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**EFFECT OF LAKE ACIDIFICATION ON
THE UPTAKE OF PHOSPHORUS BY SEDIMENTS**

by

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MANAGEMENT PERSPECTIVE

Numerous studies have been carried out on the state of phosphorus in sediments and on its mobility in aquatic ecosystems. Most of the studies, however, relate to hard water lakes with large fluxes of P. Consequently, little information is available on the mobility of P in acidic lakes.

The objective of this study was to determine the effects of lake acidification on the immobilization of phosphorus from solution by sediments. Quantitative estimates of sorption parameters of sediments allow assessment of the relative importance of pH changes in the lake versus the geochemical characteristics of sediment in regulating the dissolved P concentration in the water.

The study links together lake acidification and eutrophication and shows that acidification does not significantly influence the P-retention properties of sediments.

PERSPECTIVE-GESTION

Plusieurs études ont été réalisées sur l'état du phosphore dans les sédiments ainsi que sur sa mobilité dans les écosystèmes aquatiques. Toutefois, la majorité de ces études portaient sur des échantillons d'eau dure lacustre dont la concentration en P variait énormément. On possède donc peu de renseignements sur la mobilité du P dans les lacs acides.

Cette étude a pour objet de déterminer les effets de l'acidification des lacs sur l'immobilisation par les sédiments du phosphore en solution. Une évaluation quantitative des paramètres de sorption des sédiments a permis de déterminer l'importance relative des variations de pH dans les lacs par rapport aux caractéristiques géochimiques des sédiments dans le processus de régularisation des concentrations de P dissout dans l'eau.

L'étude permet de faire le lien entre l'acidification et l'eutrophisation des lacs; elle démontre qu'en définitive, le processus d'acidification a peu d'effets sur les propriétés de rétention du phosphore par les sédiments.

RÉSUMÉ

On a déterminé les propriétés de rétention de sédiments provenant de lacs acides et non acides dans le but d'évaluer les effets de l'acidification des lacs sur l'immobilisation par les sédiments du phosphore en solution. On a découvert que les solides retiennent le P par un mécanisme d'adsorption. On a fait appel au modèle de Langmuir pour décrire les données relatives à l'adsorption et évaluer les paramètres de sorption (maximums de sorption et constante d'équilibre de l'adsorption). Le pH de la solution et les caractéristiques chimiques et minéralogiques des sédiments font varier surtout l'échelle des maximums d'adsorption. L'énergie de liaison du complexe adsorbé est semblable dans tous les échantillons de sédiments analysés ($\Delta G = -25,3$ à $-28,5 \text{ kJmol}^{-1}$); cette force semble relativement indépendante des variations de pH ou de la composition chimique et minéralogique des sédiments.

Les résultats indiquent toutefois que le taux d'élimination du PH, suggéré par les maximums d'adsorption, est déterminé davantage par la composition chimique et minéralogique des sédiments (oxydes, hydroxydes de Al, Fe amorphes) que par le pH de l'eau.

ABSTRACT

The retention properties of acidic and non-acidic lake sediments were determined in order to assess the effects of lake acidification on the immobilization of P from solution by sediments. The uptake of P by solids was explained by an adsorption mechanism. The Langmuir model was used to describe the adsorption data and evaluate the sorption parameters (sorption maxima and equilibrium constant of adsorption). The pH of solution and the chemical and mineralogical characteristics of sediments affect mainly the magnitude of adsorption maxima. The binding strength of the adsorbed complex is similar for all the investigated sediments ($\Delta G = -25.3$ to -28.5 kJmol^{-1}) and it is affected little by variation in pH or by chemical and mineralogical composition of sediments.

The results, however, indicate that the efficiency of P removal as indicated by adsorption maxima, is determined more by sediment chemistry and mineralogy (amorphous Al/Fe oxy-hydroxides, carbonate content) than by pH of the water.

1. INTRODUCTION

The role of sediments in regulating dissolved inorganic P concentration has long been recognized (Einsele, 1938; Mortimer, 1941; Olsen, 1964; Imboden, 1974; Sonzogni et al., 1976; Bostrom et al., 1982; Janus & Vollenweider, 1984). Hence, sediments are important components of the whole-lake mass balances of phosphorus. Whereas numerous studies have been concerned with uptake of P by sediments of neutral lakes, little information is available on P immobilization by sediments of acidic lakes.

The purpose of this investigation is to evaluate the effect of pH on the sorption of P by lacustrine sediments. The retention properties of sediments are assessed by investigating the reversibility of adsorption.

Sampling was carried out to allow comparison of sediments from lakes of different geology and pH. The samples include sediments from acidic and neutral Shield lakes. The lakes are located in terrain underlain by non-calcareous bedrock of low solubility with thin glacial overburden. The lakes are oligotrophic with low alkalinity and conductivity. Their limnology and geological setting have been described in detail (Ontario Ministry of Environment 1978; 1982).

Two sediments from depositional basins of Lake Ontario, which is a mesotrophic hardwater lake (Dobson, 1980), were included for comparison. Locations of the sampling sites are shown in Figure 1.

2. MATERIALS AND METHODS

Surficial sediments from Shield lakes were obtained in the summer of 1981 using an Ekman dredge. Surface sediments from Lake Ontario locations were collected in May 1975 with a double-Shipek. The samples were frozen and subsequently freeze dried. Sediment particles less than 250 μm in diameter were used for all experiments.

Methods of determining the chemical properties of sediments included: total elemental composition by X-ray fluorescence; total and organic C (Kemp 1971); total and organic P (Williams et al. 1976); and oxalate extractable Fe and Al (McKeague 1978).

The sorption of inorganic P was evaluated by equilibrating sediment suspensions with various levels of phosphorus. The appropriate amount of P was added in 5 mL aliquots to 1.0 g of dry sediment, and placed in a pre-weighed 100 mL polypropylene centrifuge tube. Thirty-five mL of 0.1 N NaCl was added to obtain a sediment-solution ratio of 1:40. NaCl was used to facilitate particle settling during centrifugation and maintain constant ionic strength. Bacterial uptake of P was eliminated by addition of 147 μM HgCl_2 . The samples were equilibrated by shaking for 72 hrs at 21°C. On equilibration, the aqueous and solid phase were separated by centrifugation followed by filtration through a Millipore 0.45 μm membrane filter. The filtrate was analyzed colorimetrically for phosphate, (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, the recovery and removal of the supernatant and subsequent P determination were carried out as above.

To determine the effect of the ionic strength of the matrix solution on the adsorption process, sorption of P in 10^{-4} N NaCl was also evaluated. This evaluation was carried out essentially by the same method as sorption of P from 0.1 N NaCl, with the change in the ionic strength of the electrolyte being the only difference.

If the initial pH of the 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.

Controls containing the appropriate 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.

Native exchangeable P was determined by ^{32}P exchange following the procedure similar to that described above. Carrier-free ^{32}P (2.2 μCi) was added in 0.5 mL aliquot to the centrifuge tubes containing 1 g of sediment and 40 mL of 0.1 N NaCl. After equilibration and separation, the solution ^{31}P concentration was

determined by the method of Harwood et al. (1969). Solution ^{32}P concentration was determined by counting a 1 mL aliquot mixed with PCS-xylene scintillation cocktail on a Searle Mark III liquid-scintillation spectrometer. A blank aqueous extract of each sediment was used for the quench correction. Native exchangeable P was determined from isotope dilution (Li et al. 1973). The value obtained was used as an estimate of the native sorbed P which was added to all values of added P sorbed used in the analysis of P sorption data.

3. RESULTS

A summary of some chemical characteristics of the investigated sediments is given in Table I. A detailed description of the physical and chemical properties can be found elsewhere (Mayer, 1984). Oxalate extractable Fe, which measures Fe associated with amorphous oxy-hydroxides constituted a similar proportion of total Fe in all investigated sediments, except in the Windy Lake sediment. This iron rich sediment contained unusually high proportions of oxalate extractable Fe (Table I). Oxalate extractable Al was, however, significantly lower in sediments from Lake Ontario than that in Shield sediments (Table I). The low values of oxalate extractable Al in Lake Ontario sediments suggest that most of Al in these sediments is associated with clay minerals. The carbonate content of Lake Ontario sediments was also higher (Mayer, 1984) than that of Shield sediments, reflecting different lithology of lake basins.

The Langmuir model was used to describe the adsorption data. The adsorption isotherms (Figure 2) for given experimental data sets were obtained by least squares fit to the standard form of the Langmuir equation.

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

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) (Table II) through the relation $K = \exp [\Delta G^\circ/RT]$, where R = gas constant ($8.314 \text{ Jmol}^{-1}\text{K}^{-1}$) and T = absolute temperature in K (Stumm and Morgan, 1981). Each isotherm is characterized by a large change in the amount of P adsorbed at lower solution P concentrations, followed by a more gradual change in the amount of P sorbed with increasing solution P concentration. At higher solution P concentrations, the isotherms show deviation from the Langmuir function.

Values of the Langmuir parameters (K , Γ_M) and R^2 values are summarized in Table II, along with results from other studies for comparison.

The experiments with different lake sediments show a close relationship between the capacity of the sediment to adsorb and to 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 (Figure 3).

4. DISCUSSION

The adsorption data indicate discrepancy between the experimental data and the curve obtained by the least squares fit to Langmuir equation. The discrepancy may be attributed to the fact that the Langmuir model takes no account of surface charges (Parfitt, 1977; Barrow, 1978; Posner and Bowden, 1980). Thus, it describes the adsorption process better at lower concentrations. Despite this limitation, the model can be used to give an 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 an upper limit of adsorption implied from saturation of adsorption sites is a definite advantage of this model.

The results of the adsorption experiments indicate that the type and properties of sediments are reflected only in the magnitude of the sorption maxima Γ_M (Table II). 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.

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 Shield sediments. At higher phosphate solution concentrations, the Shield sediments exhibited a continued linear adsorption (Figure 2), 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 I) support this conclusion.

Values of the free energy of adsorption (ΔG) are remarkably similar for all the investigated sediments (Table II). Such similarity strongly suggests that the chemical and mineralogical characteristics of sediments do not affect the nature of the adsorption process. Neither do 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 strong chemisorption. A strong tendency towards chemical bonding between phosphate groups and metal ions in the 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.

Comparison of Γ_M values (Table II and Figure 2) reveals that more P is adsorbed by the same sediment at lower pH. For example, in the case of Wavy sediment an increase in adsorption of 4% coincided with a decrease in pH of 1.5 units. For Clearwater sediment, an adsorption increase -17% coincided with an experimental decrease in pH of 2.5 units. The observed increase in magnitude of phosphate uptake with decreasing pH is consistent with the adsorption model.

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. The results show that an 18% increase in adsorption occurred in Wavy sediment when the ionic strength of solution was increased by three orders of

magnitude. A smaller and perhaps insignificant increase occurred in Lake Ontario E-30 sediments. The increase in adsorption resulting from the increase in ionic strength is consistent with the electric double layer (EDL) theory (Parks, 1975; Stumm and Morgan, 1981).

The reversibility of adsorption evaluated from the amount of added P desorbed, indicates that calcareous Lake Ontario sediments have a lower retention ability than noncalcareous Shield sediments. Between 10-30% of added sorbed P was desorbed from Lake Ontario sediments, whereas only 0.3-4% of added P was released from the Shield lake sediments. Hence, the sediments which adsorbed the most added P tended to release the least during the subsequent desorption (Figure 3). Similar findings were reported on sediments from Wisconsin lakes by Williams et al. (1970; 1971).

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

The results of the absorption study can be summarized as follows: Sediments from three Shield lakes tend to have considerably higher adsorption capacities and better retention abilities than do Lake Ontario sediments. The difference in the magnitude of adsorption caused by the shifts of pH or ionic strength is relatively small when compared with the difference in adsorption due to the chemical and mineralogical characteristics of sediments. Therefore, the sediment

chemistry and mineralogy appears to be more important in determining the adsorption capacity of sediments than the changes in pH of the lakes.

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REFERENCES

Barrow, N.J.: 1978, 'The Description of Phosphate Adsorption Curves', J. Soil Sci. 29 , 447-462.

Bostrom, B., Janson, M. and Forsberg, C.: 1982, "Phosphorus Release from Lake Sediments", Arch. Hydrobiol. 18 , 5-59.

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

Einsele, W.:1938, 'Über Chemische und Kolloidchemische Vorgänge in Eisen-Phosphat Systemen unter Limmochemischen und Limnogeologischen Gesichtspunkten'. Arch. Hydrobiol. 33 , 361-387.

Harwood, J.E., van Steenderen, R.A., and Kuhn, A.L.: 1969, 'A Rapid Method for Orthophosphate Analysis at High Concentrations in Water.' Water Res. 3 , 417-423.

Imboden, D.M.: 1974. 'Phosphorus Model of Lake Eutrophication'. Limnol. Oceanogr. 19 , 297-304.

Janus, L.L. and Vollenweider, R.A.: 1984, 'Phosphorus Residence Time in Relation to Trophic Conditions in Lakes'. Verh. Internat. Verein. Limnol. 22 , 179-184.

Kemp, A.L.W.: 1971, 'Organic Carbon and Nitrogen in the Surface Sediments of Lakes Ontario, Erie and Huron'. J. Sediment. Petrol. 41 , 537-548.

Ku, W.C., DiGiano, F.A., and Feng, T.H.: 1978, 'Factors Affecting Phosphate Adsorption Equilibrium in Lake Sediments'. Water Res. 12 , 1069-1074.

Kuo, S. and Lotse, E.G.: 1974, 'Kinetics of Phosphate Adsorption and Desorption by Lake Sediments'. Soil Sci. Soc. Amer. Proc. 38 , 50-54.

Mayer, T.: 1984, 'Phosphorus Mobility in Lacustrine Sediments upon Lake Acidification'. M.Sc. Thesis, McMaster University, Hamilton.

McKeague, J.A. (ed): 1978, 'Manual on Soil Sampling and Methods of Analysis'. Canadian Society of Soil Science.

Mortimer, C.H.: 1941, 'The Exchange of Dissolved Substances between Mud and Water in Lakes'. J. Ecol. 29 , 280-329.

Muljadi, D., Posner, A.M., and Quirk, J.P.: 1966, 'The Mechanism of Phosphate Adsorption by Kaolinite, Gibbsite and Pseudoboehmite'. J. Soil Sci. 17 , 212-47.

Olsen, S.: 1964, 'Phosphate Equilibrium between Reduced Sediments and Water, Laboratory Experiments with Radioactive Phosphorus'. Verh. Int. Verein. Limnol. 15 , 333-341.

Li, W.C., Armstrong, D.E., and Harris, R.F.: 1973, 'Measurement of Exchangeable Inorganic Phosphate in Lake Sediments'. Environ. Sci. Technol. 7 , 454-456.

Ontario Ministry of the Environment: 1978, Extensive Monitoring of Lakes in the Greater Sudbury Area, 1974-1976. Sudbury Environmental Study.

Ontario Ministry of the Environment: 1982, Studies of Lakes and Watershed near Sudbury, Ontario. Sudbury Environmental Study. Supplementary Volume to SES 009/82.

Parfitt, R.L.: 1977, 'Phosphate Adsorption on an Oxisol'. Soil Sci. Soc. Am. J. 41 , 1064-1067.

Parfitt, R.L., Atkinson, R.J., and St. Smart, R.: 1975, 'The Mechanism of Phosphate Fixation on Iron Oxides'. Soil Sci. Soc. Am. Proc. 39 , 837-841.

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

Posner, A.M. and Bowden, J.W.: 1980, 'Adsorption Isotherms: Should they Be Split'? Journal of Soil Science. 31 , 1-10.

Ryden, J.C., McLaughlin, J.R. and Syers, J.K.: 1977, 'Mechanisms of Phosphate Sorption by Soils and Hydrous Ferric Oxide Gel'. J. Soil Sci. 28 , 72-79.

Sonzogni, W.C., Uttomark, P.C. and Lee, G.F.: 1976. 'A Phosphorus Residence Time Model: Theory and Application'. Water Res. 10 , 429-435.

Stumm, W. and Morgan, J.J.: 1970, 'Aquatic Chemistry, 1st ed.' Wiley-Interscience, New York. 583 p.

Stumm, W. and Morgan, J.J.: 1981, 'Aquatic Chemistry 2nd ed.' Wiley-Interscience, New York. 780 p.

Williams, J.D.H., Jaquet, J.M. and Thomas, R.L.: 1976, 'Forms of Phosphorus in the Surficial Sediments of Lake Erie'. J. Fish. Res. Bd. Can. 33 , 413-429.

Williams, J.D.H., Syers, J.K., Shukla, S.S., Harris, R.F. and Armstrong, D.E.: 1971, '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., Syers, J.K., Harris, R.F. and Armstrong, D.E.: 1970, 'Adsorption and Desorption of Inorganic Phosphorus by Lake Sediments in a 0.1 M NaCl System'. Environ. Sci. Technol. 4 , 517-519.

Yan, N.D. and Lafrance, C.: 1982, 'Characterization 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.

TABLE I Water chemistry data and chemical characteristics of sediments

Sample	Water				Sediment					
	pH*	Alkalinity*	Total Fe	Oxalate extract. Fe	Total Al	Oxalate extract. Al	Organic C	Organic P	Total P	
			mg g ⁻¹	mg g ⁻¹	mg g ⁻¹	mg g ⁻¹	%	μg g ⁻¹	μg g ⁻¹	μg g ⁻¹
Wavy	4.5	-0.03	26.7	4.69	34.3	16.0	12.84	742	1845	
Clearwater	4.4	-0.04	41.7	6.96	36.2	8.8	9.68	535	1142	
Windy	6.4	0.09	71.7	44.37	48.3	7.7	6.53	460	1863	
L.O. E-30	8.5	1.7	49.2	12.19	76.4	1.1	2.48	155	1108	
L.O. WB	8.5	1.7	48.5	13.76	78.9	2.3	2.72	200	1191	

*Data from Ontario Ministry of the Environment (1978; 1982)

TABLE II Langmuir parameters and the values of free energy of adsorption

Sediment Sample	pH*	I** (M)	K L μ mol ⁻¹	Γ_M μ moles 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
Lake sediments		dist. water +KH ₂ PO ₄		27.7- 48.4		-11.5 Kuo & Lotse (1974)
Lake sediments	4.8- 7.0	dist. water	0.033- 1.036	36.3- 71.6		Ku <u>et al.</u> (1978)
New Zealand soils	7	10 ⁻¹		10-104		Ryden <u>et al.</u> (1977) -28.5- -30.1

* pH of matrix solution.

** I = Ionic strength of matrix solution (NaCl).

FIGURE CAPTIONS

- Fig. 1. Location of the sampling sites.
- Fig. 2. Adsorption isotherms for (a) Wavy Lake and Lake Ontario E-30 sediments, matrix solution 10^{-4} M NaCl; (b) Wavy Lake and Lake Ontario WB sediments, matrix solution 10^{-1} M NaCl; (c) Clearwater Lake sediments matrix solution 10^{-1} M NaCl; (d) Windy Lake and Lake Ontario E-30 sediments, matrix solution 10^{-1} M NaCl. Solid lines reflect the Langmuir fit.
- Fig. 3. Proportions of P adsorbed/desorbed at different levels of added P.

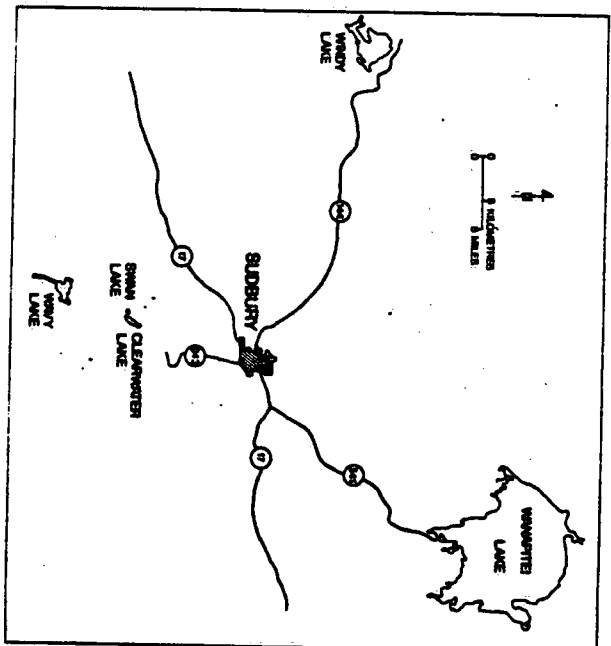
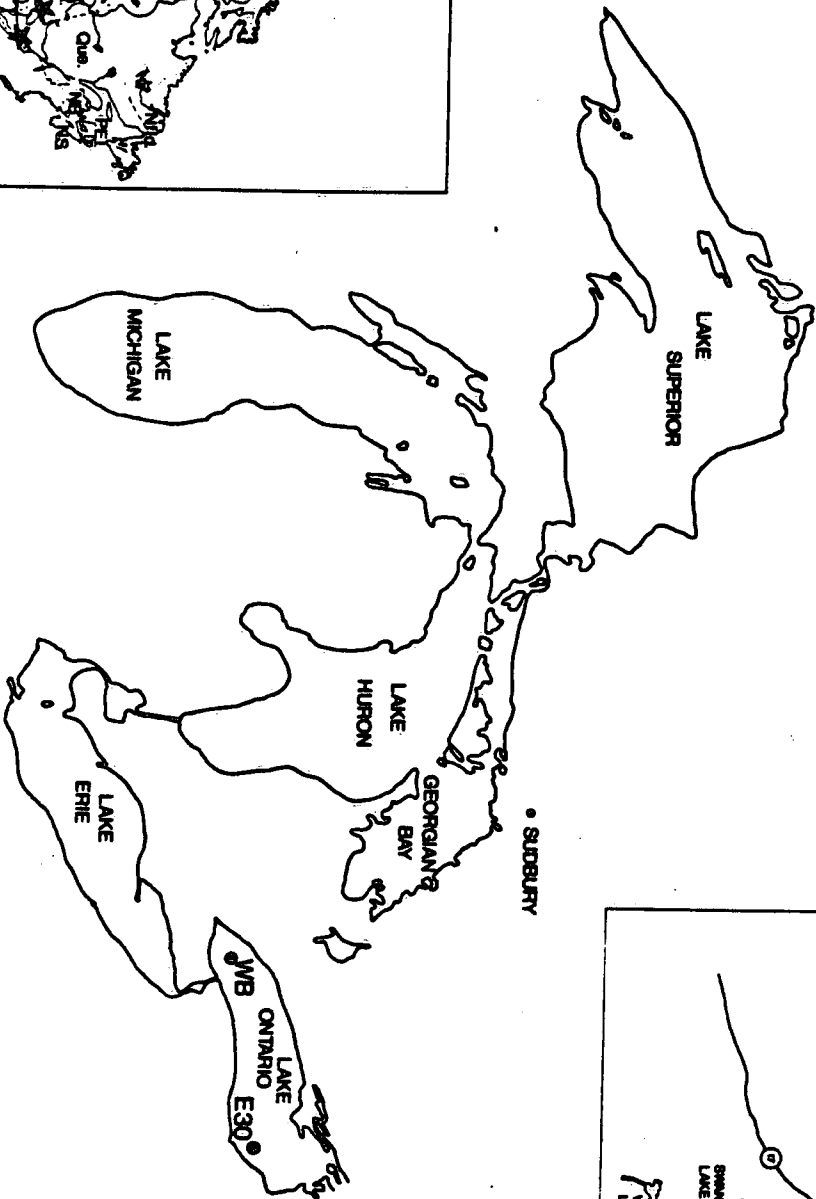
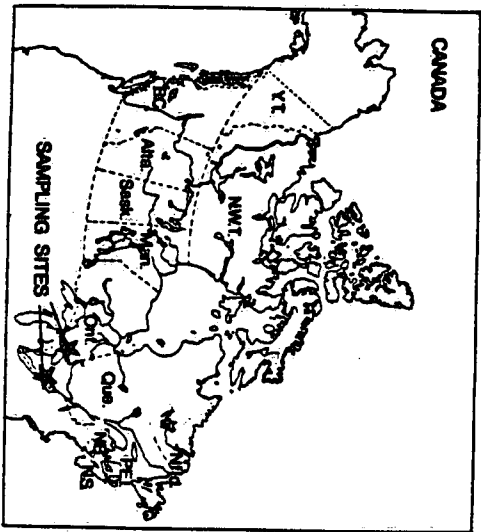


Fig. 1.

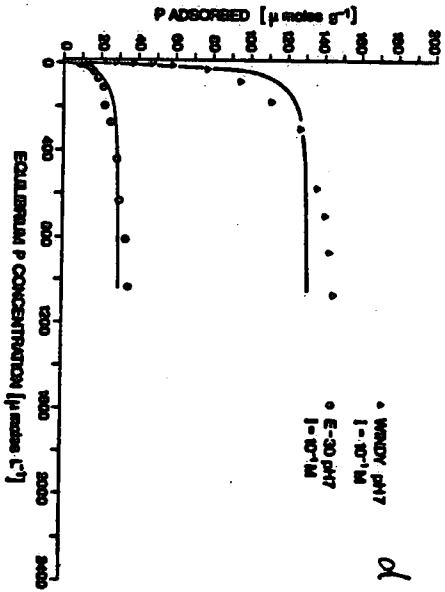
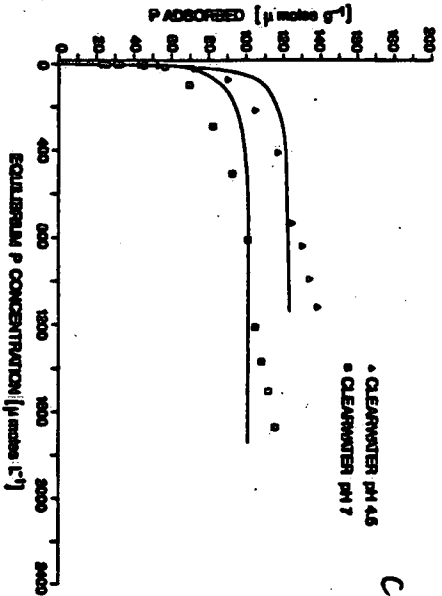
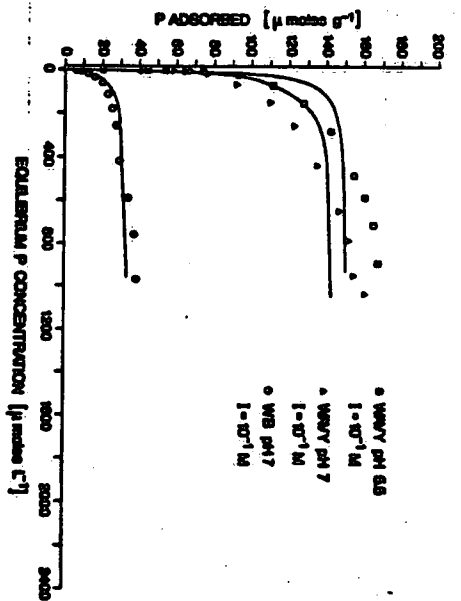
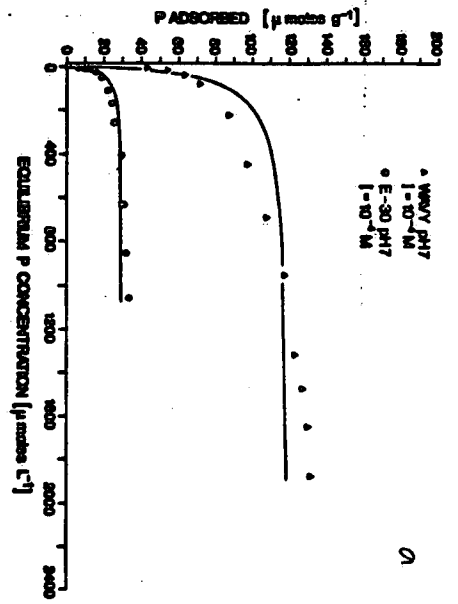
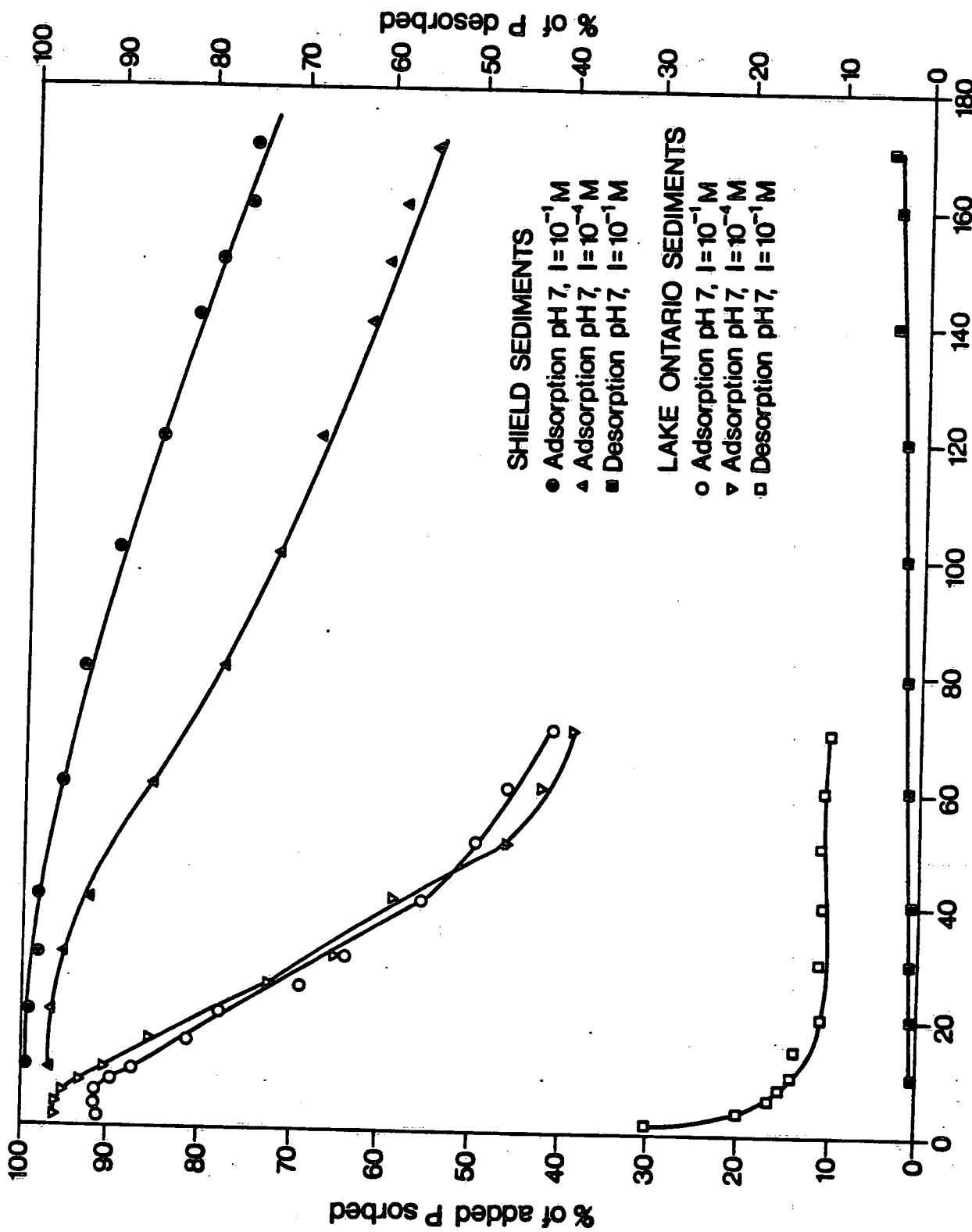


Fig. 2.



added P (mmol g⁻¹)

Fig. 3