the exchange of dissolved substances between sediment and water. Hydrobiologia. 66: 149-159.

Harvey, H., R.C. Pierce, P.J. Dillon, J.R. Kramer, and D.M. Whelpdale. 1981. Acidification in the Canadian Aquatic Environment. Publication NRCC No. 18475 of the Environmental Secretariat, National Research Council of Canada.

Harwood, J.E., R.A. van Steenderen, and A.L. Kuhn. 1969. A rapid method for orthophosphate analysis at high concentrations in water. Water Res. 3: 417-423.

Hayes, F.R. 1964. The mud-water interface. Oceanogr. Mar. Biol. Ann. Rev. 2: 121-145.

Hayes, F.R., and J.E. Phillips. 1958. Lake water and sediment. IV. Radiophosphorus equilibrium with mud, plants, and bacteria under oxidized and reduced conditions. Limnol. Oceanogr. 3: 459-475.

Hendrey, G.R. 1976. Effects of pH on the growth of periphytic algae in artificial stream channels. Sur. Nedbors Virkning pa Skog og Fisk Project IR 25/76.

Hesse, P.R. 1973. Phosphorus in lake sediments in Environmental Phosphorus Handbook. E.J. Griffith, A. Beeton, J.M. Spencer, and D.T. Mitchell (eds.) Wiley-Interscience, New York.

Hingston, F.J., R.J. Atkinson, A.M. Posner, and J.P. Quirk. 1967. Specific adsorption of anions. Nature, Lond. 215: 1459-1461.

Hingston, F.J., and A.M. Posner. 1972. Anion adsorption by geothite and gibbsite. 1. The role of the proton in determining adsorption envelopes. J. Soil Sci. 23: 177-92.

Holdren, G.C., and D.E. Armstrong. 1980. Factors affecting phosphorus release from intact lake sediment cores. Environ. Sci. Technol. 14: 79-87.

Huang, C.P. 1975. Adsorption of phosphate at the hydrous γ-Al_2O_3-electrolyte interface. Journal of Colloid and Interface Science. Vol. 53: 178-186.

Hwang, C.P., T.H. Lackie, and P.M. Huang. 1976. Adsorption of inorganic phosphorus by lake sediments. J. Water Pollut. Control Fed. 48: 2754-2760.

Jackson, T.A., and D. Schindler. 1975. The biogeochemistry of phosphorus in an experimental lake environment: evidence for the formation of humic metal-phosphate complexes. Verh. Internat. Verein. Limnol. 19: 211-221.

Keller, W., J. Gunn, and N. Conroy. 1980. Proc. Int. Conf. ecol. impact acid precip, Norway 1980. SNSF project.

Kemp, A.L.W., and R.L. Thomas. 1976. Cultural impact on the geochemistry of the sediments of Lake Ontario, Erie, and Huron. Geoscience Canada. 3: 191-207.

Kemp, A.L.W., R.L. Thomas, and J.D.H. Williams. 1977. Major elements, trace elements, sediment particle size, water content, and pH in 26 cores from Lakes Superior, Erie, and Ontario. Unpublished Report. Canada Centre for Inland Waters.

Krom, M.D., and R.A. Berner. 1980. Adsorption of phosphate in anoxic marine sediments. Limnol. Oceanogr. 25: 797-806.

Krom, M.D. and R.A. Berner. 1981. The diagenesis of phosphorus in a nearshore marine sediment. Geochimica et Cosmochimica Acta. 45: 207-216.

Ku, W.C., F.A. DiGiano, and T.H. Feng. 1978. Factors affecting phosphate adsorption equilibrium in lake sediments. Water Res. 12: 1069-1074.

Kuo, S., and E.G. Lotse. 1974. Kinetics of phosphate adsorption and desorption by lake sediments. Soil Sci. Soc. Amer. Proc. 38: 50-54.

Kimmel, B.L., and O.T. Lind. 1970. Factors influencing orthophosphate concentration decline in the water of laboratory mud-water systems. The Texas Journal of Science. 21: 339-345. No. 4.

Kramer, J.R. 1967. Equilibrium models and composition of the Great Lakes. p. 243-254. In Equilibrium concepts in natural water systems. Advances in Chemistry Series 67. Amer. Chem. Soc.

Lean, D.R.S. 1973. Phosphorus dynamics in lake water. Science. 179: 678-679.

Lean, D.R.S., and M.N. Charlton. 1976. A study of phosphorus kinetics in a lake ecosystem. In Environmental Biogeochemistry. (J.O. Nriagu, ed.). Proc. 2nd Int. Symp. (1975) 1, Ann Arbour Sci., Ann Arbor, Michigan.

Lee, C.C., R.F. Harris, J.D.H. Williams, J.K. Syers, and D.E. Armstrong. 1971. Adenosine triphosphate in lake sediments. II. Origin and significance. Soil Sci. Soc. Amer. Proc. 35: 86-91.

Lerman, A. 1979. Geochemical Processes: Water and Sediment Environments, Wiley-Interscience, New York. 481 p.

Li, W.C., D.E. Armstrong, J.D.H. Williams, R.F. Harris, and J.K. Syers. 1972. Rate and extent of inorganic phosphate exchange in lake sediments. Soil Sci. Soc. Amer. Proc. 36: 279-285.

Lijklema, L. 1980. Interaction of orthophosphate with iron (III) and aluminum hydroxides. Environ. Sci. Technol. 14: 537-541.

Logan, T.J. 1978. Chemical extraction as an index of bioavailability of phosphate in Lake Erie Basin suspended sediments. Final Project Report, Lake Erie Wastewater Management Study, U.S. Army Corps of Engineers, Buffalo, NY.

Logan, T.J., T.O. Oloya, and S.M. Yaksich. 1979. Phosphate characteristics and bioavailability of suspended sediments from streams draining into Lake Erie. J. Great Lakes Research. 5(2): 112-123.

Mackereth, F.J.H. 1966. Some chemical observations on post-glacial sediments. Phil. Trans. Roy. Soc. London Ser. B., 250: 165-213.

Manning, P.G., T. Birchall, and W. Jones. 1981. Ferric hydroxides in surficial sediments of the Great Lakes and their role in phosphorus availability: a MÖssbauer spectral study. Can. Mineral. 19: 525-530.

Manning, P.G., and W. Jones. 1982. The binding capacity of ferric hydroxides for non-apatite inorganic phosphorus in sediments of the depositional basins of Lakes Erie and Ontario. Can. Mineral. 20: 169-176.

Mattson, S., E. Alvsaker, E. Koutler-Andersson, E. Barkoff, and K. Vahtras. 1950. Phosphate relationships of soil and plant. VI. The salt effect on phosphate solubility in pedalfer soils. Lantbruk-shoegsk. Ann. 17: 141-160.

Mayer, L.W., F.P. Liotta, and S.A. Norton. 1982. Hypolimnetic redox and phosphorus cycling in hypereutrophic Lake Sebasticook, Maine. Water Res. 16: 1189-1196.

Mayer, T., and J.D.H. Williams. 1981. Modified procedures for determining the forms of phosphorus in freshwater sediments. Technical Bulletin No. 119. National Water Research Institute, Inland Waters Directorate, Canada Centre for Inland Waters, Burlington, Ontario.

McKeague, J.A. (ed). 1978. Manual on soil sampling and methods of analysis. Canadian Society of Soil Science.

McLaughlin, J.R., J.C. Ryden, and J.K. Syers. 1977. Development and evaluation of a kinetic model to describe phosphate sorption by hydrous ferric oxide gel. Geoderma. 18: 295-307.

McMaster University. 1981. Aluminum: chemistry, analysis, and biology. Environmental Geochemistry Report. 1981-2.

Mortimer, C.H. 1941. The exchange of dissolved substances between mud and water in lakes. J. Ecol. 29: 280-329.

Mortimer, C.H. 1942. The exchange of dissolved substances between mud and water in lakes. J. Ecol. 30: 147-201.

Mortimer, C.H. 1970. Physical factors with bearing on eutrophication in lakes in general and in large lakes in particular. p. 340-368. In Eutrophication: Causes, consequences, correctives. National Academy of Science, Washington, D.C.

Muljadi, D., A.M. Posner, and J.P. Quirk. 1966. The mechanism of phosphate adsorption by kaolinite, gibbsite and pseudoboehmite. J. Soil Sci. 17: 212-47.

Nembrini, G.P., J.A. Capobianco, M. Viel, and A.F. Williams. 1983. A Mössbauer and chemical study of the formation of vivianite in sediments of Lago Maggiore (Italy). Geochmica et Cosmochimica Acta. 47: 1459-1464.

Nissenbaum, A., B.J. Presley, and I.R. Kaplan. 1972. Early diagenesis in a reducing fjord, Saanich Inlet, British Columbia I: Chemical and isotopic changes in major components of interstitial waters. Geochim. Cosmochim. Acta. 32: 1007-1027.

Nriagu, J.O., and C.I. Dell. 1974. Diagenetic formation of iron phosphates in recent lake sediments. Am. Mineral. 59: 934-946.

Ohle, W. 1953. Phosphor als Initialfaktor der Gewassereutrophierung. Vom Waser. 20: 11-23.

Olsen, S. 1958. Phosphate adsorption and isotopic exchange in lake muds, experiments with P^{32}. Verh. Int. Verein. Limnol. 13: 915-922.

Olsen, S. 1964. Phosphate equilibriumm between reduced sediments and water, laboratory experiments with radioactive phosphorus. Verh. Int. Verein. Limnol. 15: 333-341.

Ontario Ministry of the Environment. 1978. Extensive monitoring of lakes in the greater Sudbury area, 1974-1976. Sudbury Environmental Study.

Ontário Ministry of the Environment. 1982. Studies of lakes and watershed near Sudbury, Ontario. Final limnological report. Sudbury Environmental Study. Supplementary Volume to SES 009/82.

Parfitt, R.L. 1977. Phosphate adsorption on an oxisol. Soil Sci. Sco. Am. J. 41: 1064-1067.

Parfitt, R.L., R.J. Atkinson, and R.St. Smart. 1975. The mechanism of phosphate fixation on iron oxides. Soil Sci. Soc. Am. Proc. 39: 837-841.

Parks, G.A. 1967. Aqueous surface chemistry and complex oxide minerals in equilibrium concepts in natural water systems. Amer. Chem. Soc. Spec. Publ. 67: 121-160.

Parks, G.A. 1975. Adsorption in the marine environment. In Chemical Oceanography, J.P. Riley and G. Skirrow (eds.). Vol. 1, 2nd ed., Academic, New York, pp. 241-308.

Petersen, G.W., and R.B. Corey. 1966. A modified Chang and Jackson procedure for routine fractionation of inorganic soil phosphates. Soil Sci. Soc. Amer. Proc. 30: 563-565.

Pomeroy, L.R., E.E. Smith, and C.M. Grant. 1965. The exchange of phosphate between estuarine water and sediment. Limnol. Oceanogr. 10: 167-172.

Posner, A.M., and J.W. Bowden. 1980. Adsorption isotherms: should they be split? Journal of Soil Science. 31: 1-10.

Rao, S.S., and B.J. Dutka. 1983. Influence of acid precipitation on bacterial populations in lakes. Hydrobiologia. 98: 153-157. ✓

Rao, S.S., A.A. Jurkovic, and J.O. Nriagu. 1984. Bacterial activity in sediments of lakes receiving acid precipitation. Env. Pollution. Accepted for publication.

Reckhow, K.H. 1979. Quantitative techniques for the assessment of lake quality. EPA Report 440/5-79-015. pp. 145.

Redfield, A.C., B.H. Ketchum, and F.A. Richards. 1963. The influence of organisms on the composition of seawater. In The Sea. M.N. Hill (ed.). Wiley-Interscience. Vol. 2. pp. 26-77.

Rittenberg, S.C., K.O. Emery, and W.L. Orr. 1955. Regeneration of nutrients in sediments of marine basins. Deap-Sea Res. 3: 23-45.

Rosenquist, I.Th. 1972. Formation of vivianite in Holocene clay sediments. Lithos. 3:327-334.

Ryden, J.C., J.R. McLaughlin, and J.K. Syers. 1977. Mechanisms of phosphate sorption by soils and hydrous ferric oxide gel. J. Soil Sci. 28: 72-79.

Ryding, S.O., and C. Forsberg. 1976. Sediments as a nutrient source in shallow polluted lakes. In H.L. Golterman (ed.). Interactions between sediments and fresh water. Junk. The Hague.

Sagher, A. 1976. Availability of soil runoff phosphorus to algae. Ph.D. thesis, Univ. Wisconsin-Madison. 192 p.

Scheider, W.A. 1978. Applicability of phosphorus budget models to small precambrian lakes, Algonquin Park, Ontario. J. Fish. Res. Board Can. 35: 300-304.

Schindler, D.W. 1974. Eutrophication and recovery in experimental lakes: Implications for lake management. Science. 184: 897-899.

Schofield, C.L. Jr. 1968. Phosphate fixation in organic lake sediments. Cornell Univ. Water Res. and Marine Sci. Cent. Tech. Rep. No. 13, 23 p.

Schroeder, D.C. 1976. Phosphate mobility in rural runoff. Ph.D. thesis, Univ. Wisconsin-Madison. 123 p.

Serruya, C. 1971. Lake Kinneret: the nutrient chemistry of the sediments. Limnol. Oceanogr. 16: 510-521.

Shukla, S.S., J.K. Syers, J.D.H. Williams, D.E. Armstrong, and R.F. Harris. 1971. Sorption of inorganic phosphate by lake sediments. Soil Sci. Soc. Amer. Proc. 35: 244-249.

Sly, P.G., and C.F.M. Lewis. 1972. The Great Lakes of Canada - Quaternary geology and limnology. 24th Int. Geol. Congr. Montreal, Que. Guide Book Trip A 43: 92 p.

Sommers, L.E., R.F. Harris, J.D.H. Williams, D.E. Armstrong, and J.K. Syers. 1972. Fractionation of organic phosphorus in lake sediments. Soil Sci. Soc. Amer. Proc. 36: 51-54.

Sonzogni, W.C., S.C. Chapra, D.E. Armstrong, and T.J. Logan. 1982. Bioavailability of phosphorus inputs to lakes. J. Environ. Qual., Vol. 11, No. 4: 555-563.

Stamm, H.-H., and H.W. Kohlschütter. 1965. Sorption of phosphate ions on iron (III) hydroxide. J. Inorg. Nucl. Chem. 27: 2103-2108.

Stokes, P. 1980. Benthic algal communities in acidic lakes. In Effects of acidic precipitation on benthos. R. Singer (ed.). Proc. of symposium sponsored by U.S. EPA/North Carolina State Acid Rain Program.

Stumm, W., R. Kummert, and L. Sigg. 1980. A ligand exchange model for the adsorption of inorganic and organic ligands at hydrous oxide interfaces. Croatica Chemica Acta. 53(2): 291-312.

Stumm, W., and J.O. Leckie. 1971. Phosphate exchange with sediments: Its role in the productivity of surface waters. Proc. 5th Int. Water Pollution Res. Conf.

Stumm, W., and J.J. Morgan. 1970. Aquatic chemistry. Wiley-Interscience, New York. 583 p.

Stumm, W., and J.J. Morgan. 1981. Aquatic chemistry. Wiley-Interscience, New York. 780 p.

Sutherland, J.C., J.R. Kramer, L. Nichols, and T.D. Kurtz. 1966. Mineral-water equilibria, Great Lakes: Silica and phosphorus. Proc. 9th Conf. Great Lakes Res. (Chicago). pp. 439-445.

Syers, J.K., R.F. Harris, and D.E. Armstrong. 1973. Phosphate chemistry in lake sediments. J. Environ. Qual. 2: 1-14.

Syers, J.K., G.W. Smillie, and J.D.H. Williams. 1972. Calcium fluoride formation during extraction of calcareous soils with fluoride. I. Implications to inorganic P fractionation schemes. Soil Sci. Soc. Amer. Proc. 36: 20-25.

Theis, T.L., and P.J. McCabe. 1978. Phosphorus dynamics in hypertrophic lake sediments. Wat. Res. 12: 677-685.

Travis, C.C., and E.L. Etnier. 1981. A survey of sorption relationships for reactive solutes in soil. J. Environ. Qual. Vol. 10, No. 1: 8-15.

Ullen, B. 1978. Seston and sediment in Lake Norrviken. III nutrient release from sediments. Schweiz. Z. Hydrol. 40: 287-304.

Verhoff, F.H., and M.R. Heffner. 1979. Rate of availability of total phosphorus in river waters. Environ. Sci. Technol. 13: 844-849.

Vollenweider, R.A. 1968. Scientific fundamentals of the eutrophication of lakes and flowing waters with particular reference to nitrogen and phosphorus as factors in eutrophication. Technical Report DAS/C81/68, Organization for Economic Cooperation and Development, Paris.

Warry, N.D., and J.R. Kramer. 1976. Some factors affecting the synthesis of cryptocrystalline strengite from an amorphous phosphate complex. Canadian Mineralogist. 14: 40-46.

Watanabe, F.S., and S.R. Olsen. 1962. Colorimetric determination of phosphorus in water extracts of soil. Soil Sci. 93: 183-188.

Wentz, D.A., and G.F. Lee. 1969. Sedimentary phosphorus in lake cores: Observations on depositional pattern in Lake Mendota. Environ. Sci. Technol. 3:754-759.

Wetzel, R.G. 1975. Limnology, W.B. Sanders, Philadelphia. 743 p.

Williams, J.D.H., J.M. Jaquet, and R.L. Thomas. 1976a. Forms of phosphorus in the surficial sediments of Lake Erie. J. Fish. Res. Bd. Can. 33: 413-429.

Williams, J.D.H., T.P. Murphy, and T. Mayer. 1976b. Rates of accumulation of phosphorus forms in Lake Erie sediments. J. Fish. Res. Bd. Can. 33: 430-439.

Williams, J.D.H., T. Mayer, and J.P. Nriagu. 1980a. Extractability of phosphorus from phosphate minerals common in soils and sediments. Soil Sci. Soc. Am. J. 44: 462-465.

Williams, J.D.H., and T. Mayer. 1972. Effects of sediment diagenesis and regeneration of phosphorus with special reference to Lakes Erie and Ontario. In Nutrients in Natural Waters, H.E. Allen and J.R. Kramer (eds.). Wiley-Interscience, New York. pp 281-315.

Williams, J.D.H., J.K. Syers, and T.W. Walker. 1967. Fractionation of soil inorganic phosphate by a modification of Chang and Jackson's procedure. Soil Sci. Soc. Amer. Proc. 31: 736-739.

Williams, J.D.H., J.K. Syers, R.F. Harris, and D.E. Armstrong. 1970. Adsorption and desorption of inorganic phosphorus by lake sediments in a 0.1M NaCl system. Environ. Sci. Technol. 4: 517-519.

Williams, J.D.H., J.K. Syers, R.F. Harris, and D.E. Armstrong. 1971a. Fractionation of inorganic phosphate in calcareous lake sediments. Soil Sci. Soc. Amer. Proc. 35: 250-255.

Williams, J.D.H., J.K. Syers, D.E. Armstrong, and R.F. Harris. 1971b. Characterization of inorganic phosphate in noncalcareous lake sediments. Soil Sci. Soc. Amer. Proc. 35: 556-561.

Williams, J.D.H., J.K. Syers, S.S. Shukla, R.F. Harris, and D.E. Armstrong. 1971c. Levels of inorganic and total phosphorus in lake sediments as related to other sediment parameters. Environ. Sci. Technol. 5: 1113-1120.

Williams, J.D.H., H. Shear, and R.L. Thomas. 1980b. Availability to scenedesmus quadricauda of different forms of phosphorus in sedimentary materials from the Great Lakes. Limnol. Oceanogr. 25(1): 1-11.

Yan, N.D. 1979. Phytoplankton community of an acidified, heavy-metal-contaminated lake near Sudbury, Ontario 1973-1977. Water, Air and Soil Pollution. 11: 43-55.

Yan, N.D., and Lafrance. 1982. Experimental fertilization of lakes near Sudbury, Ontario. In Studies of Lakes and Watersheds Near Sudbury, Ontario: Final Limnological Report SES 009/82, Ontario Ministry of the Environment.

Yan, N.D., and G.E. Miller. 1982. Characterization of lakes nesr Sudbury, Ontario. In Studies of Lakes and Watersheds Near Sudbury, Ontario: Final Limnological Report SES 009/82, Ontario Ministry of the Environment.