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EQUILIBRIUM ADSORPTION OF INORGANIC PHOSPHATE BY LAKE SEDIMENTS

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ENVIRONMENTAL ENGINEERING
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Preface

This report is devoted to one phase of a comprehensive study on control of benthic deposits in lakes which has been undertaken by the Environmental Engineering group at the University of Massachusetts since 1967. The laboratory work of this particular phase of the study was planned and performed by Wen-Chi Ku, then a doctoral candidate and now, after the completion of his doctoral study, a consulting engineer with the Dufresne-Henry Engineering Corporation, North Springfield, Vermont. During Dr. Ku's three year research on the subject, the following faculty members of the University of Massachusetts contributed generously their valuable advice and suggestions:

Dr. G. W. Foess, former Assistant Professor of Civil Engineering
Dr. F. A. DiGiano, Assistant Professor of Civil Engineering
Dr. J. H. Baker, Associate Professor of Plant and Soil Sciences
Dr. O. T. Zajicek, Assistant Professor of Chemistry.

Specifically Dr. G. L. Stewart and Professor J. Stryker offered their assistance in the radioisotope study and Professor A. Costa, Mr. A. Glazier, and Mr. L. Lieu and Mr. C. Liu assisted in the fabrication of equipment and sample collection.

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ABSTRACT

Equilibrium Adsorption of Inorganic Phosphate by Lake Sediments

Wen-Chi Ku and Tsuan Hua Feng

Eutrophication caused by excessive addition of plant nutrients to natural waters has become a problem of national concern. Among all the essential nutrients needed by aquatic plants, phosphorus has long been considered to be one of the most important limiting factors. An understanding of its behavior in different waters is therefore essential to the inauguration of proper measures to control eutrophication.

Inorganic phosphate adsorption studies were conducted on the surface sediments from two western Massachusetts lakes. The experimental parameters studied were pH, temperature and redox potential. Phosphorus attached to the surface of the sediments (surface phosphorus) was determined by the isotopic exchange method using P^{32} and was used in the determination of adsorption maxima. Glucose was used to obtain redox potentials in the range -110 to -274 mv in the sediment-water mixtures. The chemical characteristics of the sediments and the major sediment components responsible for the adsorption of phosphate were also investigated.

Under the experimental conditions studied (pH 4.8 to 7.0; temperature 11^{o} to $20^{o}C$; redox potential, E_c, -274 mv to 460 mv), the phosphate adsorption data for the two lake sediments could be described by the

Langmuir adsorption equation. The adsorption capacities of the two sediments increased with decrease in pH and temperature but with increase in redox potential.

Both iron and aluminum were found to be important in the fixation of phosphate in lake sediments. The relative importance of these elements for phosphate fixation seemed to depend on the type of sediment and the environmental conditions prevailing in the sediment.

Under low redox potential conditions, the sediments released large amounts of iron to the solutions, and the phosphate adsorption capacities of both sediments reduced accordingly. The adsorption capacity of the Lake Warner sediment was more sensitive to changes in redox potentials than that of the Lake Wyola sediment. This could be attributed to the fact that in the Lake Warner sediment both the native phosphate and the newly adsorbed phosphate were retained more by the iron in the sediment than by the aluminum in the sediment, while in the Lake Wyola sediment the reverse was true. Changing in redox potential caused a corresponding change in the amount of iron released from the sediment but the status of aluminum in the sediment was not affected by the change in redox potential. The sediment that relied more on iron than on aluminum to adsorb phosphate was therefore more sensitive to changes in redox potential than the one that relied more on aluminum than on iron.

The close relationships observed between redox potential and the iron concentration in the equilibrated solution and the quantity of

~~of~~ added phosphate adsorbed suggested that redox potential could be used as a valuable parameter for sediment phosphate adsorption studies.

The equilibrium adsorption data derived herein are valuable for the derivation of the mathematical models used for the prediction of the phosphate exchange processes between lake sediments and the overlying waters.

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CHAPTER I

INTRODUCTION

Eutrophication caused by excessive addition of plant nutrients to natural waters has become a problem of national concern. Among all the essential nutrients needed by aquatic plants, phosphorus has long been considered to be one of the most important limiting factors (Weiss, 1969; Shannon and Brezonik, 1972; Edmondson, *et al*. 1956). An understanding of its behavior in different waters is, therefore, essential to the inauguration of proper measures to control eutrophication.

In lakes, sediments have profound effects on the overlying water quality (Fitzgerald, 1970; Gahler, 1969; Golterman, 1967; McKee, *et al*. 1970a, b; Serruya, 1971). The sediment is not only a sink for nutrient deposition, but also a supplier of nutrients for aquatic growth under proper conditions. Thus, even though the sources of nutrients are eliminated from a lake, the eutrophication problem may still prevail for some time.

Throughout the years, many investigators have studied the effect of sediments on the nutrient conditions in lake waters. Generally speaking most of the work is qualitative in nature. While qualitative work is still needed for better understanding of the nutrient behavior, it is felt that more quantitative data should be gathered in lake nutrient studies. For example, Lorenzen (1973) has summarized three models using different simplification assumptions to describe the change of nutrient concentrations with time in a lake. The models were to be used for the prediction of the effects of nutrient diversion on lake recovery. Using hypothetical lake data to fit the models, he found that different assumptions about nutrient exchange processes used in deriving these models resulted in substantial difference in the prediction of lake recovery. The collection of quantitative data regarding the nutrient exchange processes would therefore be essential to the development of a more realistic model.

DiGiano (1970) has also developed several mathematical models to describe the rate of nutrient transport between lake sediments and the overlying waters. In the development of these models, many simplifying assumptions have been made. The verification of these assumptions and the final development of these models will also need quantitative data.

The transport of nutrients between lake sediment and the overlying water is to say the least very complicated. To develop a model to describe this phenomenon completely, the physical, chemical and biological aspects of both the sediment and the lake water should all be studied and incorporated into this model. Without going into much details initially, however, one can assume that the interchange of nutrients between the sediment and the overlying water consists of transport of physical nature only. With this assumption, the nutrient release from the sediment to the overlying lake water can be conceived as consists of the following steps: (1) migration of nutrient in the interstitial water from the deep layer of the sediment to the upper layer, (2) emergence through the sediment-water interface to the water immediately above, and (3) dispersion throughout the lake water

(DiGiano, 1970). A simple pore diffusion model can be derived to describe the transport of nutrients through the interstitial water of the sediment based on the above assumptions.

However, in the study of the interchange of nutrients between lake sediment and water, one should always bear in mind the fact that sediment particles all have certain capacity to adsorb plant nutrients such as phosphorus. Before equilibrium is reached, the sediment particles will always adsorb some of the nutrient molecules from the interstitial water as they diffuse through. Therefore, a model that considers both pore diffusion and adsorption seems to be more realistic than the one that considers only pore diffusion (DiGiano, 1970). For the derivation of such a model and for its successful application, equilibrium adsorption data is essential. The adsorption pattern varies depending on the nature of the adsorbent (sediment), the nature of the adsorbate (nutrients) and the different environmental conditions such as pH, temperature and redox potential. Although there were some previous studies involving the adsorption of phosphate on lake sediments (e.g., Kuo and Lotse, 1974, Harter, 1968), most of these studies were designed to investigate the mechanisms involved in the adsorption. Quantitative adsorption data that can be applied to the derivation of the above mentioned pore diffusion-adsorption model are still lacking.

The general purpose of this research was to study the equilibrium adsorption of inorganic phosphate by the surface sediments of two western Massachusetts lakes. The specific objectives were:

1. To characterize the chemical nature of the surface sediments from the lakes.
2. To develop a method for the determination of the phosphorus attached to the surface of lake sediments, referred to hereinafter as surface phosphorus.
3. To study the effects of pH, temperature and redox potential on the equilibrium adsorption of inorganic phosphate by lake sediments.
4. To fit the adsorption data with a proper adsorption equation which can be applied for the derivation of mathematical models which describe the transport of inorganic phosphate between lake sediments and the overlying waters.
5. To determine the applicability of using redox potential as an operational parameter in sediment adsorption studies.
6. To determine the relative importance of sediment iron and aluminum in the sorption of inorganic phosphate.

CHAPTER II

LITERATURE REVIEW

Phosphorus in Lake Sediments

It is generally recognized that lake sediments serve as a sink for phosphorus and other nutrients. In an analysis of the sediment cores taken from Lake Mendota, Wisconsin, Bortleson and Lee (1972) found that man's activity during postcultural period had caused a steady increase in concentrations of phosphorus and other nutrients in the sediments of that lake. Frink (1967) also showed that sediments of a eutrophic lake were greatly enriched in phosphorus. Snow and DiGiano (1973) analyzed the phosphate concentrations in lake waters and in the interstitial water of the sediments of several western Massachusetts lakes. It was found that a lake with high concentration of phosphate in the overlying water usually contained a high concentration of phosphate in the interstitial water of its sediment.

The proportion of organic phosphorus in sediments varies among lakes. Frink (1969) reported that more than half of the sediment phosphorus he analyzed was in the inorganic form. The data of Sommers et al. (1970) also indicated that, with one exception, all the lakes they studied contained a higher percentage of inorganic phosphorus than organic phosphorus. Golterman (1973) stated that due to the geochemical instability of the C-O-P bonding, organic phosphate compounds could occur in sediments for only a short period of time.

Wenz and Lee (1969) found in studies of calcareous sediments that the inorganic phosphorus was associated with $CaCO_3$. Williams <u>et al.</u> (1971b), however, showed that iron-containing components might be even more important than $CaCO_3$ in influencing the levels of inorganic phosphorus in calcareous lake sediments. They found that the conventional inorganic phosphorus fractionation scheme (Chang and Jackson (1957)) had underestimated non-occluded iron and aluminum-bound phosphorus and overestimated calcium-bound phosphorus and occluded iron-bound phosphorus in calcareous soils and lake sediments. Livingstone and Boykin (1962) used water, 0.1 N HCl and nitric-perchloric acid digestion to extract phosphorus from the sediments of Linsley Pond in Connecticut and found that even in this moderately calcareous lake a large portion of the phosphorus in the sediment was not in the apatite form. This observation is different from the terrestrial soils, where phosphorus is usually bound as one of a series of minerals of apatite type at high pH.

In noncalcareous lake sediments, Williams <u>et al.</u> (1971a, c) showed that inorganic phosphorus was associated with short-range-order hydrated iron-oxides extractable by acid ammonium oxalate or neutral citrate-dithionite-bicarbonate. The apatite content in noncalcareous lakes was generally low. Williams <u>et al.</u> (1971a) suggested that the short order iron complex responsible for the retention of inorganic phosphorus in both calcareous and noncalcareous lakes was not $Fe(OH)_3$ or $Fe_2O_3 \cdot nH_2O$ but was chemically related to $Fe(OH)_2$. They also showed that organic phosphorus interacted with different components of sediments than inorganic phosphorus. Organic phosphorus was partly associated with oxalate-and citrate-dithionite-bicarbonate-extractable forms of aluminum and was partly a constituent of organic matter which was independent of both iron and aluminum.

Distribution of elements in lakes is not uniform. Delfino et al. (1969) found that in Lake Mendota there was a high correlation between Mn, Fe and P concentrations in the sediment and the depth of water overlying the sampling point. Data of Bortleson and Lee (1972) showed that the phosphorus in the center of Lake Mendota was associated with the finer fraction of the sediment. This indicated that a natural grading process might have occurred in this lake, resulting in the accumulating of finer particles and the associated P, Mn and Fe in the center of the lake. Similarly, Frink (1969) observed that at the center of a eutrophic lake there were more clay, organic matter, N and P than around the edge of the lake or in the soil in the watershed.

Golterman (1967) stated that the phosphorus ions in lake sediments are dominated by two chemical systems: the Fe-S-phosphorus system and the Ca-CO_3-phosphorus system. The Fe-S-phosphorus system is sensitive to the oxidation-reduction potentials in the mud or in the water. The Ca-CO_3-phosphorus system is independent of redox conditions and is probably most important in the hard water lakes. Both systems are pH dependent. Other sorption processes such as the iron-humus-phosphorus system and iron or aluminum-silicon-humus system may also be important, but have not been properly investigated.

Interaction of Phosphorus with Sediments

Phosphorus in lake water was observed to exchange constantly with that in the sediment by a number of investigators. It was generally concluded that the sediment involved in the exchange process consisted of only a very thin layer of the surface mud. For example, Hayes et al. (1952) added radioactive phosphorus to a small unstratified lake in Nova Scotia and noticed the rapid loss of the phosphorus from the water and uptake by aquatic organisms and mud. They postulated that there was an active exchange process between the water-phase phosphorus and participating phosphorus in the lake solids (including the organisms and mud). They also noticed the actual exchange thickness of mud is of the order of 1 mm and suggested that only one tenth of the phosphorus exchange was with the mud in the lake. Zicker et al. (1956) placed radioactive phosphate fertilizer at various depths below the lake mud surface in an undisturbed mud-water system and found that there was virtually no phosphorus release from depths greater than 1/4 inch below the mud surface. Holden (1961) found that most of the removed phosphate remained in the upper aerobic zone of the bottom deposits, which extended normally to a depth of about 20 mm. Hayes (1955) observed that the phosphorus exchange between mud and water was considerably less in an acid bog lake (surrounded by Sphagnum, pH 5.5) than in a neutral, mesotrophic lake.

A few investigators also studied the sorption and desorption of phosphate by lake sediment. Harter (1968) and Williams et al. (1970)

both showed that sediments of eutrophic lakes could still adsorb a large quantity of added phosphorus in the water. However, it was noted that a large portion of the adsorbed phosphorus was only loosely bound and could be released later to the water. Williams et al. (1970) and Shukla et al. (1971) found that noncalcareous lake sediments generally adsorbed and retained more added inorganic phosphorus than calcareous lake sediments.

Kuo and Lotse (1974) found that the adsorption of phosphorus by lake sediments could be described by the Freundlich equation over a wide range of phosphorus concentration. But at low phosphorus concentrations the Langmuir equation provided a good fit. The amount of the phosphorus adsorbed (x) was found to relate to the reaction time (t) by an equation $x = kC_0t^{1/m}$ where C_0 was the initial phosphorus concentration, and k and 1/m were both constants. The authors also showed the capacity of $EDTA^=$, OH^-, F^- and $HC_2O_4^-$ to release phosphorus from sediments decreased in the order $EDTA^= > OH^- > F > HC_2O_4^-$. Freshly adsorbed phosphorus was shown to have a higher exchangeability than native phosphorus.

Data of Gumerman (1970) indicated that at low phosphate concentrations, the adsorption of phosphate by Lake Erie sediment could be described by the Langmuir equation. Gumerman also found that release of adsorbed phosphorus from Lake Erie sediments was sufficient to maintain a minimum phosphorus concentration of 0.1 mg/l in the water phase.

In their study of the release of phosphorus from the sediments in the Upper Klamath Lake, Oregon, Wildung and Schmidt (1973) found the release of phosphorus was largely from the non-occluded Fe-P, but phosphorus adsorbed from the water phase was primarily in the form of non-occluded Al-P on the sediment. Altogether, the phosphorus in the forms of Al-P, Fe-P and Fe- and Al-oxide occluded P accounted for approximately 85 percent of the seasonal changes in total sediment phosphorus of that lake in a one-year period.

There are quite a number of factors that may influence the interaction between phosphorus and sediment. Among these are the redox potential, pH, temperature, sediment chemical composition, and biological activity. These factors have been explored by a number of researchers throughout the years.

Redox Potential. Redox potential affects the phosphorus status in lake sediments through its influence on the chemical forms of iron in the sediments. Early in the 40's, Pearsall and Mortimer (1939) and Mortimer (1941, 1942) already observed the importance of redox potential on the sorption and release of phosphorus and other nutrients from lake sediments. During the summer and winter stagnation periods, the level of dissolved oxygen in the hypolimnion of a lake dropped rapidly, with an accompanying drop in redox potential in the sediment-water interface. As a result of this reduction, iron was reduced from Fe^{+3} to Fe^{+2}, and phosphorus, presumably sorbed by a thin layer of colloidal ferric hydroxide gel in the interface during oxidized conditions released to the overlying water.

Olsen (1958, 1964) showed that under oxidized conditions lake sediments adsorbed more phosphorus than under reduced conditions.

Similarly, Spear (1970) noted that under anoxic conditions lake sediments released more phosphate and at a higher rate than under oxic conditions. Snow and DiGiano (1973) observed the release of large quantities of iron from sediment cores stored for a few months in the laboratory. However, the corresponding release of orthophosphate was very small. The authors explained that the plastic core barrels might have sorbed the released phosphate.

Fillos and Molof (1972) found that changing the DO level in the overlying water affected the redox potential of only a thin layer of the surface mud. It was suggested that the increased release of phosphate and ammonia under anaerobic conditions resulted from the changes within a thin layer of surface mud.

pH. It is generally observed that lake sediments sorb maximum amounts of phosphate in the pH range 4.0-6.5; the sorption capacity decreases at pH values outside this range. Carritt and Goodgal (1954) showed that maximum sorption of PO_4 by solids (river sediments, bentollite and fullers earth) occurred in the pH range of four to six where $H_2PO_4^-$ is the predominent species. At high pH the return of phosphorus to solution from a sorption complex is favored. Gumerman (1970) found that maximal removal of phosphorus by Lakes Erie and Superior sediments occurred in the pH range 4.5 to 6.5. Ohle (1937) found that ferric hydroxide gels could sorb phosphate ions. The ferric hydroxide gels are amphoteric in nature, being electropositive in acid pH and electronegative in the alkaline pH range. The adsorption of negatively charged

PO_4 ions onto the ferric hydroxide gels can happen therefore only in the acid range of pH.

MacPherson et al. (1958) found that minimal release of phosphorus from lake sediments occurred at pH 5.5-6.5. Spear (1970) also found that the release of phosphorus from sediments increased with increasing pH. Zicker et al. (1956) observed that when calcium carbonate was added to the water phase of mud-water systems, a thin crust was formed at the mud-water interface which restricted the diffusion of phosphorus from the mud to the overlying water. Acidification of a previously limed mud-water system would effectively release the phosphorus in the mud.

Temperature. Olsen (1966) stated that the phosphorus sorbing capacity of lake sediments decreased with increasing temperature. The results of Gumerman (1970), however, showed that the reverse was true. On the other hand, data of both Spear (1970) and Wildung and Schmidt (1973) showed that the release of phosphorus from sediments increased with increasing temperature. Spear (1970) observed that in a mud-water mixture, under anoxic condition, when the temperature was reduced from $24^{o} \pm 2^{o}C$ to $11 \pm 1^{o}C$, a more than two-fold reduction in phosphorus release rate and total amount resulted.

Organic Matter. Struthere and Sieling (1950) and Swenson et al. (1949) showed that organic anions such as citric, oxalic, tortaric, malonic, malic and lactic acids, which were produced in soil by microorganisms decomposing organic matter, were able to complex with iron and aluminum and prevent phosphate precipitation with both iron and aluminum. The effectiveness of these organic acids on preventing phosphorus fixation was dependent on pH. Organic matter added to soils also retarded the phosphorus fixation (Dalton et al., 1952). Easily decomposable organic matter was more effective in this regard. Hepher (1958) also noticed that a decrease in phosphorus fixation was associated with an increase in organic matter in the clay colloid.

Harter (1969), however, found that organic matter was responsible for the initial adsorption of added phosphorus by soils and sediments. Weir and Soper (1963) showed that the iron-humic acid complex could adsorb phosphate ions. Although the phosphate thus fixed was nearly all exchangeable with P^{32}, only a portion of it was available for plant use.

Biological Effects. Many investigators also noticed the importance of biological effects on phosphorus exchange in the mud-water systems. Pomeroy et al. (1965) observed that the exchange of phosphate between an estuarine water and its sediment was a combination of a pure physico-chemical sorption reaction and a biologically controlled exchange process. They noticed that the biological effect was more pronounced when the sediments were well mixed with the water than when the sediment cores were undisturbed.

Hayes and Phillips (1958) observed that in lake water-mud systems, bacteria competedwith both plants and muds for phosphorus. They postulated that bacteria in the water would take up phosphorus and produce an organic-phosphorus compound which could not enter the chemical or colloidal adsorption mechanism of the mud and could not be assimilated by plants. At the same time, bacteria in the mud would rapidly return phosphorus to the water. Thus, in a system where bacteria were present, when equilibrium was reached there would be more phosphorus in the water than in systems where bacteria were absent. When there is an increase in organic matter in the mud due to plankton sedimentation, the increased activity of bacteria would cause rapid phosphorus uptake from the water.

Holden (1961) found that a large portion of the adsorbed phosphorus on the mud was not extractable by dilute (1/10 N) hydrochloric acid or by neutral ammonium fluoride. It was suggested that the phosphorus was converted to the stable organic form by bacteria in the mud; therefore it would not be available for release to the overlying water during anaerobic conditions in the surface mud.

Hayes (1955) noticed that under aerobic conditions bacteria played an important role in promoting the exchange of P^{32} at the mud-water interface. Under anaerobic conditions, the effect of bacteria was small and the inorganic mechanisms played a major part. Spear (1970) also noticed that under anoxic conditions the biological effect on phosphorus release was negligible, whereas under oxic conditions organisms increased both the phosphorus release rate and total amount.

In contrast, Kimmel and Lind (1970) studied the orthophosphate sorption properties of a reservoir sediment that contained mainly clays in approximately equal proportions of calcium-montmorillonite, illite and Kaolinite. It was found that the phosphate removal was primarily by adsorption to the mud surface. Both bacteria and plankton had little effect on the phosphate removal. Removal of phosphate by aerobic precipitation with iron was also not significant.

Henrici and McCoy (1938) observed that bacterial counts were highest at the mud-water interface and decreased exponentially with sediment depth. The bacterial counts in the littoral sediments were much higher than those in the profundal sediments if the shore-ward zone was occupied by aquatic plants. In eutrophic and dystrophic lakes the total bacterial counts at the mud were higher than in oligotrophic lakes.

Mechanisms of Phosphate Fixation by Soils, Soil Minerals, and Lake Sediments

The literature contains very few papers directly related to the mechanisms of phosphate fixation by lake sediments. Our understanding of these mechanisms can only be derived from studies done with soil and soil minerals. Although lake sediments and terrestrial soils are situated in quite different environmental conditions, sediments usually originate from soils and should possess similar properties as soils. Therefore, a review of the phosphate fixation mechanisms in soils and soil minerals will certainly shed some light on mechanisms involved with sediments.

Soil literature contains numerous papers discussing the mechanisms of phosphate fixation. However, the abundance of literature leads one only to confusion. Although there were several attempts to present a unified theory of phosphate fixation, not a single theory has yet received general acceptance. Three major theories have been developed through the years. They are:

1. Isomorphous substitution
2. Adsorption
3. Chemical precipitation

A thorough survey of the literature on the subject of phosphate fixation is beyond the scope of this thesis. In this section only a few relatively important papers will be reviewed to present a picture of the more recent developments in this area.

The adsorption of phosphate by calcite was found by Stumm and Leckie (1970) to consist of three steps: (1) initial chemisorption of phosphate accompanied by heterogeneous formation of nuclei of amorphous calcium phosphate, (2) a slow transformation of these nuclei into crystalline apatite, and (3) crystal growth of apatite. Results of Griffin and Jurinak (1973, 1974) supported the finding of Stumm and Leckie. The kinetic data of Griffin and Jurinak (1974) showed that two simultaneous reactions were involved in the adsorption of phosphate by calcite. The first reaction was second-order and was related to the adsorption of phosphate on the surface of the calcite. The second reaction was first-order and was ascribed to the surface arrangement of phosphorus ion clusters into the calcium phosphate heteronuclei prior to the crystal growth.

Kuo and Lotse (1972) found that at low phosphate concentrations in solution, the phosphate adsorption by calcium carbonate and Ca-kaolinite could both be described by the Langmuir adsorption isotherm.

This indicated that phosphate adsorbed by both calcium carbonate and Ca-kaolinite formed a monolayer on the surfaces of these minerals. Cole et al. (1953) also noticed a rapid monolayer sorption of phosphate on $CaCO_3$ surfaces at low phosphate concentrations. But, at high phosphate concentrations, precipitation of dicalcium phosphate or similar compounds could be formed.

The mechanisms for the fixation of phosphate by kaolinite seems to depend on the concentration of phosphate solution, too. In strong phosphate solutions (1 M), kaolinite was shown to decompose and the released aluminum reacted with phosphate to form crystalline aluminum phosphate compounds whose composition depended on the predominant cations available in the solution. This solution-precipitation phenomenon was in accord with the aluminum-dissociation and solubility-products principles (Low and Black, 1950; Kittrick and Jackson, 1954, 1956).

In dilute phosphate solutions, over a short period of time, on the other hand, decomposition of kaolinite would not occur, and the phosphate fixation was caused by a chemical adsorption which obeyed the Freundlich equation (Low and Black, 1950; Russel and Low, 1954). The chemical adsorption was caused by the presence of adsorbed reactive aluminum which precipitated phosphate as an aluminum phosphate on the kaolinite surface. The reactive aluminum could be resulted from the weathering of the clay crystal and took the form of adsorbed aluminum ions or hydrous aluminum oxide films on the clay particles, or was simply the lattice aluminum on the exposed corners or edges of the kaolinite crystals.

In a more recent study, Chen et al. (1973) showed that crystals of new solid phase could be detected when α-Al_2O_3 was reacted with a very diluted phosphate solution (3×10^{-4}M). The crystals were very similar to those reported to form when kaolinite reacted with 1M phosphate solution (Kittrick and Jackson, 1956). But, the growth of the new solid phase was possibly more complicated than a simple stoichiometric reaction to form $AlPO_4 \cdot nH_2O$. In the kaolinite-phosphate system, however, the authors were not certain a similar new solid phase was also formed at low phosphate concentrations and for short reaction periods. The authors also eliminated as a rate-determining step either the release of aluminum ions from the lattice of alumina or kaolinite, or the diffusion of phosphate from solution to react with the aluminum ions. Instead, they hypothesized that the nucleation and growth of the new solid phase were the rate-determining steps.

While many workers favored the theory of solution-precipitation in explaining the phosphate fixation mechanism, as described above, some authors suggested that the fixation involved the exchange of edge hydroxyl groups of clay lattice by phosphate ions (Kelly and Midgley, 1943; Muljadi, et al. 1966a, b; Kafkafi et al. 1967). Kuo and Lotse (1972) described the phosphate adsorption by kaolinite as the replacement by phosphate ions of coordinated H_2O group and/or coordinated anions of the crystal lattice to form an outer octahedral complex of aluminum phosphate. A more detailed explanation of this type of exchange mechanism based on surface charge considerations was given by Hingston et al. (1972) in their study of the anion adsorption by goethite and gibbsite.

The reaction of phosphate with alumina and kaolinite also showed an initial rapid adsorption step followed by a slow process. The initial rapid adsorption step could be described by a second-order kinetic equation, suggesting that both the phosphate concentration and the surface saturation of the adsorbent were important in the adsorption process (Kuo and Lotse, 1972). The slow reaction was shown by Chen et al. (1973) to be first-order and was related only to the total soluble phosphate remaining in solution.

Muljadi et al. (1966 a, b) showed that the adsorption isotherms for the phosphate-kaolinite system could not be represented by a single isotherm type. In the phosphate concentration ranging from 0 to 10^{-1}M, the isotherm could actually be divided into three distinct regions, indicating that at least three energetically different reactive sites existed on the clay mineral. It was suggested that the sites for the first two regions (corresponding to the adsorption in the low phosphate concentration range) were located on the edge $-Al(OH)_2$ of the mineral and the third adsorption site was in some amorphous region of the clay surface. Adsorption isotherms for phosphate-gibbsite and phosphate-pseudoboehmite systems followed the same pattern as that for the phosphate-kaolinite system, but the number of adsorption sites differed. In their study of phosphate adsorption by three soils in Brazil, Syers et al. (1973) also indicated that three populations of adsorption sites with different capacities existed in these soils, and the adsorption isotherms could not be represented by a single Langmuir isotherm. However, Kuo and Lotse (1973), in their study of the kinetics of phosphate adsorption by hematite and gibbsite, explained that the surface of the clay minerals might not necessarily contain reactive sites of different energy levels. The reason that the phosphate molecules were held at different energy levels was because of the interactions between the adsorbed molecules.

Haseman et al. (1950) found that the fixation of phosphate by montmorillonite, illite, kaolinite, gibbsite and goethite could all be characterized by an initial rapid and subsequent slower stage. It was suggested that some chemical reactions were involved in these two stages. The rapid fixation might have resulted from the reaction of phosphate with readily available Al and Fe from these minerals, while the slower fixation might have involved the reaction of phosphates with Al and Fe released through decomposition of the minerals. The authors further identified that compounds chemically similar to palmerite were formed when montmorillonite, illite, kaolinite, limonite and goethite were treated with solutions of sodium, potassium and ammonium phosphates, and, when kaolinite and illite were treated with magnesium phosphate, compounds in the variscite-barrandite-strengite isomorphous series were formed. Similarly, Coleman et al. (1960) suggested that phosphate fixation by soil and montmorillonite was caused by a reaction that involved exchangeable aluminum or its hydrolysis products. An aluminum phosphate compound of composition similar to that of variscite was formed by this reaction. Hsu (1964), however, found that in a relatively dilute, neutral, phosphate solution phosphate was not fixed as variscite or strengite-type compounds, but was adsorbed on amorphous aluminum hydroxides and iron oxides or hydroxides in soils.

The sorption of phosphates by gibbsite and hydrous ferric oxide were found by Bache (1964) to consist of three stages: (1) a high energy chemisorption of small amounts of phosphate, (2) with larger amounts of phosphate, precipitation of insoluble phosphates, and (3) a low energy sorption of phosphate which might be physical adsorption or replacement of phosphate ions diffused into the solids. Hall and Baker (1971) found that stable aluminum polymers existed within the interlayer spaces of vermiculite. Increasing pH would cause an increase in the formation of the stable interlayer aluminum polymers and reduce the specific surface of reactive Al and phosphate adsorption site.

Kittrick and Jackson (1956) cited literature to prove that isomorphous substitution of P for Si in tetrahedral structural units in soil silicate minerals was not possible. The replacement of PO_4 for OH in a crystal structure was also unlikely since the phosphate tetrahedron was too large to occupy a hydroxyl site. While it was possible for the phosphate ions to replace hydroxyl ions at the edge of layer silicate clay particles, it was considered as an adsorption phenomenon. The adsorption mechanism could only be used to explain the initial reactions between phosphate and soil minerals. In order to explain all the observed facts in phosphate fixation experiments, the authors proposed a unified theory of phosphate fixation in soils. Essentially, this theory stated that the fixation of phosphate by soils was a chemical precipitation phenomenon. The chemistry of the formation and growth of separate-phase phosphate precipitates was controlled by solubility product principles. It was also suggested that precipitation and chemical adsorption were basically the same mechanism, both resulting from the interaction between phosphate and aluminum or iron.

Hsu (1965) further described adsorption as a special case of precipitation in the fixation of phosphate by soils. While, in precipitation,discrete phase of aluminum or iron phosphate was formed as a result of the attractive force between phosphate and aluminum or iron, in adsorption, aluminum (or iron) remained as the constituent of the original phase but reacted with phosphate by the residual force on the surface. The author also noted that at pH 5 or above, the activity of Al^{3+} or Fe^{3+} was negligible. The factors that dominated the process of phosphate fixation in ordinary soils were, therefore, not Al^{3+} or Fe^{3+}, but the surface-reactive amorphous aluminum hydroxides and iron oxides.

Soil organic matter may also play a role in the phosphate adsorption mechanism. Harter (1969) suggested that the added phosphate was initially adsorbed by organic matter in soil through some type of anion exchange, possibly involving a substitution of phosphate ions for hydroxyl ions in the organic matter. The adsorbed phosphate ions were readily exchangeable. But with time, the phosphate was transformed into less soluble aluminum and iron phosphates.

Lake sediments are different from soil in that the former are always water-saturated and may have an alternation of aerobic and anaerobic conditions. The soils usually contain a higher proportion of occluded phosphorus and apatite than lake sediments. This is reflected in the observation that the degree of exchangeability of native sediment phosphorus is higher than that of terrestrial soils (Li et al. 1971). It might nevertheless be true that major phosphate-sorbing components and the mechanisms of phosphate fixation in lake sediment are similar to those in soil.

In their study of the exchange of phosphate between estuarine water and sediments, Pomeroy et al. (1965) found that the sorption of phosphate by sediments consisted of two processes of different rates. It was postulated that the more rapid process was an initial surface sorption and slower process was subsequent combination of phosphate ions into the crystal lattice of clay particles. Carritt and Goodgal (1954) also explained the rapid process as an adsorption process and the slower process as a diffusion controlled reaction.

Kuo and Lotse (1973) suggested that the initial rapid adsorption was a high energy adsorption. The subsequent slower reaction was resulted from (1) an increase in surface negative charge, (2) an increase in interaction energy, and (3) a decrease in adsorption energy. The authors also found that the activation energy of phosphate adsorption was low, indicating that the adsorption was controlled by diffusion.

Livingstone, and Boykin (1962) suggested that sedimentary phosphorus was bound by sorption reactions, particularly ion-exchange, with mineral materials. The exchange capacity of the mud and the ionic activity of the water must therefore be the most important factors governing the phosphorus release from mud.

In his phosphorus adsorption study of the surface mud taken from a Connecticut lake, Harter (1968) found that aluminum in the mud was important in the sorption of added phosphorus. He based his finding on the fact that large amounts of adsorbed phosphorus could be recovered by extracting the mud with NH_4F which supposedly removed aluminum bound phosphorus. Bromfield (1965), however, found that the NH_4F reagent is not specific for aluminum bound phosphorus. In fact, NH_4F can also extract 1/2-3/4 of the phosphorus on phosphoratized iron oxides.

Shukla et al. (1971) postulated that an amorphous iron hydrous oxide gel complex which contained a small amount of Al_2O_3, $Si(OH)_4$ and organic matter was the major phosphorus-sorbing component of lake sediments studied. The clay fractions were mainly amorphous alumino-silicate which were not a major phosphorus sorption component. After the amorphous iron complex was removed by extracting with acid ammonium oxalate or citrate-dithionite-bicarbonate, the phosphorus sorption capacity of the sediments was greatly reduced. Their results, however, were discordant with those of Harter (1968) who found that after extracting with H_2SO_4, citrate-dithionate and NH_4F which removed calcium carbonate, iron oxides and aluminum, respectively, the mud still adsorbed large quantities of added phosphorus.

Li et al. (1971) found that both the native inorganic phosphorus and the adsorbed phosphorus exhibited a high degree and rapid rate of exchangeability. This concluded that a large portion of the inorganic phosphorus in the sediments must exist in the non-occluded form and the amorphous iron hydrous oxide gel complex as proposed by Shukla et al. (1971) and by Williams et al. (1971a) was indeed the major phosphorus sorption component for both native inorganic phosphorus and the added phosphorus. They also found that the total exchangeable inorganic P^{31} in lake sediments was about the same in both aerobic and anaerobic conditions. This observation provided indirect evidence to the fact that the inorganic phosphorus in the sediments was not in discrete iron-phosphate form (e.g. strengite). Otherwise, dissolution of crystalline iron phosphate under anaerobic conditions would be expected to increase markedly the total exchangeable inorganic P^{31}. On the other hand, Shapiro et al. (1971) discovered that in some parts of Lake Washington sediments, several types of particles with high iron content were responsible for the very high concentrations of phosphorus.

Although $CaCO_3$ may not be the major component responsible for the sorption of added phosphorus by calcareous lake sediments (Williams et al. 1970), Shukla et al. (1971) have suggested that when the added phosphorus concentration is high, precipitation of discrete calcium phosphate may occur. Hepher (1958) observed the disappearance of added superphosphate to some fishponds that had alkaline water and high calcium content and explained that most of the added phosphate was precipitated as $Ca_3(PO_4)_2$. In the alkaline conditions the mud was believed to fix the added phosphorus partly by anion-exchange reaction with the clay colloids and partly by reaction with calcium carbonate. Phosphorus adsorption on compounds of iron, manganese and aluminum might not be possible under high pH and low concentrations of these metals.

Redox Potential and Its Application in Lake Sediment Studies

A chemical reaction reaches equilibrium when the free energy of the products equals that of the remaining reactants. In a reversible oxidation-reduction reaction that has reached equilibrium, Oxidant + ne^- = Reductant, the free energy change can be related to the activities of the oxidizing and reducing species of the reaction by the following relationship:

$$\Delta G = \Delta G^o + RT \ln \frac{(Ox)}{(Red)} \qquad (1)$$

where (Ox) = the activity of the oxidant

(Red) = the activity of the reductant

ΔG = free energy change of the reaction

ΔG^o = the free energy change when the activities of both the oxidant and reductant are unity.

R = Gas constant

T = Absolute temperature.

The free energy change is related to electrical energy by

$$\Delta G = -n\ E\ F \tag{2}$$

Substituting equation (2) into (1), we get the Nernst Equation:

$$E_h = E^o + \frac{RT}{nF}\ \ln \frac{(OX)}{(Red)} \tag{3}$$

where E_h = Oxidation-Reduction potential or reduction potential, which is the potential of the half-cell that forms a complete cell with the hydrogen half-cell

$$\frac{1}{2} H_2 = H^+ + e^-$$

E^o = the standard oxidation-reduction potential. It is the potential when the activity of the oxidant equals that of the reductant or when both have unity activity.

n = the number of electrons invovled in the reaction

F = Faraday's constant.

From this derivation, it is known that the Nernst equation and the measured E_h are valid only if the reaction is reversible and is at equilibrium with constant temperature and pressure.

In an ideal case, when a number of redox couples are mixed together and allowed to reach true equilibrium, and assuming that the electron exchanges between the oxidized and reduced species and between them and the electrode are reversible, then the measured electrode potential, E_h, can be related to all the redox couples present according to the Nernst equation, i.e.

$$
\begin{aligned}
E_h &= E_1^o + \frac{RT}{nF} \ln \frac{(Ox)_2}{(Red)_1} \\
&= E_2^o + \frac{RT}{nF} \ln \frac{(Ox)_2}{(Red)_2} \\
&= \ldots
\end{aligned}
\tag{4}
$$

where the numerical subscripts refer to individual redox couples (Bohn, 1968).

On the other hand, in a non-equilibrium mixture of redox couples, the above relationship no longer holds. Although a null potential can still be registered by a potentiometer in such system, the potential represents merely a mixed potential which has no simple or Nernstian relationship to the redox couples in the system. Bohn (1971) stated that the mixed potential could be approximately expressed as a weighted average of the potentials of all the redox couples present in a system, and the weighing of each couple depended on its exchange current, i^o. Thus, for a system that contained m numbers of redox couples, the mixed potentials could be expressed as

$$E = \sum_{j=1}^{m} \frac{|i_j^o|}{\sum |i_j^o|} \left[E_j^o + \frac{RT}{n_j F} \ln \frac{(Ox)_j}{(Red)_j}\right] \tag{5}$$

The exchange current, which is the current between the redox couple and the electrode, is related to the concentrations of the oxidizing and reducing species, C_{ox} and C_{Red}, respectively, by the following equation

$$i^o = nFAk^o(C_{ox})^\alpha (C_{Red})^{1-\alpha} \tag{6}$$

where k^o is the combined rate constant, A is the surface area of the electrode and α is the transfer coefficient. When the concentrations of one or both members of a redox couple are low, the couple is not able to exert a potential on the electrode. Exchange currents from other couples in the mixture will create a mixed potential.

Since 1930, when Karsinkin, et al.(Mortimer, 1942) first published data on potential measurements in muds and pointed out their relation to the redox condition in the water, many investigators have used redox potential as a parameter in lake studies. Pearsall and Mortimer (1939) have shown a positive correlation between the measured potential and the oxidation-reduction conditions in soil, lake water and sediments. They observed that $E_5 = + 0.350$ V (where E_5 is the redox potential at pH = 5) was always the dividing point between oxidizing (appearance of Fe^{3+}, NO_3^- and $SO_4^=$) and reducing (appearance of Fe^{2+}, NH_4^+ and $S^=$) conditions. They suggested that the mechanism of potential formation in all three systems was similar in nature. Mortimer (1941, 1942, 1971) later showed that ferric iron reduced to ferrous at the water-mud interface at a fairly definite redox potential (about $E_7 = + 0.25$ volts) and low oxygen concentration (about 0.5 mg/1). In the overlying water, the concentrations of iron, ammonia, silicate, phosphorus, alkalinity, conductivity and substances reducing permanganese increased rapidly after the potential at the mud surface had fallen below $E_7 = 0.24$ volt.

Allgeier, et al. (1941), however, did not observe such a sharp changeover in the Wisconsin lakes they studied. Hayes, et al. (1958)

had difficulties in getting reproducible results in their potential measurements of lake muds. Hutchinson (1957) stated that in well-oxygenated surface water, the oxygen potential, $O_2 + 2\ H_2O + 4\ e^- = 4OH^-$, should dominate and gave a potential of $E_7 = 0.80$ V at 25°C. However, actual measurements in different lake waters showed that the best value for natural water was 0.52 volts. Hutchinson believed that the discrepancy was due to the presence of a cracked film of platinum oxide on the surface of the platinum electrodes used in the potential measurements. As a result, a truly reversible system no longer existed.

Doyle (1968) found that the measured redox potentials of natural waters often was the Nernst potential for the ferrous ion-ferric oxide reaction:

$$Fe^{++} + 2\ H_2O = \gamma\text{-FeOOH} + 3\ H^+ + e^- \tag{7}$$

$$E_h = 0.965 - 0.177\ \text{pH} - 0.059\ \log A_{Fe}{}^{++} \tag{8}$$

This potential could be recorded even if the equilibrium concentration of Fe^{++} ion was several orders of magnitude too low to influence the potential of an inert electrode. A deposit of ferric oxide (probably γ-FeOOH) was found on the platinum electrode. The real redox potential of a solution containing ferrous iron may therefore never be measured. Doyle also noticed that in a strongly reduced natural water the deposition of ferric oxide would not occur. Another unknown potential determining reaction might have existed for the platinum electrode which gave a potential reading that was much lower than a value predicted from the ferrous ion-ferric oxide reaction.

As a matter of fact, natural waters are not in an equilibrium state with regard to oxidation-reduction. The major cause of nonequilibrium conditions in natural waters is photosynthesis. Through photosynthesis, the light energy is converted to chemical energy in the form of compounds of high free energy, this causes an accumulation of nonequilibrium concentrations of these compounds in the waters. The nonphotosynthetic organisms, on the other hand, tend to restore the equilibrium by catalytically decomposing the endproducts of photosynthesis to derive energy for their metabolism. However, as long as new photosynthetic products continue to be put in, a state of eqilibrium can nver be reached. Potential measurements in lake waters, therefore, represent mixed potentials that cannot be interpreted in the thermodynamic sense (Morris and Stumn, 1967; Stumm, 1967). Furthermore, the measurement of redox potentials in sediments is subject to a number of limitations. (Hayes et al. 1958; Morris and Stumm, 1968; Whitfield, 1969). They are listed as follows:

(1) Mechanical disturbance during sampling and during inserting of the electrodes into the sample may disturb the natural environment and cause the entrapped gases to escape. It may also introduce air to the sample.

(2) In a poorly poised system, such as many lake muds, the electrode surface area is critical. Larger surface area gives more accurate readings, but large surface area also magnifies the

effects of trace impurities or adsorption of surface-active materials.

(3) The reproducibility of repeated measurements depends on the degree of poising of the system and on whether oxygen is present. In general, the higher the potential, the greater the reproducibility. Dilution causes a reduction in reproducibility.

(4) Some compounds in the natural system such as hydrogen sulfide may attach to the electrode metal surface and cause irreversible reaction potentials.

(5) In natural systems the redox reactions are usually poorly coupled, and, as a result, the measured potential may reflect some highly reversible redox reactions that may have little significance in the overall chemistry of the environment.

(6) Microenvironments in a natural system may be active in the formation of many mineral deposits. These microenvironments are usually inaccessible to the potential measurement.

Because of these limitations, one should be very careful in commencing the measurement of potentials in sediments and in interpreting of the data.

Nevertheless, the redox potential can be used as an operational parameter in sediment studies. Although, being a mixed potential, the measured potential cannot be interpreted thermodynamically, it reflects qualitatively the oxidation-reduction status of a system. Many investigators have found consistently direct relationships between the measured redox potentials in sediments and the important parameters they were interested in (Krumbein and Garels, 1952; Mortimer, 1941, 1942; Mortimer, 1971; Pearsall and Mortimer, 1939; Whitfield, 1969). The measurement of redox potentials has also been practiced in the studies of other complex natural systems such as bacterial cultures (Hanke and Katz, 1943), sewage treatment processes (Dirasian, 1968b; Dirasian et al. 1963; Grune and Chueh, 1958; Henry, 1960; Hood, 1948; Rohlich et al.,1941), industrial waste (Eckenfelder and Hood, 1951), and soil (Armstrong, 1967, Gotoh and Patrick, 1974; Patrick et al. 1973; Ponnamperuma et al. 1967; Savant and Ellis, 1964; Williams and Patrick, 1973).

Ponnamperuma, et al.(1967) tried to study the redox equilibria in flooded soils and interpreted them in the thermodynamic sense. They stated that the dominant inorganic redox system or systems in flooded soils depended on the content of nitrate, manganese (IV, III) oxide hydrates, iron (III) oxide hydrates and sulfate. In soils that were high in iron and low in manganese and sulfate the dominant redox systems were the iron hydroxide systems as nitrates disappear rapidly in flooded soils. Assuming that the principal solid species involved in the iron (III) - iron (II) hydroxide equilibria in reduced soils were the metastable hydrated oxides, $Fe(OH)_3$ and $Fe_3(OH)_8$, they proved that in reduced soils that were not unduly high in sulfide, the principal redox systems were $Fe(OH)_3$-Fe^{++}, $Fe(OH)_3$-$Fe_3(OH)_8$ and the $Fe_3(OH)_8$-Fe^{++} systems.

$\underline{Fe(OH)_3 - Fe^{++} \text{ system}}$

$$Fe(OH)_{3c} + 3\ H_{aq}^{+} + e = Fe_{aq}^{++} + 3\ H_2O \qquad (9)$$

$$E_h = 1.058 - 0.059 \log (Fe^{++}) - 0.177\ pH \qquad (10)$$

$\underline{Fe(OH)_3 - Fe_3(OH)_8 \text{ system}}$

$$3\ Fe(OH)_{3c} + H_{aq}^{+} + e = Fe_3(OH)_{8c} + H_2O \qquad (11)$$

$$E_h = 0.429 - 0.059\ pH \qquad (12)$$

$\underline{Fe_3(OH)_8 - Fe^{++} \text{ system}}$

$$Fe_3(OH)_{8c} + 8\ H_{aq}^{+} + 2e = 3\ Fe_{aq}^{++} + 8\ H_2O \qquad (13)$$

$$E_h = 1.373 - 0.0885 \log (Fe^{++}) - 0.236\ pH \qquad (14)$$

Gotoh and Patrick (1974) also showed that the $Fe^{2+} - Fe(OH)_3$ system was present in a waterlogged soil.

Beside iron, other predominant participating elements in redox reactions in natural waters and soils are: carbon, oxygen, nitrogen, sulfur and manganese. An excellent review of the redox systems involving these elements in waterlogged soils and sediments has been given by Ponnamperuma (in press).

The oxidation-reduction reactions in natural systems are mediated or catalyzed by organisms. Organisms, however, can carry out only those reactions that are thermodynamically possible, i.e. those leading to a decrease in free energy. In a closed aqueous system containing organic matters, successive biologically-mediated redox reactions will occur in the order of their thermodynamic possibility, as the redox potential was lowered gradually (Morris and Stumm, 1967). Table 1 shows the succession of events occurring in a waterlogged soil as the redox potential decreases (Parr, 1969). A similar sequence may also have occurred in lake sediments (Keeney et al. 1971).

Table 1

Succession of Events Occurring in A Waterlogged Soil as Related to Redox Potential (Parr, 1969)

Stage of Reduction	Process	Redox Potential, E_h, mv	Biological Metabolism	Formation of Organic Acids
First Stage	Disappearance of O_2	+600 to + 500	Aerobes	None
	NO_3^- reduction	+500 to +300	Facultative Anaerobes	Some accumulation after addition of organic matter
	Mn^{4+} reduction	+400 to +200		
	Fe^{3+} reduction	+300 to +100		
Second Stage	SO_4^{2-} reduction	0 to -150	Obligate Anaerobes	Rapid accumulation
	H_2 production	-150 to -220		Rapid decrease
	CH_4 production	-150 to -220		

CHAPTER III

EXPERIMENTAL APPARATUS

Platinum Electrodes

Platinum electrodes were needed for redox potential measurements. Commercially available foil type electrodes were expensive and the foil broke away easily after short periods of usage. It was therefore decided to construct some electrodes with platinum wires. The construction procedure was similar to that described by Dirasian (1968a). A typical electrode is shown in Figure 1. The working portion (i.e. the exposed end of the platinum wire) of the electrode has a surface area of about 0.162 sq. cm.

Once the electrode was constructed and each time before its use, it had to be standardized. The solution used for the standardization was a buffered solution of quinhydrone. It was prepared by adding 2 grams of primary standard grade quinhydrone to each liter of a 0.05M potassium hydrogen phthalate buffer solution. At 25°C this solution has a pH of 4.008 and a redox potential of +218 mv when measured against a saturated calomel half cell (Dirasian, 1968a). After standardization the unsatisfactory electrodes were reconstructed and tested again or simply discarded. The standardized electrodes were soaked in distilled water until use.

To insure proper functioning, the electrode must be cleaned after each usage to remove the surface film that might accumulate on the electrode surface. This was done by first washing with tap water and

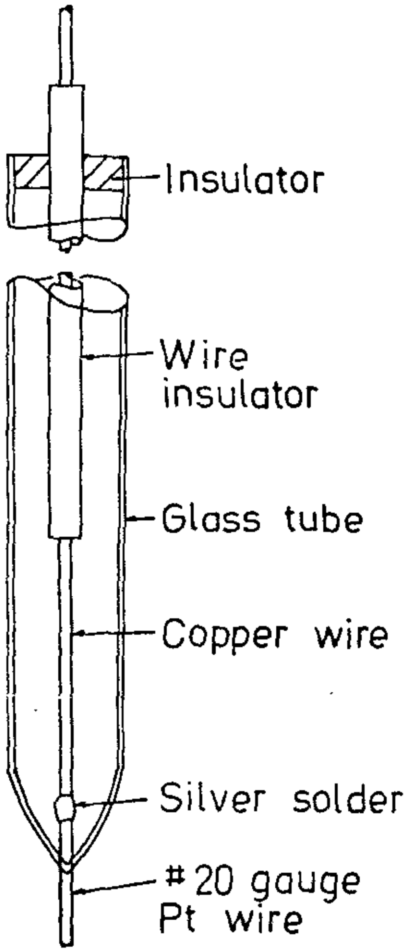

Figure 1. A Typical Platinum Electrode

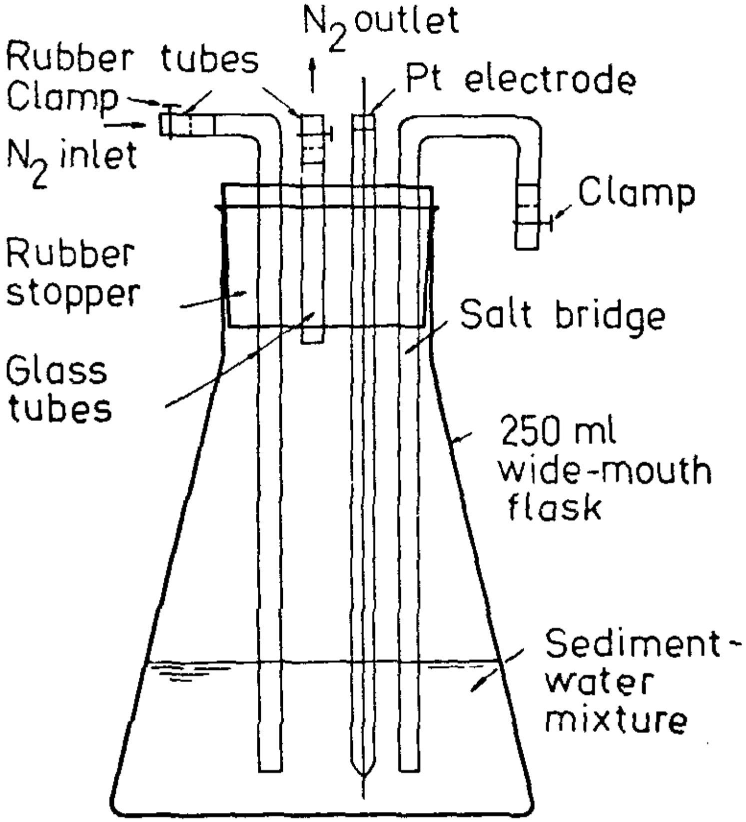

Figure 2. Typical Reaction Unit for Adsorption Study under Anaerobic Conditions.

scouring with powdered alumina, followed by immersing in a 10 percent nitric acid solution for about 10 minutes. Finally, the electrode was washed several times with distilled water. Once the electrode was cleansed, it had to be stored in distilled water for at least 30 minutes before next usage (Dirasian, 1968a).

Salt Bridge

In the phosphate adsorption experiments under low redox potential conditions, a salt bridge was used for the convenience of potential measurement. The salt bridges were constructed according to the procedures outlined by Davies and Kelly (1967). Approximately 16 grams of potassium chloride were dissolved in 50 ml of hot distilled water. 1.5 grams of plain agar were then added and the mixture was boiled for at least 15 minutes. Water was added from time to time to make up the evaporation loss. At the end of the boiling period, the solution was poured into pre-bent glass tubes having a nominal diameter of 7 mm. After cooling in the air for a few minutes, the salt bridge was ready to use. In order to prevent contamination, new salt bridges were constructed for each set of new samples.

Apparatus for Adsorption Studies

For adsorption experiments conducted under high redox potential conditions, the apparatus used was nothing more than a number of 500 ml widemouth glass flasks or 4-oz widemouth glass jars with proper rubber stoppers and/or screw-on caps.

For experiments under low redox potential conditions, 250 ml widemouth glass flasks and rubber stoppers were used. On each of the rubber stopper four holes were drilled to accommodate 7 mm diameter glass tubings. The holes should be drilled as small as possible to insure air-tightness when the tubings were inserted. To these four holes, a platinum electrode, a salt bridge and two 7 mm diameter glass tubes, were properly introduced. One of the glass tubes served as the inlet and the other served as the outlet for the nitrogen gas to be used for purging the air out of a sample mixture. The salt bridge was installed along with the platinum electrode so that the redox potentials could be measured without removing the stoppers from the containers, thus preventing air from entering the samples. Air was found to change the redox potential of a sample from negative values to positive values in a very short period of time. The use of a salt bridge has one additional advantage. That is, only one reference electrode is needed for the measurement of the potentials of a number of samples. A schematic diagram of a typical reaction unit for low redox potential adsorption studies is shown in Figure 2.

When measuring redox potentials, the free end of the salt bridge was, together with a reference electrode, dipped into a saturated KCl solution. The leading wires of the platinum electrode and the reference electrode were connected to a pH meter to complete a circuit. A Radiometer, Type PHM-28, pH meter was used for the potential measurement. A saturated calomel electrode was used as the reference electrode. All the potential measurements reported in this thesis are relative to the saturated calomel electrode (E_c). For potential measurements in samples under high redox potentials, the reference electrode was dipped into the samples directly; no salt bridges were used. The potential drops across the salt bridges were found to be negligibly small.

Liquid Scintillation System

Radioactive P^{32} was used to determine the amount of surface phosphorus existing on the sediment particles. The radioactivity of P^{32} was counted by the liquid scintillation counting technique. The major components involved in this technique are a scintillator system and a liquid scintillation counter. The scintillator system consists of an organic solvent or solvent mixture, a primary fluor and a secondary fluor. For counting in aqueous solutions, an additional polar solvent is often needed to improve the miscibility of the aqueous solution with the organic solvent(s).

In operation, the radoactive sample material is mixed with the scintillator system and the polar solvent (if needed) in a vial. The vial is then put into the sample compartment of the liquid scintillation counter for counting. In the sample-scintillator system mixture, the radiation energy from the sample is first transferred to the organic solvent and, then, to the primary fluor. Upon receiving the radiation energy, the primary fluor emits a burst or scintillation of light photons. The secondary fluor absorbs these photons and re-emits them at a longer wavelength which is closer to the wavelength of maximum response of the photomultiplier tube in the counter. The photons are then absorbed by the photocathode of a photomultiplier tube which converts them into an electronic pulse. After suitable amplification, the pulse is registered as a count corresponding to the emission of the radiation (Radiochemical Centre, 1967).

"Quenching" is a decrease in counting efficiency caused by materials which interfere with the production of light photons in the liquid scintillator and its transmission to the photomultiplier tube of the counter. Many materials, including dissolved oxygen, act as quenchers in the liquid scintillator, and it is almost impossible to predict the counting efficiency of a given sample. Presently, there are three methods available for the determination of counting efficiencies. They are: (1) internal standard method, (2) external standard method and (3) channel ratios method. Details of these methods are described in Principles of Radioisotope Methodology by Chase and Rabinowitz (1967) and many other text books.

The liquid scintillation counter used for the experiment reported herein was a Beckman LS-100 Liquid Scintillation System, manufactured by Beckman Instruments, Incorporated, and was located in the laboratory of the Department of Plant and Soil Sciences, University of Massachusetts, Amherst. The instrument is an ambient-temperature soft-beta spectrometer. It has built-in quench calibration which is performed by the combined external standard-channel ratios method. The scintillator system used was a diluted solution of Beckman Fluoralloy TLY and had the following composition

PPO (2,5-diphenyloxazole)		4 g
POPOP [1,4-bis-2-(5-phenyloxazolyl)-benzene]		67 mg
Toluene	to make	1000 ml

The toluene used for the dilution had a purity of 99 mole and was manufactured by Fisher Scientific Company. To improve the miscibility of sample solutions with toluene, Beckman Bio-Solv Solubilizer BBS-1 was also used. Polyethylene vials (Beckman Poly Q vials) were used to contain sample-scintillator mixtures for activity counting.

CHAPTER IV

MATERIALS AND METHODS

Sediment Sources, Collection and Storage

The sediments under study were taken from two small lakes in western Massachusetts. Lake Warner, located in North Hadley, Hampshire County, has a surface area of 68 acres and a maximum depth of 10 feet (McCann, 1970). It is a eutrophic lake with abundant algal growth during summer months. Lake Wyola, located in Shutesbury, Franklin County, has a surface area of 129 acres and a maximum depth of 34 feet. It is a relatively clean lake and can be classified as a mesotrophic lake (Snow and DiGiano, 1973). The general morphology of these two lakes are shown in Figures 3 and 4.

Sediment samples were taken from the western end of Lake Warner at a water depth of 5 feet and from a location near the center of Lake Wyola at a depth of 28 feet. An Ekman dredge was used for sample collection. Only the surface three inches of each grab was collected and the rest discarded. All samples were kept in plastic bags in the field. Brought back to the laboratory, always within the same day, the samples from each lake were mixed thoroughly, stored in glass bottles, sealed and refrigerated at 4^{o}C in the dark until use.

Analytical Methods for Sediment Characteristics Determination

The pH of the wet sediment samples was determined at 20^{o}C without diluting with water by using a Radiometer, Type PHM-28, pH meter. The

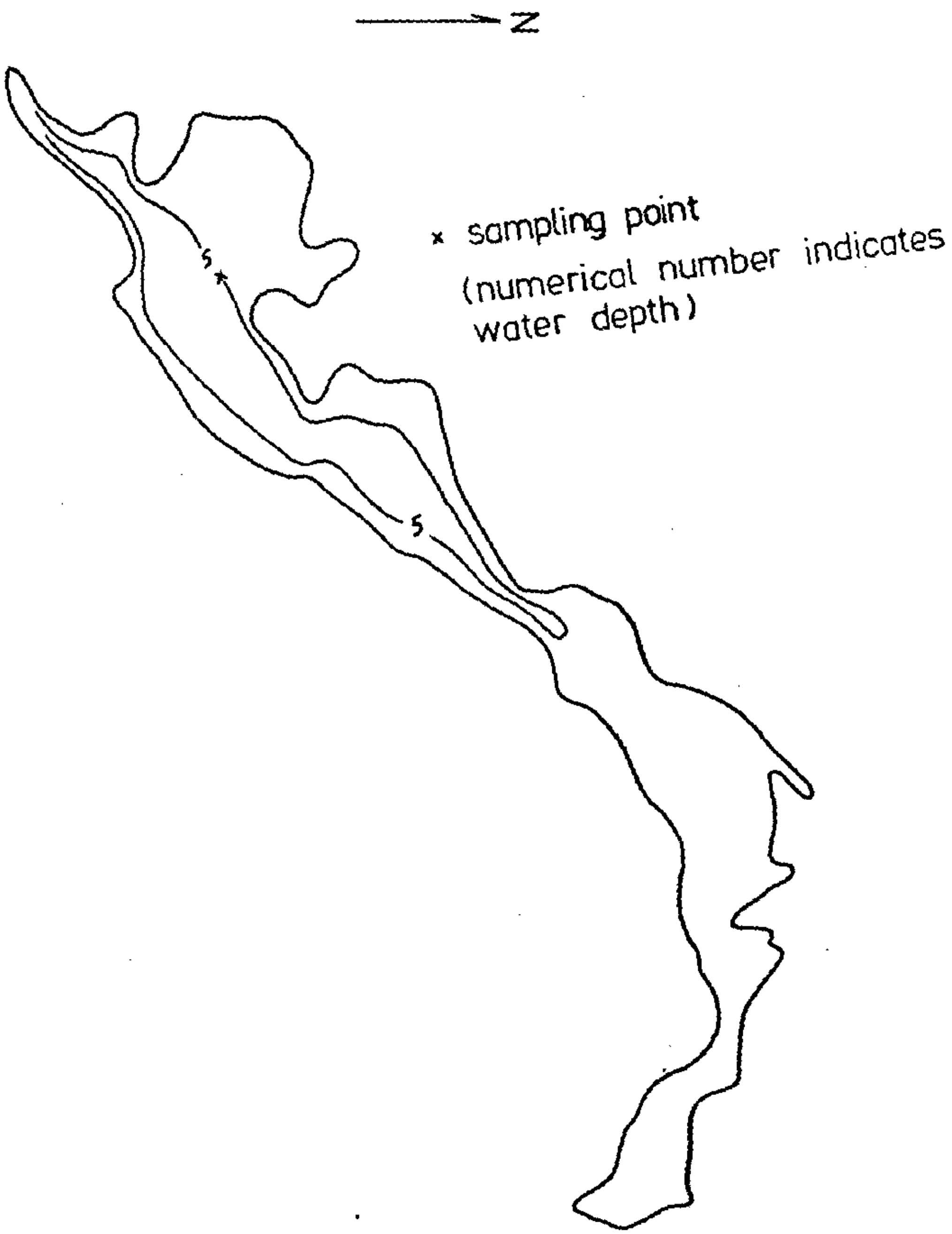

Figure 3. Map of Lake Warner

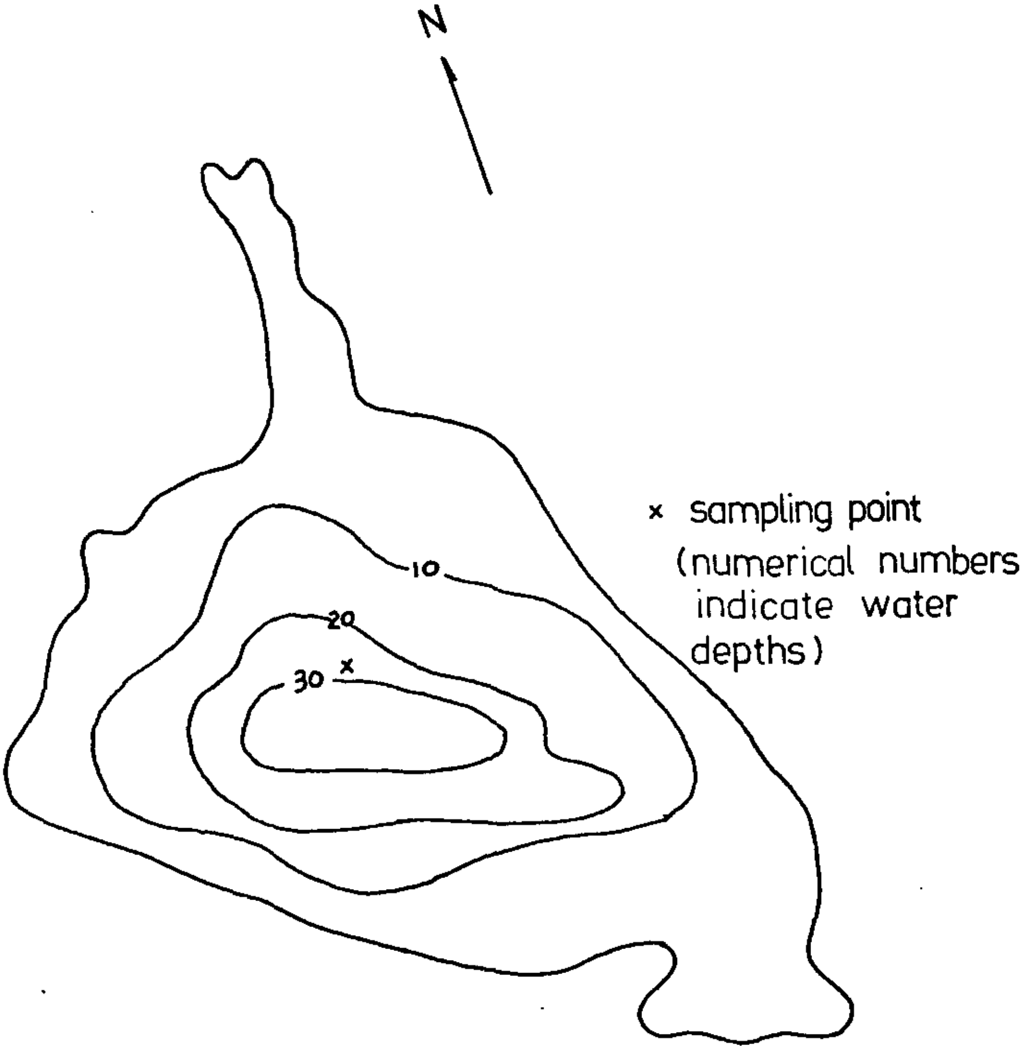

Figure 4. Map of Lake Wyola.

organic matter content was determined by evaporating the wet sediment in a cruscible, oven drying it at 110°C for 24 hours, and then burning it at 600°C for 24 hours. The percentage of the weight of the oven-dried sample lost in the combustion period was counted as the organic matter content (Jackson, 1958).

Portions of the well mixed sediment samples were air dried and ground to the size of 100-mesh for the determination of carbonates, total organic phosphorus, total P, Fe, Al, Ca and Mn. The carbonates content was determined by a rapid gasometric method reported by Leo (1963). Total organic phosphorus was determined by the extraction procedure of Mehta et al. (1954). For determining total P, Fe, Al, Ca and Mn, samples were prepared by fusion with sodium carbonate (Na_2CO_3) and dissolving the fusion cake in 9N H_2SO_4 (Jackson, 1958). The diluted solutions were then used for the determination of total P by the method of Fogg and Wilkinson (1958), total Fe and Al by the Ferron method (Rainwater and Thatcher, 1960) and total Ca and Mn by atomic absorption spectrophotometry (Standard Methods, 1971).

Undried sediment samples were used for inorganic phosphate fractionation, oxalate extraction and citrate-dithionite-bicarbonate extraction. Inorganic phosphate was fractionated following a modified Chang and Jackson procedure (Petersen and Corey, 1966). The oxalate extraction and citrate-dithionite-bicarbonate extractions were carried out by the procedures described by Williams et al. (1971a). The total P in the extracts was determined by the ascorbic acid method (EPA, 1971), the inorganic phosphorus by the isobutanol extraction method (Appendix A), Fe and Al by the Ferron method (Rainwater and Thatcher, 1960), and Mn by atomic absorption spectrophotometry.

The weights of all the elements analyzed herein are reported as mg per gm of oven dried sediment. The oven dried weight of a unit weight of wet sediment sample was determined by heating at 110°C for 24 hours.

Surface Phosphorus Determination

Phosphorus existing on the sediment particles or, the surface phosphorus, was determined by the method used by McAuliffe _et al_. (1947) for the determination of surface phosphorus on soil particles. In this method, a small volume of a P^{32} solution is added to the sediment-water mixture that has reached equilibrium (with respect to P^{31} in the solution). When P^{32} is added to the sediment solution, it exchanges immediately with P^{31} on the sediment particles. The exchange reaction can be represented by the following equation:

$$P^{32}_{\text{solution}} + P^{31}_{\text{surface}} \rightleftharpoons P^{32}_{\text{surface}} + P^{31}_{\text{solution}} \tag{15}$$

where $P^{32}_{\text{solution}} = P^{32}$ in solution

$P^{32}_{\text{surface}} = P^{32}$ on sediment particles

$P^{31}_{\text{solution}} = P^{31}$ in solution

$P^{31}_{\text{surface}} = P^{31}$ on sediment particles

The equilibrium constant, K, of this reaction is

$$\frac{P^{32}_{\text{surface}} \cdot P^{31}_{\text{solution}}}{P^{32}_{\text{solution}} \cdot P^{31}_{\text{surface}}} = K = 1 \qquad (16)$$

K is unity because the two isotopes (P^{31} and P^{32}) behave almost identically. Equation (16) can be rearranged to give

$$P^{31}_{\text{surface}} = \frac{P^{32}_{\text{surface}} \; P^{31}_{\text{solution}}}{P^{32}_{\text{solution}}} \qquad (17)$$

Equation (17) is used for the determination of surface phosphorus. Detailed procedures for this determination is discussed in Chapter V. The laboratory procedure is described as follows.

Undried sediment sample equivalent to 0.5 gm of oven-dried material was shaken continuously with 50 ml of distilled water in 250 ml plastic centrifuge bottles. The bottles were capped during the equilibration period. From time to time, the caps were removed from the bottles for a few seconds to let air enter the bottle so as to keep an aerobic condition in the sample mixtures. Light was excluded and temperature was maintained at 20 ± 1°C in an air-conditioned room. The sediment-water mixture was equilibrated until sample filtrates showed a constant level in phosphate concentration. This took about four days. To make sure a true equilibrium was reached, the samples were shaken continuously for another ten days. At the end of the shaking period, 1 ml of a carrier free P^{32} solution* of known activity was added to the sample

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*The carrier free P^{32} solution was in the form of $H_3P^*O_4$ in 0.02N HCl solution, and was purchased from New England Nuclear, Catalog No. NEX 054. The solution was diluted with distilled water to the desired activity level before use.

mixtures and the shaking was resumed. After shaking for a predetermined period of time, the sediment mixture in one centrifuge bottle was filtered through a 0.45μ pore size Millipore filter paper. The filtrate was immediately determined for P^{32} by the liquid scintillation technique. This was repeated until after 14 days, the last sample was filtered and the P^{32} activity in the filtrate determined.

The ortho-phosphate concentration in each filtrate was also determined. The ascorbic method (EPA, 1971) was used for all samples except Lake Wyola sediment samples. Since the phosphate concentration was very low in the Lake Wyola sediment-water mixture, the more sensitive isobutanol extraction method (see Appendix A) was used for its determination.

In using the liquid scintillation technique for the determination of P^{32} activities, the first task was to determine the optimal combination of the sample, the BioSolv and the scintillator system to obtain a maximum counting efficiency. The next task was to determine the quench calibration curve. As mentioned previously, the Beckman LS-100 Liquid Scintillation System uses the combined external standard-channel ratios method for quench calibration. For each sample counted, the System will print out an External Standard Ratio. The latter is related to the counting efficiency by the quench calibration curve. The curve varies for each element being counted by the System. The quench calibration curve for P^{32} was determined and is shown in Figure 5. The optimal combination of the sample, the BioSolv and the scintillator system was found to be 1 ml sample solution + 1.65 ml BioSolv + 9 ml scintillator

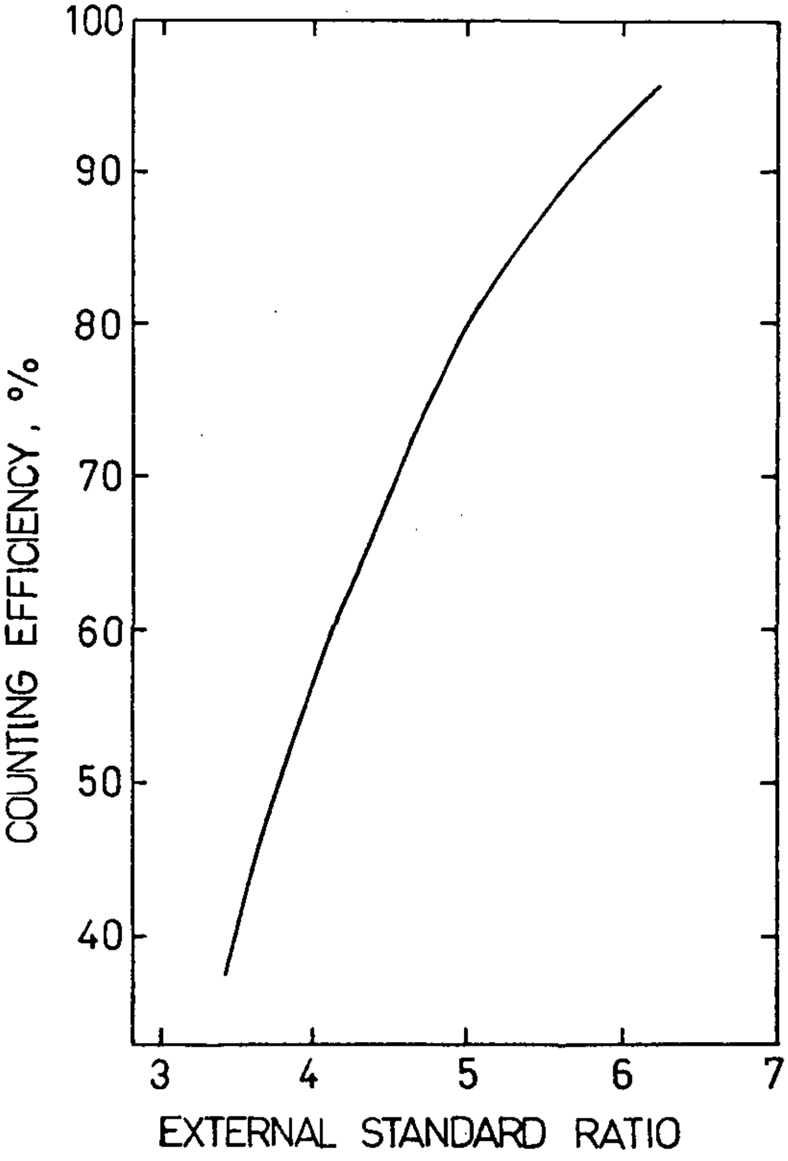

Figure 5. Quench Calibration Curve.

system. Detailed description of the procedures used for these determinations as well as for the natural decay and background corrections are shown in Appendix B.

Inorganic Phosphate Adsorption Studies

Adsorption Under High Redox Potential Conditions. For adsorption studies under high redox potential conditions, a carefully weighed undried sediment equivalent to 2 grams (for the Lake Warner sediment) or 2.11 grams (for the Lake Wyola sediment) of oven-dried material (oven dried at 110°C for 24 hours) and 190 ml of distilled water were added to a series of 500 ml widemouth Erlenmeyer flasks or 4-oz glass jars. The pH of the mixtures was adjusted by HCl or NaOH* to the desired values and checked periodically. Several days were generally required for the pH of the mixtures to become stabilized. At the end of this stabilization period, 10 ml of phosphate solutions in the form of KH_2PO_4 and in concentrations ranging from 0 to 300 mg-P/l were added to the mixtures. The pH of the mixtures was re-adjusted. Constant pH was maintained during the experiment by the addition of HCl or NaOH solution. Initially such adjustment was needed frequently. When the adsorption rate decreased, one pH adjustment per day was sufficient. Throughout the equilibrium period, the mixtures were

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*No suitable pH buffer system could be found for the control of the pH of the sediment-water mixture. Two buffer systems, i.e. the sodium acetate-acetic acid system and the phthalate-NaOH system, were tested and found to interfere with the interaction of phosphate and sediment. CO_2 gas is not suitable for the control of the pH of a noncalcareous sediment.

shaken by hand 2-3 times a day. During shaking, the stoppers or covers were removed so as to let air into and maintain the mixtures in aerobic conditions. The sample flasks were stored in the dark to prevent the growth of algae during the experiment. The experiments were performed in constant temperature rooms having temperatures 20 ± 0.5°C and 11 ± 0.5°C, respectively.

In order to make certain that the equilibrium was reached, the phosphorus concentration of the sample mixture to which was initially added 10 ml of a 100 mg-P/l phosphate solution was checked periodically. This was done by drawing out a portion of the well mixed sample from the container and filtering it immediately through a 0.45μ poresize Millipore filter paper. The ortho-phosphate concentration of the filtrate was then determined. When the results showed that equilibrium reached, all the sample mixtures were then filtered through 0.45μ pore size Millipore filter paper. The filtrates were analyzed for orthophosphate, total phosphorus and total iron. The redox potentials of the samples were measured with platinum electrodes just before the samples were filtered.

Adsorption Under Low Redox Potential Conditions. For the study of the equilibrium adsorption of phosphate by lake sediments under low redox potential conditions, the most difficult task is to reduce the redox potential in the sediment-water mixture and to keep it constant at a desired value for a period of time long enough for the adsorption to reach equilibrium. The job becomes more difficult if the pH of the system is also to be kept at a desired value since no suitable buffer can be used for the pH control in the sediment-water mixture without added interference (see footnote p. 52).

Hanke and Katz (1943) have successfully used an electrolytic method for the control of the redox potential in their bacteriological culture media for a few hours. Using the same technique, Dirasian (1968b) controlled the redox potentials of the sludges in his anaerobic digestion studies. Allen (1970) used a similar approach to control the redox potential in a lake sediment-water system. Essentially, the method involves the application of an electrical voltage through a pair of inert metal (such as platinum) electrodes to the sample system. One of the electrodes is inserted directly in the sample for which the redox potential is to be controlled, and the other electrode is inserted in a saturated KCl solution. The sample and the KCl solution is connected by a KCl-agar bridge to complete the electrical circuit. With the application of electrical voltage, the sample will be reduced if the electrode inserted in it is connected to the cathode of the direct current power supply; it will be oxidized if the electrode is connected to the anode of the power supply. In applying this method, it is very important to keep the samples free of oxygen, as oxygen can easily change the redox potential of the samples by oxidizing the chemical species reduced by the applied electrical potential. Oxygen was driven out of the samples by purging the samples with pure nitrogen gas. The sample containers were sealed throughout the experiment.

However, attempts to use the electrolytic method for the control of redox potential in the sediment-water systems under study proved to be fruitless. Initially, the method failed because the sample containers were not properly sealed. Continuous diffusion of minute amount of air into the sample mixture through the gaps between the stopper and the neck of the container had made it impossible to keep the system at a constant low redox potential long enough for the adsorption to reach equilibrium. Although this problem was later detected and corrected by proper sealing, another problem could not be overcome. When the redox potential of the sample-water mixture was being reduced by the electrolytic method, the pH of the mixture was also increased drastically. This was caused by the production of hydroxyl ions during the electrolysis of water according to the following reaction:

$$H_2O + e^- \rightarrow OH^- + 1/2H_2 \qquad (18)$$

Without a proper buffer, the pH of the mixture increased to a level (greater than 8) that does not normally exist in a non-calcareous lake sediment. The so-called "controlled potential electrolysis" method (Lingane, 1953) was tried to surmount this problem. This method is similar to the electrolytic method described above except that the potential of the working electrode, i.e. the electrode inserted in the sample, is maintained at the desired redox potential level by appropriately adjusting the total applied voltage. In the experiment, the samples were first deaerated with pure nitrogen gas and sealed. An electrical potential was then applied to each sample. It was intended to use this method to obtain redox potentials between 0 and -350 mv (relative to the saturated calomel electrode). Therefore, the applied electrical potential was adjusted such that the potential of the working electrode was at a desired value between 0 and -350 mv. For redox potentials in this range the reaction shown in Eq. (18) will not occur, as water will not be reduced to hydrogen gas until the redox potential is lowered to -828 mv (Murray and Reilley, 1963). Because of this, the pH of the sample should stay unchanged by the electrolysis process. But this approach was also unsuccessful. The electrolysis process proceeded so slow that after several days, the redox potential in the systems, when measured with a separate platinum electrode, still remained almost the same as before the electrolysis.

In searching for another method to control the redox potential in the sediment-water mixture, it was found that glucose could be used for reducing the redox potential in soil-water mixtures (Patrick et al. 1973). Preliminary tests showed that glucose could be used to reduce the redox potential of the Lake Warner sediment and water mixture to about -200 mv. For a period of 25 days, the redox potential of the mixture stayed in the range -150 to -250 mv, while the pH of the mixture remained constant at 4.8. It was, therefore, decided to use glucose for the subsequent studies.

The experimental procedure for the equilibrium adsorption of phosphate under low redox potential conditions is described in the following paragraph.

A carefully weighed undried sediment sample equivalent to 1 gram of oven-dried material and 90 ml of distilled water were transferred to a 250 ml widemouth Erlenmeyer flask. This was followed by adding 1 ml of a glucose solution that contained 0.05 gm of dextrose per ml. Ten ml of phosphate solutions in the form of KH_2PO_4 and containing 0,25, 50, 75 and 100 μg of P per ml were then added to the sediment-water mixture in each separate flask. The flasks were stoppered with the rubber stoppers specially prepared as described in Chapter III (Figure 2) and sealed tightly with masking tape. The content of each flask was purged with pure nitrogen gas for ten minutes, and, then, the inlet and outlet were closed tightly. The samples were agitated continuously with a wrist-action shaker. Experiments were performed in a constant (20 $\pm .5^{o}C$) temperature room. All sample flasks were wrapped with aluminum foil to prevent the samples from being exposed to the light in the room. The redox potential in each sample was checked periodically with a platinum electrode inserted in the sample. To make certain the equilibrium was reached, another series of samples was prepared. These samples were prepared and shaken in exactly the same manner as those described above with the exception that to each of these samples, the added 10 ml of phosphate solution all contained 50 μg of P per ml. The redox potentials of these samples were also measured periodically. From time to time, one of these latter samples were filtered* through a 0.45μ pore size Millipore filter paper, and the filtrate was analyzed for orthophosphate concentration. When the phosphate concentrations in several consecutive samples taken in different dates showed a constant level, the equilibrium

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*The reduced sediment is very sensitive to the presence of oxygen. In order to prevent the precipitation of phosphate with ferric iron upon oxidation of the sediment, the sample could not be allowed to contact with air during filtration. This was accomplished by covering the filtration funnel with polyethylene paper and let pure nitrogen flow over the sample during filtration.

condition was presumably reached. All the rest of the samples were then filtered through 0.45μ pore size Millipore filter paper, and the filtrates were analyzed for orthophosphate, total phosphorus and total iron.

Phosphate-Sorbing Components Studies

Three differently designed experiments were performed to investigate the relative importance of Fe and Al as the phosphate-sorbing components in the sediments under study. The experimental procedures of these three experiments are described as follows.

Experiment 1. Equilibrium Adsorption of Inorganic Phosphate by Oxalate Extracted Sediments. Undried lake sediments were first extracted by the oxalate reagents according to the procedure given by Williams et al. (1971a). After the extraction, the sediment residuals were mixed well. A portion of these residuals was weighed and oven dried at 110°C for 24 hours. The weight of the oven-dried sediment residual in a unit weight of the undried sediment residual was determined. A carefully weighed undried sediment residual equivalent to 2 grams of oven-dried sediment residual and 150 ml of distilled water were transferred to a 500 ml widemouth Erlenmeyer flask. Fifty ml of phosphate solutions in the form of KH_2PO_4 and in concentrations ranging from 0 to 40 mg P/l were then added to each separate flask. The pH of the sample mixtures was adjusted to 7.0 with HCl or NaOH and checked periodically. The flasks were shaken continuously on a wrist-action shaker. The experiment was performed in a constant temperature room having a temperature of 20 ± 0.5°C. All flasks were wrapped with aluminum foil to prevent the samples from being exposed to the light. Periodically, a portion of the sample mixture in the flask to which was added 50 ml of 30 mg P/l phosphate solution initially was filtered through the 0.45μ pore size Millipore filter paper and the orthophosphate in the filtrate was determined. When the phosphate concentrations of the samples taken from different dates reached a constant level, the equilibrium was presumably achieved. All the samples were then filtered through 0.45μ pore size Millipore filter paper and the filtrates were analyzed for orthophosphate. The redox potential in the samples were measured with platinum electrodes just before the samples were filtered.

Experiment 2. Effect of pH on the Dissolution of Phosphorus, Iron and Aluminum from Lake Sediments. Undried sediment samples equivalent to 2 grams of oven-dried sediment samples and 200 ml of distilled water were mixed together in 500 ml widemouth Erlenmeyer flasks. The pH of the mixtures was adjusted to different values of 4.0 to 7.0 and checked and readjusted periodically. The flasks were stoppered and stored in the dark. The experiment was performed in a constant temperature room having a temperature of 20 ± 0.5°C. The samples were shaken by hand twice a day for seven days. At the end of the seventh day, the samples were filtered through 0.45μ pore size Millipore filter paper and the filtrates were analyzed for orthophosphate by the isobutanol extraction method (Appendix A), and total iron and total aluminum by the Ferron method (Rainwater and Thatcher, 1960).

Experiment 3. Inorganic Phosphate Fractionation of Sediments After Equilibrium Adsorption. To determine the forms of the adsorbed inorganic phosphate on the sediments under study, the inorganic phosphate in four selected sediment samples taken from the equilibrium adsorption studies were fractionated according to the modified Chang and Jackson procedure (Petersen and Corey, 1966). Before fractionation the samples that had reached equilibrium were centrifuged at 10,000 rpm for 20 minutes to separate the solids from the liquid. The supernatant was collected for the analyses of phosphorus and iron as described in the section on Adsorption Under High Redox Potential Conditions. The solids were used for the inorganic phosphate fractionation.

Analytical Methods

Unless otherwise noted in this thesis, the analytical methods used for the determinations of orthophosphate, total phosphorus and total iron were as follows:

Orthophosphate and total phosphorus: by the ascorbic acid method as outlined in the Methods for Chemical Analysis of Water and Wastes (EPA, 1971). But, for phosphate concentrations lower than about 0.02 mg/1, the isobutanol extraction method as described in Appendix A was used for higher sensitivity.

Total iron: by the phenanthroline method as described in the Standard Methods (1971).

CHAPTER V

RESULTS

Sediment Characterization

The chemical characteristics of the sediments from Lake Warner and Lake Wyola are listed in Table 2. All the values in Table 2 are the averages of 2-3 separate analyses.

Carbonates and pH. The sediments of both lakes contained very low quantities of carbonates, indicating that the lakes are both non-calcareous. Both sediments were slightly acidic, with the pH of the Lake Warner sediment more close to neutrality than the Lake Wyola sediment. Aside from these two apparent similarities, however, the two sediments are quite different in chemical characteristics.

Phosphorus. The Lake Warner sediment contained a total phosphorus of 2.44 mg/g which was almost twice the amount of that existed in the Lake Wyola sediment. In a previous study, Snow and DiGiano (1973) showed that Lake Warner was a eutrophic lake and Lake Wyola was a mesotrophic lake. The relative amounts of the total phosphorus in the sediments of these two lakes analyzed herein may have well reflected this fact. The organic portion of the total phosphorus of both lakes were low. Almost 90 percent of the total phosphorus in the Lake Warner sediment was inorganic phosphorus, while in the Lake Wyola sediment, 85 percent of the total phosphorus was inorganic in nature.

In order to gain some insight to the nature of the inorganic phosphorus in these two sediments, a fractionation of the inorganic

Table 2. Chemical Characteristics of Sediments

Characteristics	Content[a]	
	Lake Warner Sediment	Lake Wyola Sediment
Total P	2.44	1.29
Organic P	0.25	0.19
Inorganic P	2.19	1.10
Inorganic Phosphate Fractionation, as P		
$Al-PO_4$	0.42	0.20
$Fe-PO_4$	0.47	0.09
$Ca-PO_4$	0.19	0.03
Reductant-Soluble PO_4	0.24	0.14
Occluded Al-Fe phosphate and P in residue[b]	0.87	0.64
Total Fe	37.2	14.5
Total Al	75.5	40.0
Total Ca	3.6	1.5
Total Mn	0.68	0.30
Carbonates, %	0.4	1.3
Organic Matter, %	13.7	27.8
pH	6.9	6.0
Oxalate Extraction		
Fe extracted	10.7	5.3
Al extracted	6.8	11.1
Total P extracted	1.76	0.72
Inorganic P extracted	1.52	0.41[c]
Mn extracted	0.04	0.02

Table 2, continued

Characteristics	Content[a]	
	Lake Warner Sediment	Lake Wyola Sediment
Citrate-Dithionate-Bicarbonate extraction		
Fe extracted	11.4	6.0
Al extracted	4.4	7.4
Total P extracted	1.33	0.48
Inorganic P extracted	1.10	0.29
Mn extracted	0.25	0.17

[a] Unless otherwise indicated, all contents have the unit mg/g of oven-dried sediment. All values are averages of 2-3 separate analyses.

[b] Calculated values.

[c] Value in doubt

phosphates into $Al-PO_4$, $Fe-PO_4$, $Ca-PO_4$ and reductant soluble-PO_4 was performed according to a modified Chang and Jackson procedure (Petersen and Corey, 1966). For the Lake Warner sediment, it was found that a major portion (ca. 2/3) of the extractable inorganic phosphates was in the forms of iron phosphate and aluminum phosphate. The iron phosphate content was 0.47 mg/g oven-dried sediment, which was only slightly higher than the aluminum phosphorus content. Calcium phosphate, which may in the forms of apatite, monocalcium, dicalcium and octacalcium phosphate (Chang and Jackson, 1957), was relatively unimportant in this sediment. The content of the iron oxides coated phosphates, i.e. the reductant-soluble phosphate, was also relatively low. In the Lake Wyola sediment, however, the aluminum phosphate and the reductant soluble phosphate were the major inorganic phosphates extractable by the fractionation procedure. The iron phosphate content was only about one-half, and the calcium phosphate content only one-seventh, of the aluminum phosphate.

However, it should be noted that a large portion of the total inorganic phosphorus could not be extracted by the reagents used in the fractionation procedure and did not fall into any of the above four categories. Chang and Jackson (1957) designated these as the barrandite-like aluminum-iron phosphate as they could be extracted by NaOH or NH_4F after the dithionite-citrate treatment of the soil. And, there are always some residue phosphorus which cannot be extracted by any of the above-mentioned procedures. Calculations showed that the sum of the aluminum-iron phosphate and residue phosphorus amounted to 36 percent and 50 percent of the total phosphorus in the sediments of Lake Warner and Lake Wyola, respectively.

Total Fe, Al, Ca, Mn and Organic Matter. The contents of total iron, aluminum, calcium and manganese in the Lake Warner sediment were, respectively 37.2, 75.5, 3.6 and 0.68 mg/g of oven-dried sediment. The content of the same metals in the Lake Wyola sediment were about half of those of the Lake Warner sediment. But, the organic matter content in the Lake Wyola sediment (27.8 percent of oven-dried sediment) was about twice the amount in the Lake Warner sediment. The results showed that the contents of calcium and manganese were both much less than the contents of iron or aluminum, and that in both lakes aluminum content were almost three times as much as the iron content. The amounts of the total iron and total aluminum in sediments, however, do not necessarily reflect their phosphorus-sorbing capacity. This is because Al can be present as primary and secondary alumino-silicates, such as feldspars, phyllosillicates, etc., while Fe can occur in Fe-containing layer silicate minerals. All these latter minerals possess much lower phosphorus-sorbing capacity than amorphous Al and Fe.

Oxalate and Citrate-Dithionate-Bicarbonate Extractions. Oxalate treatment extracted 28.8 percent of the total iron and 9 percent of the total aluminum from the Lake Warner sediment. Along with these, 72.2 percent of the total phosphorus and 69.5 percent of the total inorganic phosphorus were also extracted. For the Lake Wyola sediment, oxalate extraction released 36.5, 27.8 and 55.8 percent of the total iron, aluminum and phosphorus, respectively. The oxalate extraction removes iron in amorphous forms only (Saunders, 1965), whereas the citrate-dithionate-bicarbonate extraction removes iron in both amorphous and crystalline forms (Jackson, 1956). Results in Table 2 show that the citrate-dithionate-bicarbonate extraction extracted only a slightly more iron from both sediments than the oxalate extraction. This indicated that the crystalline iron compounds such as goethite and hematite were absent or present in only small quantities in both sediments. The amounts of the total aluminum, total phosphorus and total inorganic phosphorus extracted by the citrate-dithionate-bicarbonate extraction were all less than those extracted by the oxalate extraction. Williams et al.(1971a) showed that the chemicals of both of the above two extraction methods attacked the same form(s) of iron in all sediments. The reduction in the amounts of the phosphorus (both total and inorganic) released by the citrate-dithionate-bicarbonate extraction was therefore seemingly related to the reduction in the amount of the aluminum extracted.

Both of the above-mentioned extraction procedures extracted only the amorphous iron-containing components and the amorphous aluminum-containing components from soils and sediments (Saunders, 1965; Shukla et al. 1971). Therefore, a high percentage (about one-third) of the total iron in the sediments of the two lakes studied was in amorphous form. In the Lake Warner sediment, most of the aluminum was probably in the crystalline minerals, as only 9 percent of the total aluminum was extractable by the oxalate extraction and even less amount was extractable by the other extraction method. In contrast, the amount of the amorphous aluminum components in the Lake Wyola sediment was rather high (27.8 percent by oxalate extraction). As the amorphous forms of both iron and aluminum are more potent phosphorus-sorbing agents than their crystalline forms (Shukla et al. 1971; Williams et al. 1971a), it seems that, although iron may be a relatively more important component in retaining phosphorus in the Lake Warner sediment, aluminum may have played a more important role in the retention of phosphorus in the Lake Wyola sediment. This fact is also reflected in the results of the fractionation of inorganic phosphates of the two sediments, as discussed previously.

The oxalate extraction extracted very low percentage of the total manganese, while the citrate-dithionate-bicarbonate extraction extracted more than half of the total manganese from both sediments. Williams et al. (1971a) showed that manganese was not directly responsible for the accumulation of phosphorus in lake sediments.

Surface Phosphorus Determination

The determination of phosphorus adsorption maxima of soils and sediments is complicated by the fact that there are always some phosphorus existing on the surface of the soil or sediment particles initially. The adsorption maxima of a given sample cannot be determined accurately without knowing the amount of the existing surface phosphorus. Some authors used the distilled water-washed sediments for the phosphorus adsorption experiment (Kuo and Lotse, 1974). Washing may remove the phosphorus in the interstitial water and some loosely bonded phosphorus, but it may not remove all the surface phosphorus. Besides, there is a possibility that some important sediment constituents, such as colloidal Al and Fe particles, which may be important for phosphorus adsorption, are washed away as well.

For many years, soil scientists have used an isotopic exchange method for the determination of surface phosphorus on soil (McAuliffe et al. 1947; Olsen and Watanabe, 1957) and soil minerals (Olsen, 1952). This method is adopted for the determination of surface phosphorus on lake sediments in this thesis. The experimental procedures have been described in Chapter IV. The results are shown in Table 3. In this table, the values of the radioactivity remaining in solution, $P^{32}_{solution}$, at each sampling time are the averages of 2-3 measurements and have been corrected for quench, natural decay and background counts. The P^{32} adsorbed to the sediment surface, $P^{32}_{surface}$ is calculated by deducting the value of $P^{32}_{solution}$, corrected for decay, at each sampling time from the value of $P^{32}_{solution}$ at time zero.

Figure 6 is a plot of the data in Table 3, showing the disappearance of P^{32} from solution with time. The curves in Figure 6 indicate that the exchange between P^{32} in solution and P^{31} in sediment consists of an initial rapid reaction and a subsequent much slower reaction. The rapid reaction corresponds to the exchange between the P^{32} in solution and the P^{31} on the sediment surface (McAuliffe et al. 1947). The slower reaction may involve the exchange of P^{32} with phosphate of lower

Table 3. Change in Activity Ratio with Time for Lake Warner and Lake Wyola Sediments

Sample	Time, hours	$P^{32}_{solution}$*, DPM/ml	$P^{32}_{surface}$ DPM/ml	Activity Ratio, $P^{32}_{surface}/P^{32}_{solution}$
Warner	0	66554	0	0
	1	5937	60617	10.21
	4	3086	63468	20.56
	10	2114	64440	30.48
	24	1565	64989	41.52
	48	1171	65383	55.83
	121	1277	65277	51.11
	336	671	65883	98.2
Wyola Run 2	0	42180	0	0
	0.083	1105	41075	37.17
	0.25	755	41425	54.87
	0.50	514	41666	81.1
	1	364	41816	115
	2	284	41896	148
Wyola Run 1	0	63876	0	0
	1	463	63413	137
	4	231	63645	276
	10	142	63734	449
	24	131	63745	487
	48	78.3	63797.7	815
	121	98.6	63777.4	647
	336	82.0	63794.0	778

*All values have been corrected for natural decay and background; all values are the average of 2-3 measurements.

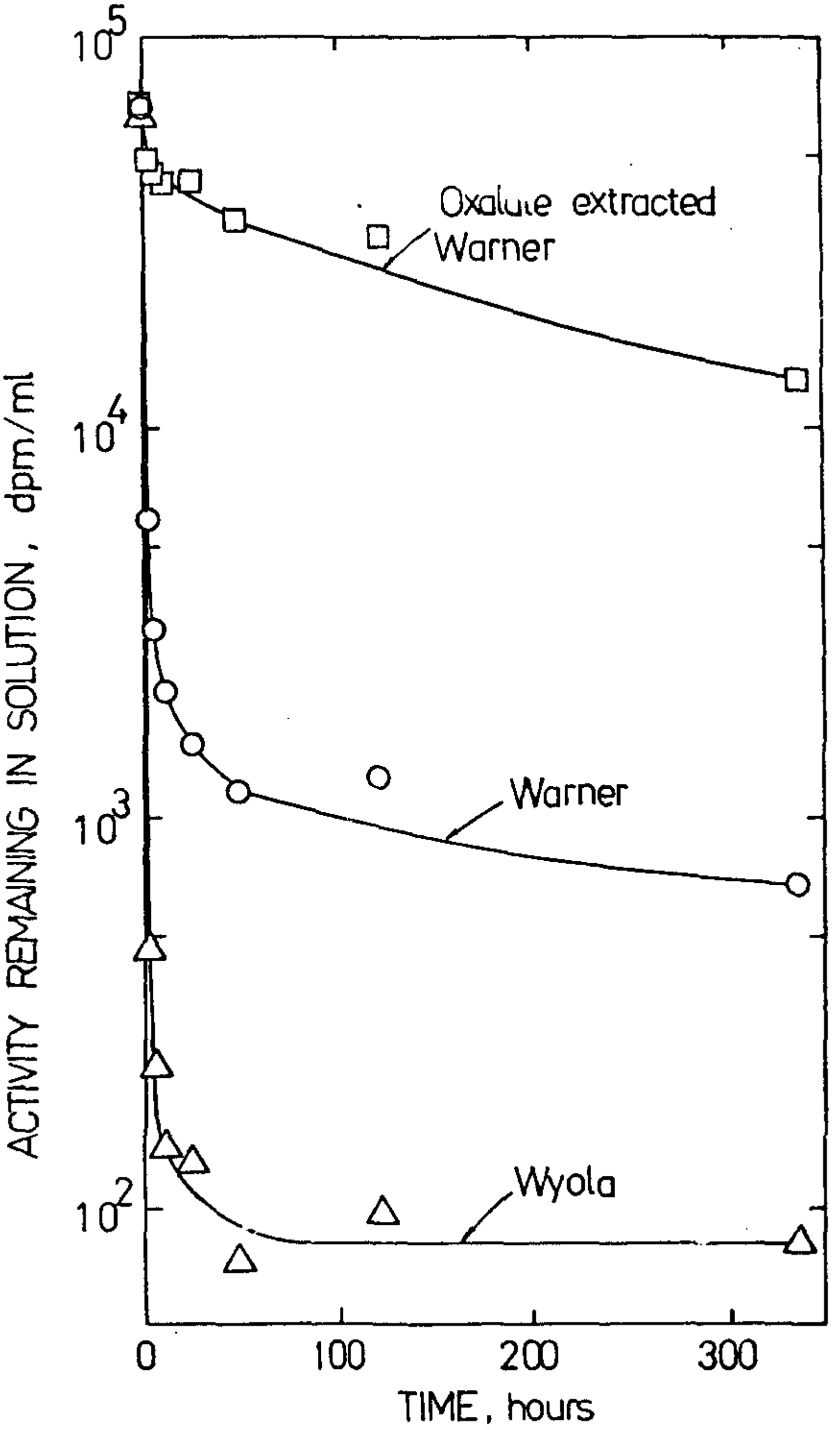
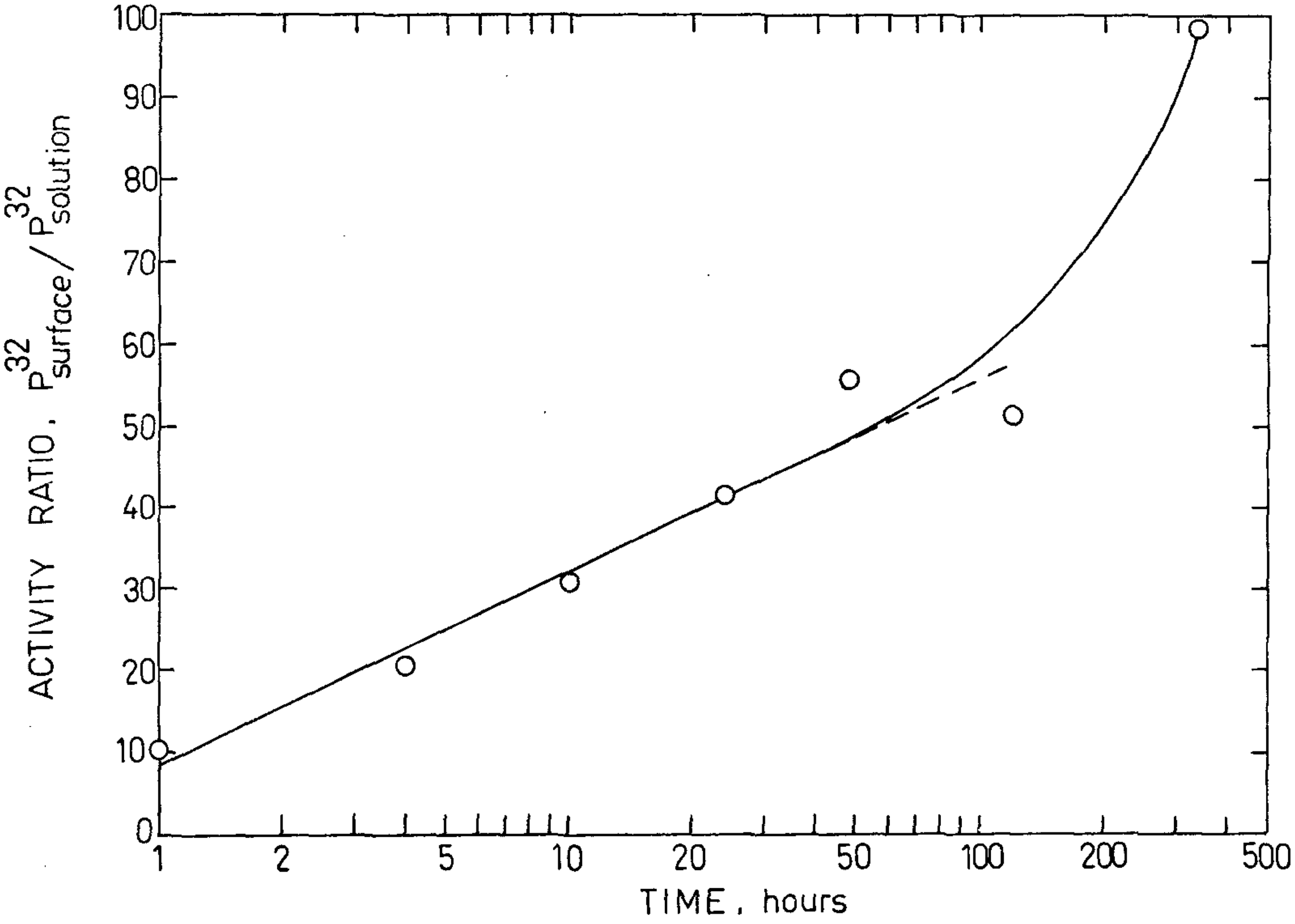


Figure 6. Disappearance of P^{32} from Sediment Solutions with Time.

exchangeability, or with phosphate inside the sediment particles (Black, 1957).

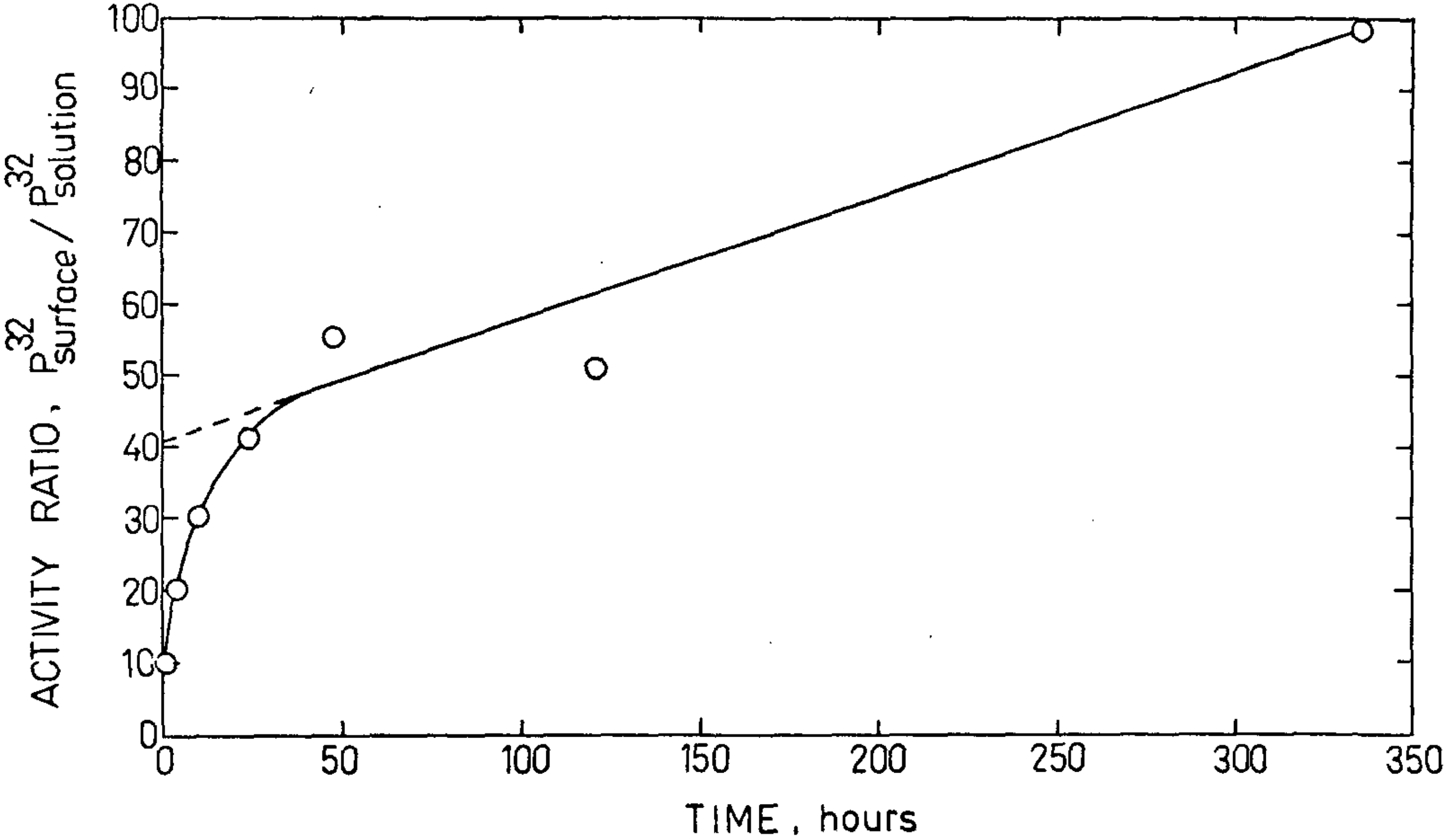
To calculate the surface phosphorus on each sediment, the activity ratio, $P^{32}_{surface}/P^{32}_{solution}$, is first computed and plotted against time (Figures 7 and 8). It is noted that the two distinct reactions mentioned above also show up in the curves of this plot. Since surface phosphorus is related to the initial rapid exchange reaction, the activity ratio corresponding to the time that marks the end of the rapid reaction is used for the calculation of surface phosphorus using equation (17), Chapter IV.

For the Lake Warner sediment, the point that separates the rapid logarithmic reaction region and the subsequent slower reaction region falls on the 24th hour after the addition of P^{32} to the equilibrated sediment solution (Figure 7). The activity ratio at this point is 41.52. For the Lake Wyola sediment, the initial exchange reaction was much more rapid. In the first experimental run for this latter sediment, samples were taken for P^{32} determination starting at one hour after the addition of P^{32} to the sediment solution. Subsequent samples were taken after 4, 10, 24, 48, 121 and 336 hours. However, the curve in the plot of the ratio $P^{32}_{surface}/P^{32}_{solution}$ vs. time did not show the expected two reaction regions. Therefore, a second test was run for this sediment with samples taken for P^{32} determinations at 5, 15, 30, 60 and 120 minutes after the P^{32} addition. The plotted data for this second run did show the two distinct reaction regions and



(a)

Figure 7. Exchange of Solution Phosphorus (P^{32}) with Surface Phosphorus (P^{31}) on Lake Warner Sediment.



(b)

Figure 7, continued

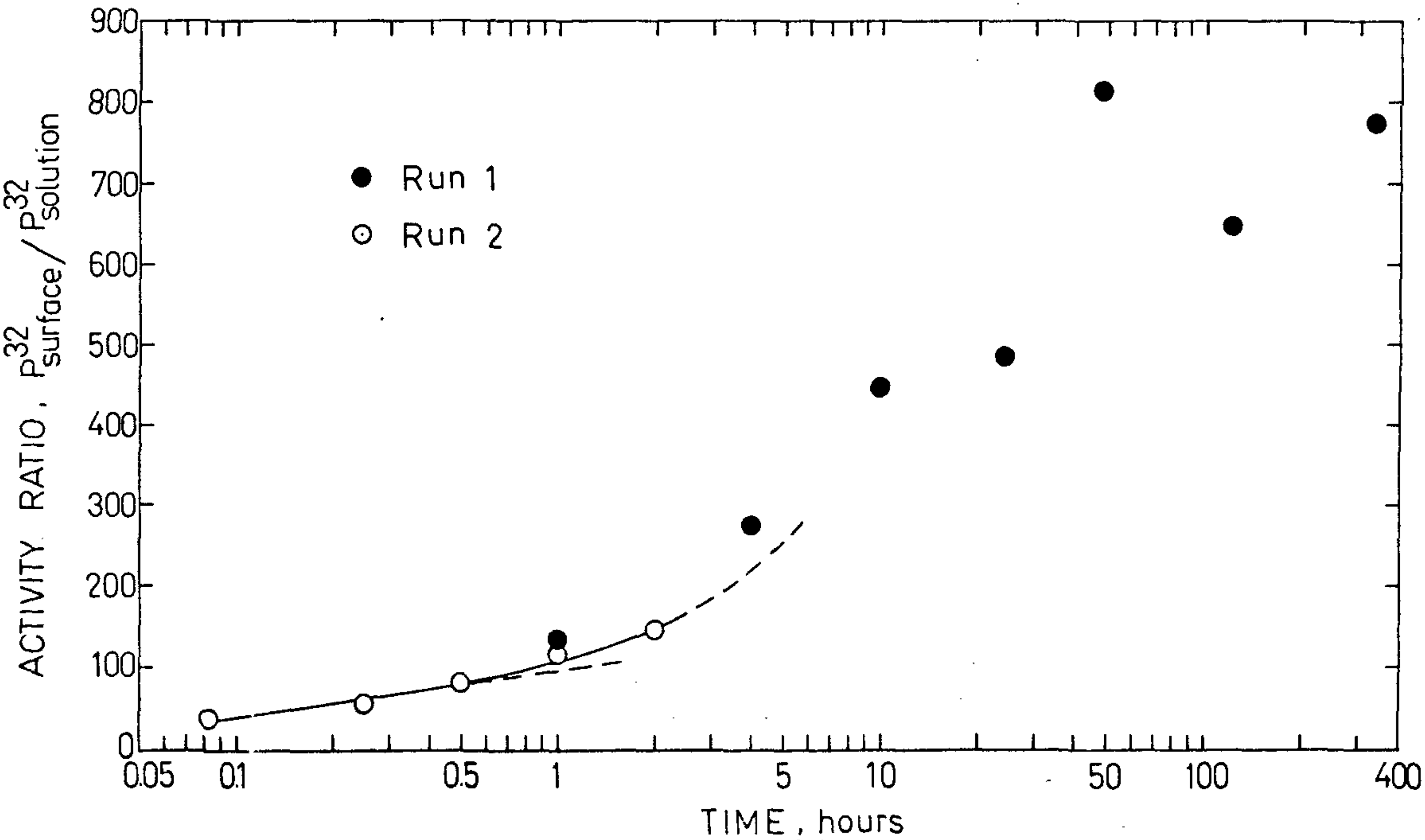
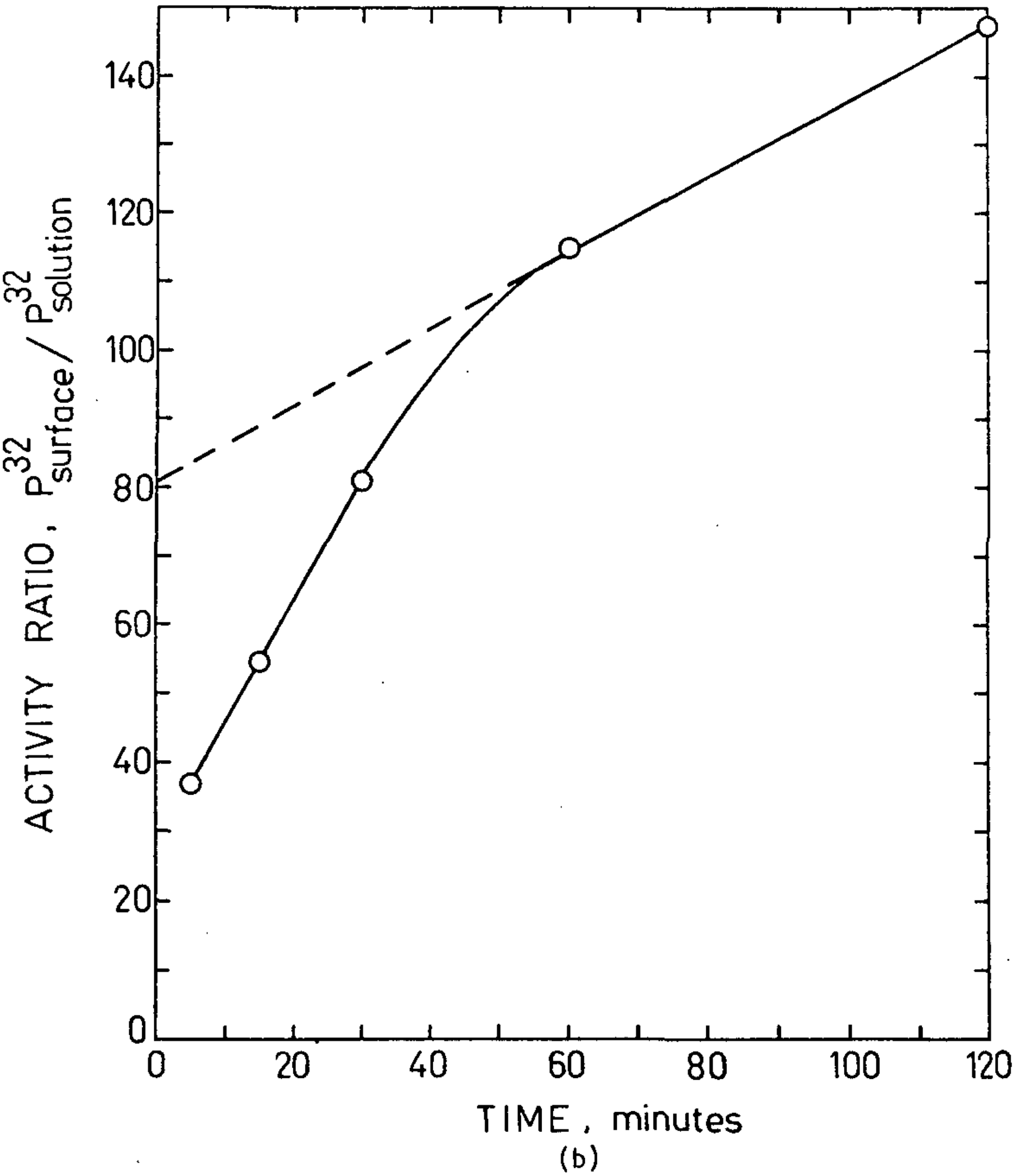


Figure 8. Exchange of Solution Phosphorus (P^{32}) with Surface Phosphorus (P^{31}) On Lake Wyola Sediment.[a]



Fiqure 8, continued

the changing point was corresponding to a time 60 minutes after the P^{32} addition (Figure 8). The activity ratio at this point is 81.10.

The values of the surface phosphorus, $P^{31}_{surface}$, as calculated using Equation (17), Chapter IV, are 261 μg/g and 44.6 μg/g for the Lake Warner sediment and the Lake Wyola sediment, respectively (Table 4). If the phosphorus released to the sediment solution is also counted, the total amounts of the phosphorus that exist both on the surface of the sediment and in the interstitial water of the sediments are 267 μg/g and 45 μg/g (both on oven-dried weight basis) for Lake Warner and Lake Wyola sediments, respectively (Table 4). These latter values are used for the surface phosphorus corrections in the calculations of the phosphorus adsorption maximums of the two sediments (see section on Adsorption Isotherms, this chapter).

The values of the $P^{31}_{solution}$ in Table 4 are the equilibrium phosphorus concentrations in the sediment-water mixtures, measured before P^{32} was added. Addition of P^{32} solutions to the equilibrated sediment-water mixtures would essentially not change the equilibria of the mixtures. This is because the added P^{32} solutions contained less than 7 x 10^{-12} gram of P^{32} (i.e. less than 2 microcuries of P^{32}) and the volume of the added solutions (1 ml) was also small compared to those of the sample mixtures (about 50 ml). Analysis of the P^{31} concentrations in sample mixtures after the addition of P^{32} gave values very close to those before the P^{32} addition. This proved that the above argument is correct.

Table 4. Determination of Surface Phosphorus

Sample	$P^{31}_{solution}$ mg/l	$P^{31}_{solution}$ μg/g	$P^{32}_{surface}/P^{32}_{solution}$	$P^{32}_{surface}$, μg/g	$P^{31}_{surface} + P^{32}_{solution}$, μg/g
Warner	0.060	6.3	41.52	261	267
Wyola	0.005	0.55	81.1	44.6	45
Oxalate Extracted Lake Warner	0.232	24.2	0.445	10.8	35

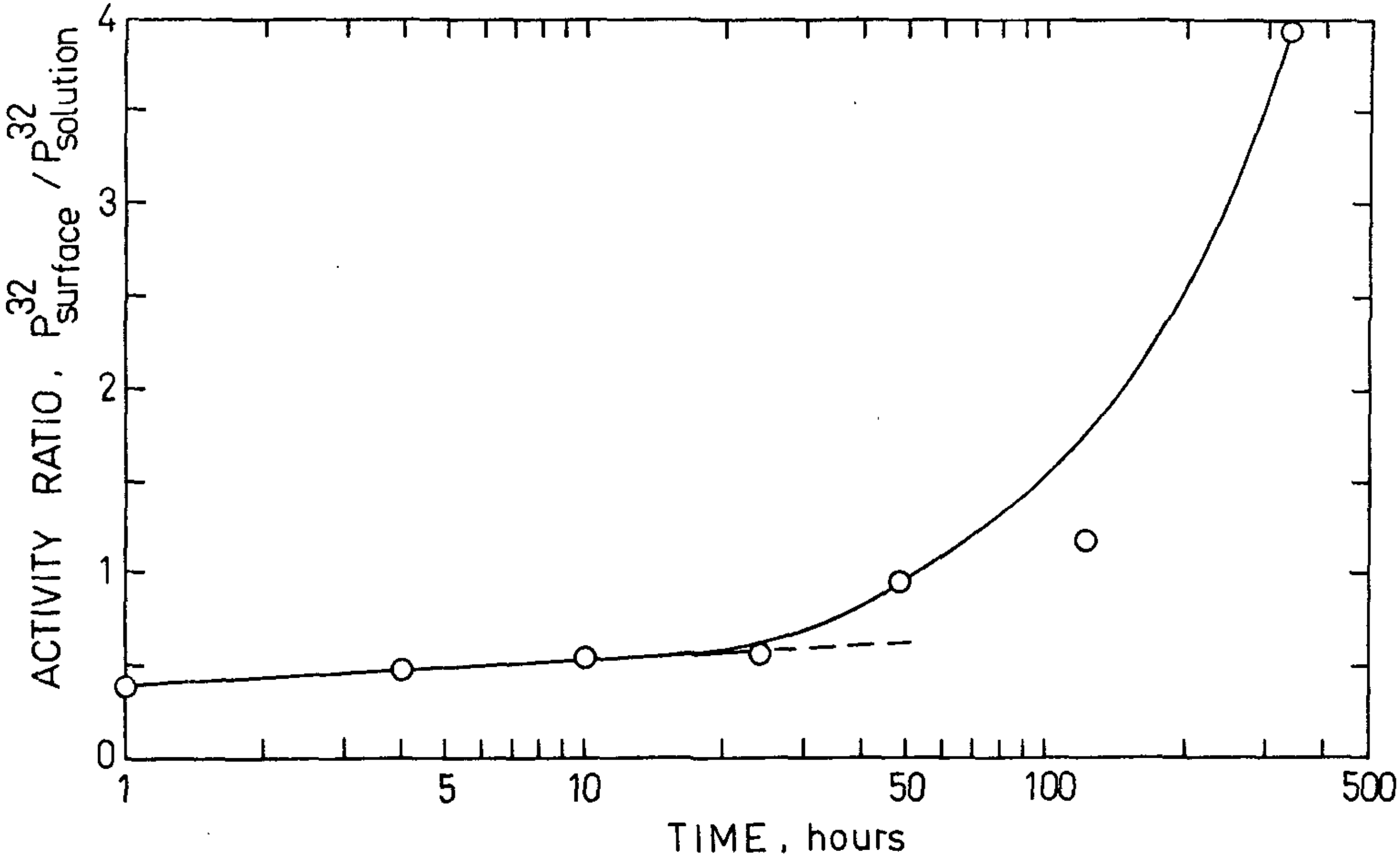
The results indicated that in the sediments of the two lakes studied, the amounts of surface phosphorus were both very low comparing to the total phosphorus contents of these sediments. Since the surface phosphorus thus determined represents that portion of the sediment phosphorus which has a high degree of exchangeability, the results suggested that although the sediment of a lake might contain a high quantity of phosphorus, only a small portion of this phosphorus was readily exchangeable with the phosphorus in the surrounding water. The fact that the Lake Warner sediment contained a greater amount of surface phosphorus than the Lake Wyola sediment suggested that when the phosphorus concentration in the surrounding water is reduced, the Lake Warner sediment would release a greater amount of phosphorus from its surface than the Lake Wyola sediment would.

In order to determine whether the oxalate extraction removed any of the surface phosphorus from lake sediments, the surface phosphorus of the oxalate extracted Lake Warner sediment was also determined exactly in the same manner as for the original sediments. The data are shown in Tables 4 and 5 and in Figures 6 and 9. The results indicate that the oxalate extracted Lake Warner sediment contained a surface phosphorus of 10.8 μg/g of oven-dried material. Or, if the phosphorus released to the solution is also considered, the total phosphorus on particles of the oxalated extracted sediment and their surrounding solution is 35 μg/g of oven-dried material. Both of these values are much smaller than the corresponding values of the unextracted sediment.

Table 5. Change in Activity Ratio with Time for Oxalate Extracted Lake Warner Sediment

Sample	Time, hours	$P^{32}_{solution}$*, DPM/ml	$P^{32}_{surface}$, DPM/ml	Activity Ratio, $P^{32}_{surface}/P^{32}_{solution}$
Oxalate	0	67185	0	0
extracted	1	48213	18972	0.3935
Lake Warner	4	45135	22050	0.4885
Sediment	10	43347	23838	0.5499
	24	43009	24176	0.5621
	48	34239	32946	0.9622
	121	30746	36439	1.1852
	336	13561	53624	3.9543

*All values have been corrected for natural decay and background; all values are the average of 2-3 measurements.



(a)

Figure 9. Exchange of Solution Phosphorus (P^{32}) with Surface Phosphorus (P^{31}) on Oxalate Extracted - Lake Warner Sediment.

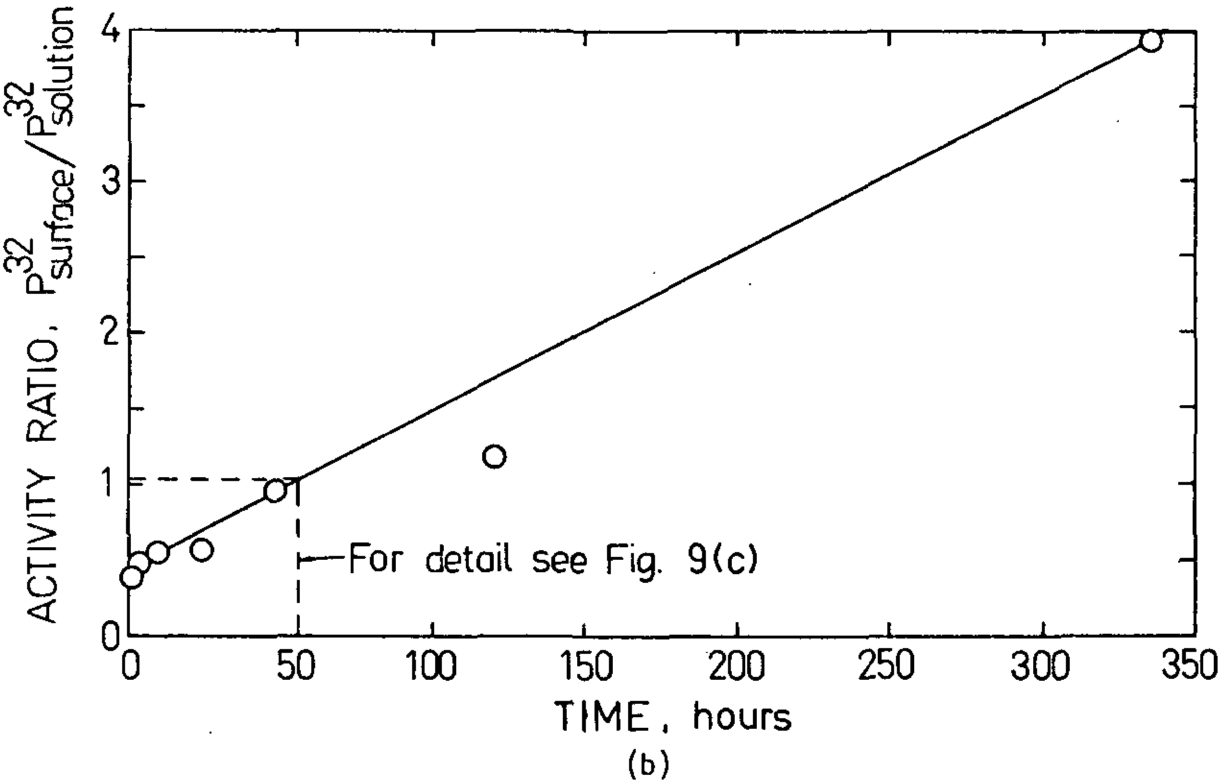


Figure 9, Continued

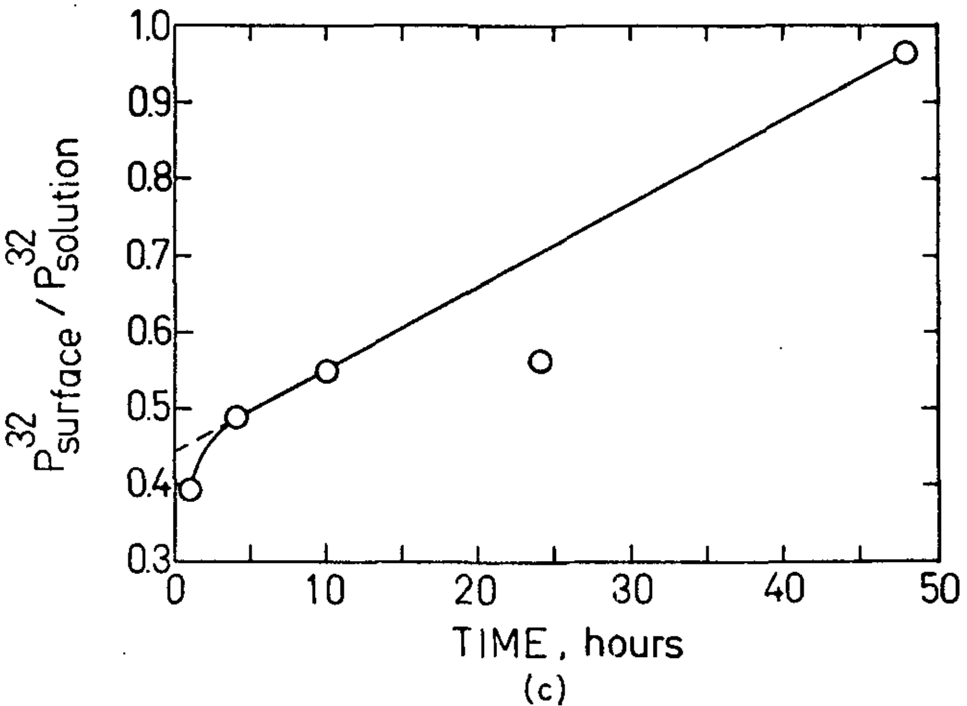


Figure 9, Continued

It is therefore concluded that oxalate extraction can remove large quantities of phosphorus from the surface of sediment particles.

Inorganic Phosphate Adsorption Studies

Inorganic phosphate adsorption capacities of sediments from Lake Warner and Lake Wyola have been studied under different pH, temperature and redox potentials. All adsorption experiments were run to such an extent that equilibrium was reached as close as possible before the final concentrations of phosphate were determined. Two to three replicate samples were used for each experimental condition, but only the averages of the results are plotted in the figures shown in the following sections.

Besides inorganic phosphate (determined as orthophosphate), total phosphorus was also determined for the equilibrated samples. The total phosphorus concentrations were generally very close to the inorganic phosphate concentrations, indicating that, under most conditions, only the inorganic phosphate was involved in the interactions between the added inorganic phosphate and the lake sediment. One possible exception was the case of the equilibrated solutions of the Lake Wyola sediment adsorbing inorganic phosphate at pH 7.0, 20°C and a redox potential of +390 mv. In these solutions, the total phosphorus concentrations were slightly higher than the inorganic phosphate concentrations. This was possibly due to the dissolution of some organic matters (such as humic acids) with part of attached organic phosphorus from the sediment at this pH.

Also analyzed were the total iron concentrations in the equilibrated samples. The significance of this analysis will be discussed later in an appropriate section.

Phosphate Adsorption under High Redox Potential Conditions. Results for the phosphate adsorption studies under high redox potential conditions are shown in Figures 10-19. The equilibrium adsorption data are shown in Appendix C. The redox potentials shown in Figures 10-19 are the averages of several measurements performed at the end of the equilibration period for each adsorption experiment (see tables in Appendix C). The measured potentials were the potentials of the sediment-water mixtures under the laboratory conditions. No attempt was made to control the potentials other than shaking and exposing the sample mixtures to the air for a few minutes, 2-3 times a day to keep them aerobic during the equilibration period. Preliminary tests showed that the redox potential of a sediment-water mixture stayed essentially constant by this approach.

For the potential measurements, the platinum electrodes were immersed in the samples for a period of 1 1/2 hours before potential readings were taken. (Tests showed that at least 1 1/2 hours was required for the potential readings to reach stable values). During the equilibration period, the samples were stirred constantly with magnetic stirring devices to provide a surface renewal of the platinum electrodes.

Although, for all adsorption studies, the samples were handled in essentially the same manner except for the differences in pH and temperatures, the redox potentials are shown to vary with the pH and the temperature of the sample mixtures. The redox potential is higher as pH decreases and as temperature increases. This relationship actually conforms to that predicted from the Nernst equation, although for a mixed potential as measured here, the Nernst equation does not strictly apply.

A. Rate of Phosphate Adsorption. The kinetic data for the removal of phosphate by Lake Warner and Lake Wyola sediments under high redox potential conditions and at different temperature and pH values are shown in Figures 10-13. The rate of removal was generally rapid initially and decreased with reaction time. The initial rate of adsorption increased as pH decreased and as temperature decreased.

The initial rapid removal step might have involved the adsorption of the phosphate in the solution to the sediment surface. The subsequent slower step might have involved a number of concurrent reactions, such as (1) diffusion of some of the phosphate to the interior of the sediment particles (Carrit and Goodgal, 1954), (2) nucleation and growth of new solid phases between the adsorbed phosphate and the minerals in the sediment (Chen et al. 1973; Stumm and Leckie, 1970), and (3) decomposition of the clay minerals in the sediment and reaction of the released iron and aluminum with the phosphate in solution (Haseman et al. 1950). Because of the complexity in composition of these lake sediments, it is very unlikely that only one kind of reaction was involved.

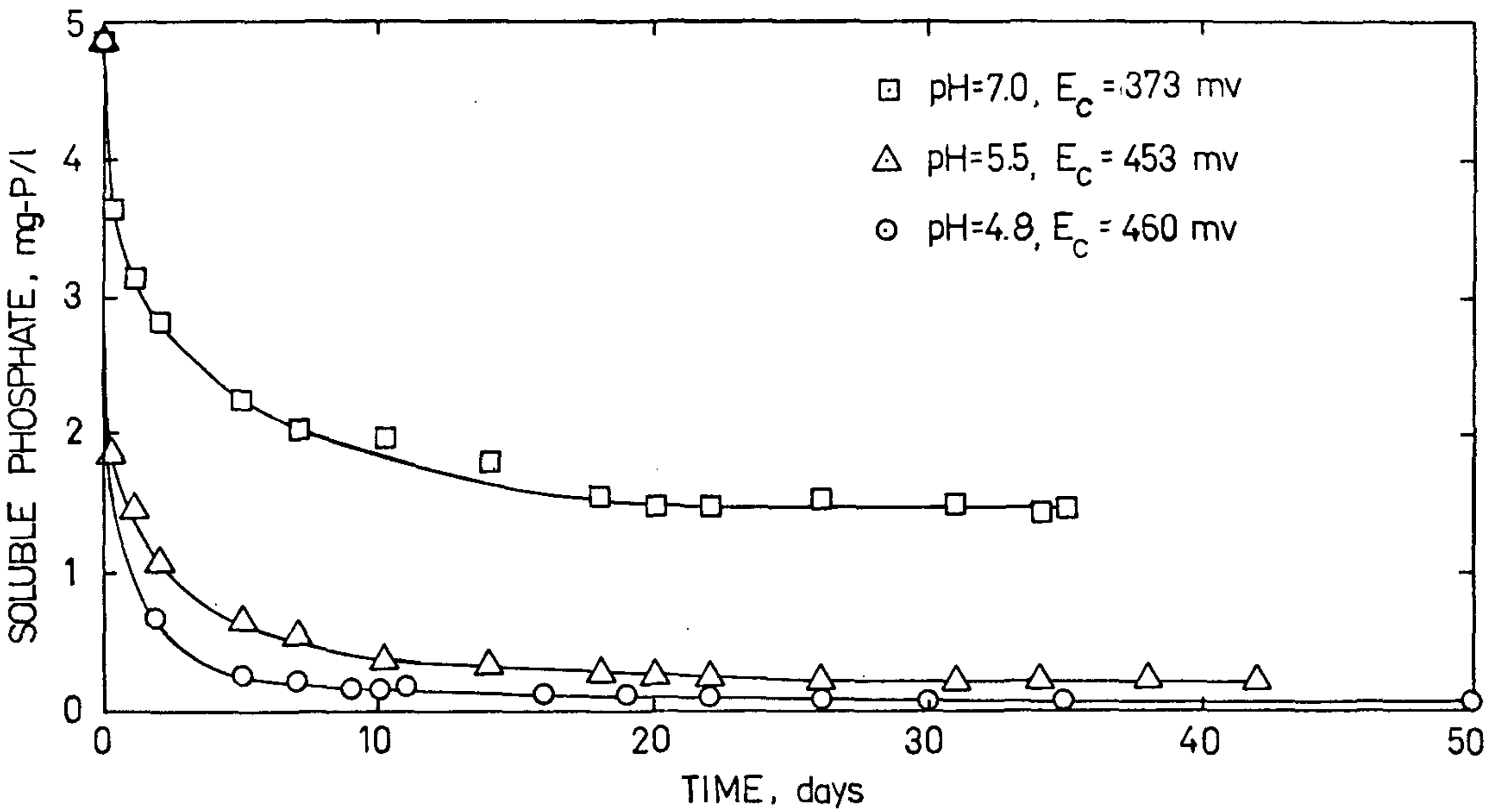


Figure 10. Phosphate Adsorption by Lake Warner Sediment at 20°C.

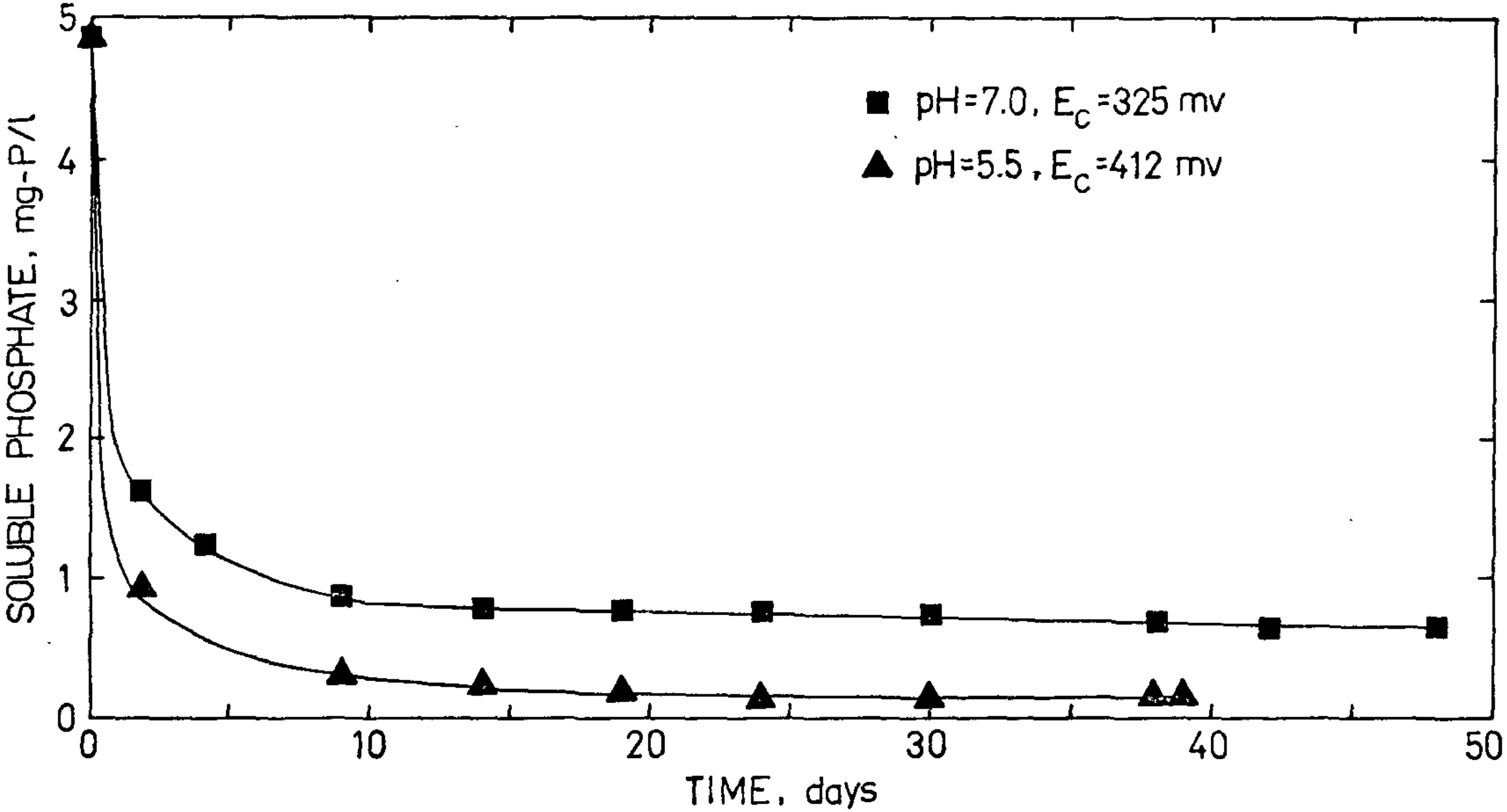


Figure 11. Phosphate Adsorption by Lake Warner Sediment at 11°C.

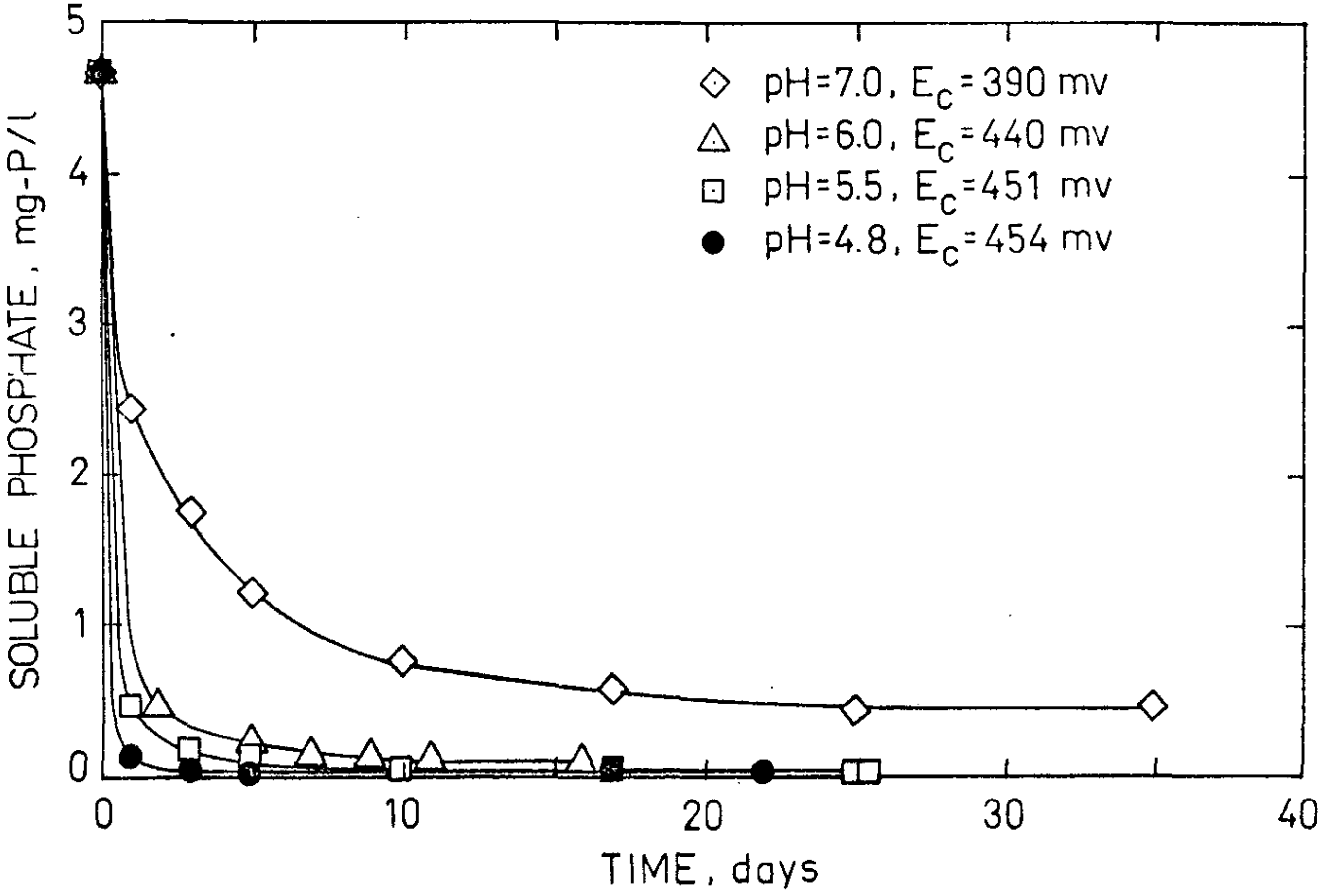


Figure 12. Phosphate Adsorption by Lake Wyola Sediment at 20°C.

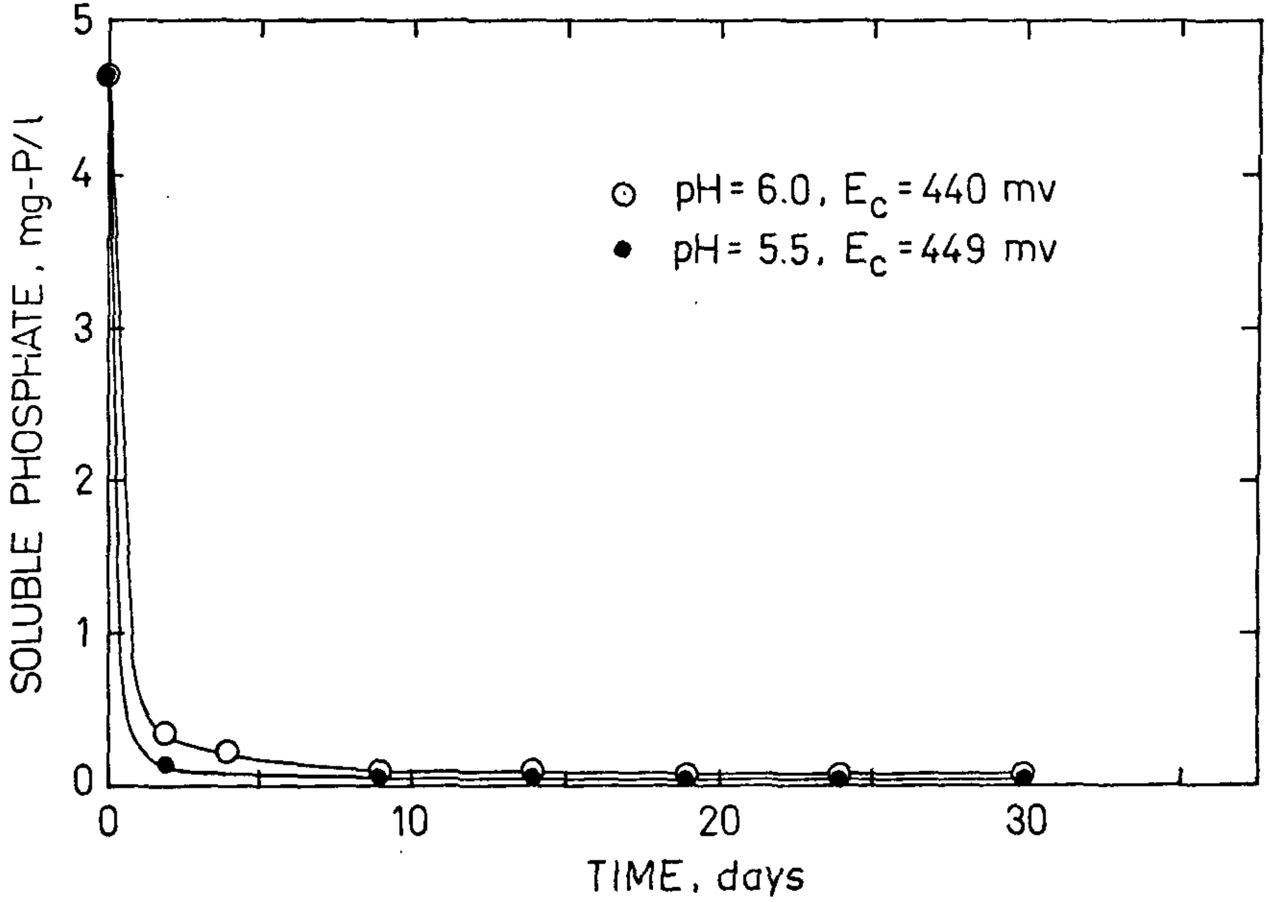


Figure 13. Phosphate Adsorption by Lake Wyola Sediment at 11°C.

B. Effect of pH on Phosphate Adsorption. The amount of phosphate adsorption by the sediments of both lakes is shown to be proportional to the amount of phosphate added initially (Figures 14-17). When the amount of added phosphate was small, a straight-line relationship on log-log plotting was noticed between the phosphate added and phosphate adsorbed. But, as the amount of the added phosphate increased, the curves started to reduce their slopes. This change in slopes of the curves started at a lower amount of added phosphate for solutions at a higher pH. Thus, for example, for Lake Warner sediment at 20°C, at a pH of 4.8, the slope of the straight line relating the added phosphate and the phosphate adsorbed did not change until the phosphate addition was increased to greater than 0.1 μg/g, while at pH 7.0, the change in slope of the straight line occurred at an added phosphate of 0.05 μg/g (Figure 14).

The data also show that the amount of the phosphate adsorbed by both sediments increased with decrease in pH of the sediment solution at all levels of added phosphate. This pH effect seemed to be more pronounced at a higher temperature than at a lower temperature. Generally, for the same amount of added phosphate, the Lake Wyola sediment adsorbed more than the Lake Warner sediment, but the change in pH had a greater effect on the phosphate adsorption capacity for the Lake Warner sediment than for the Lake Wyola sediment.

C. Effect of Temperature on Phosphate Adsorption. Both the Lake Warner and the Lake Wyola sediments showed a greater phosphate

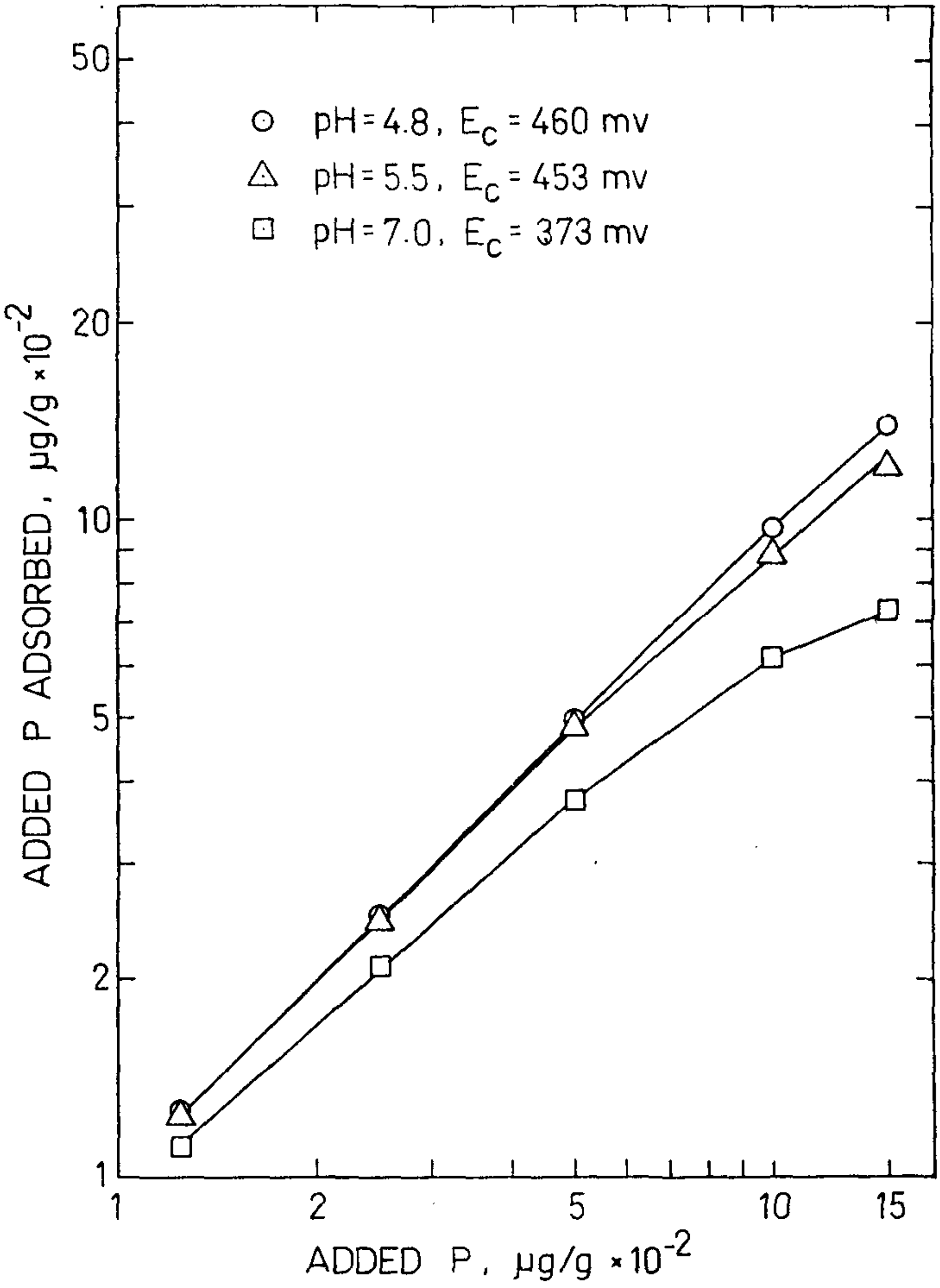


Figure 14. Effect of pH on Phosphate Adsorption by Lake Warner Sediment at 20°C.

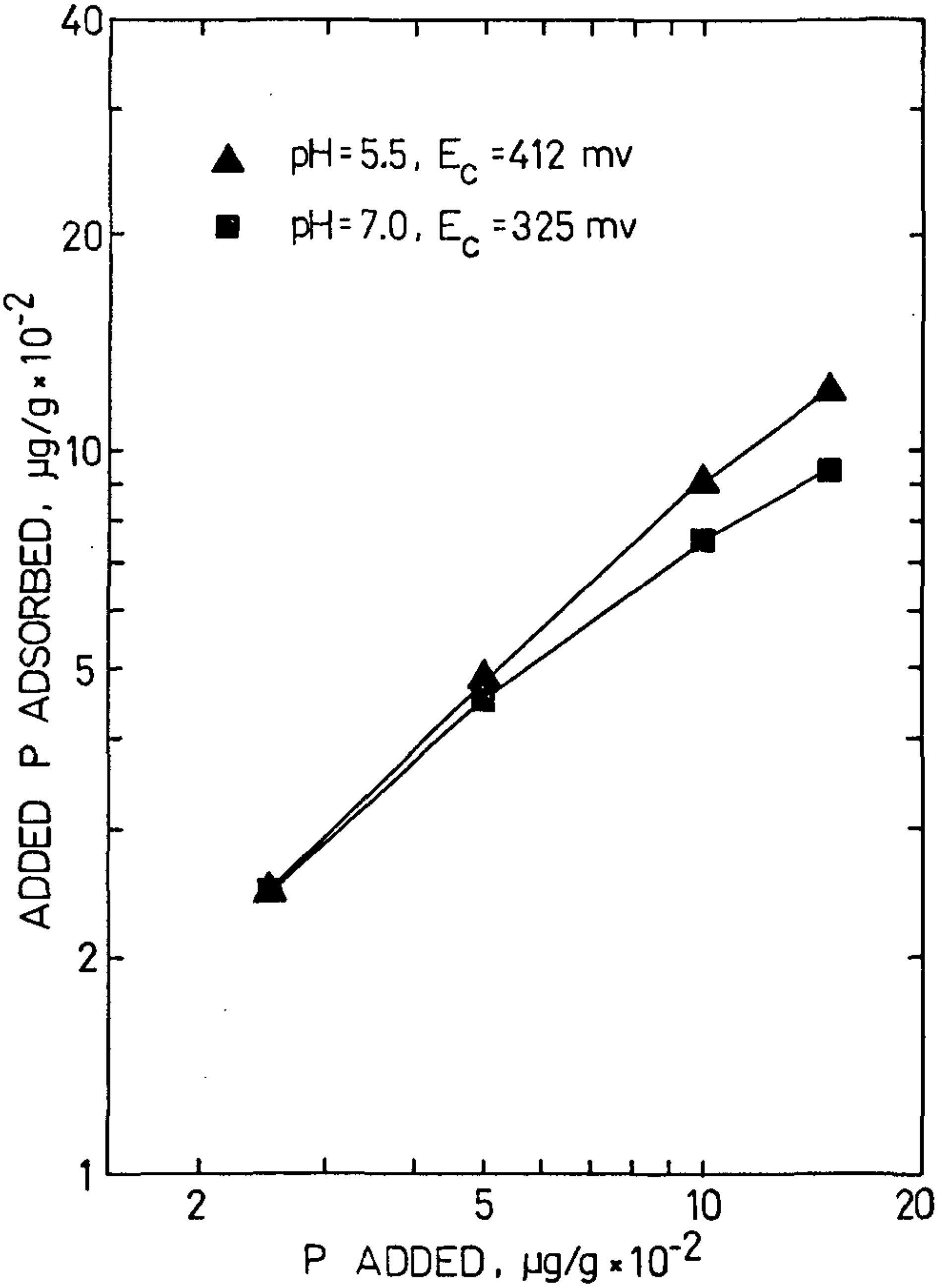


Figure 15. Effect of pH on Phosphate Adsorption by Lake Warner Sediment at 11°C.

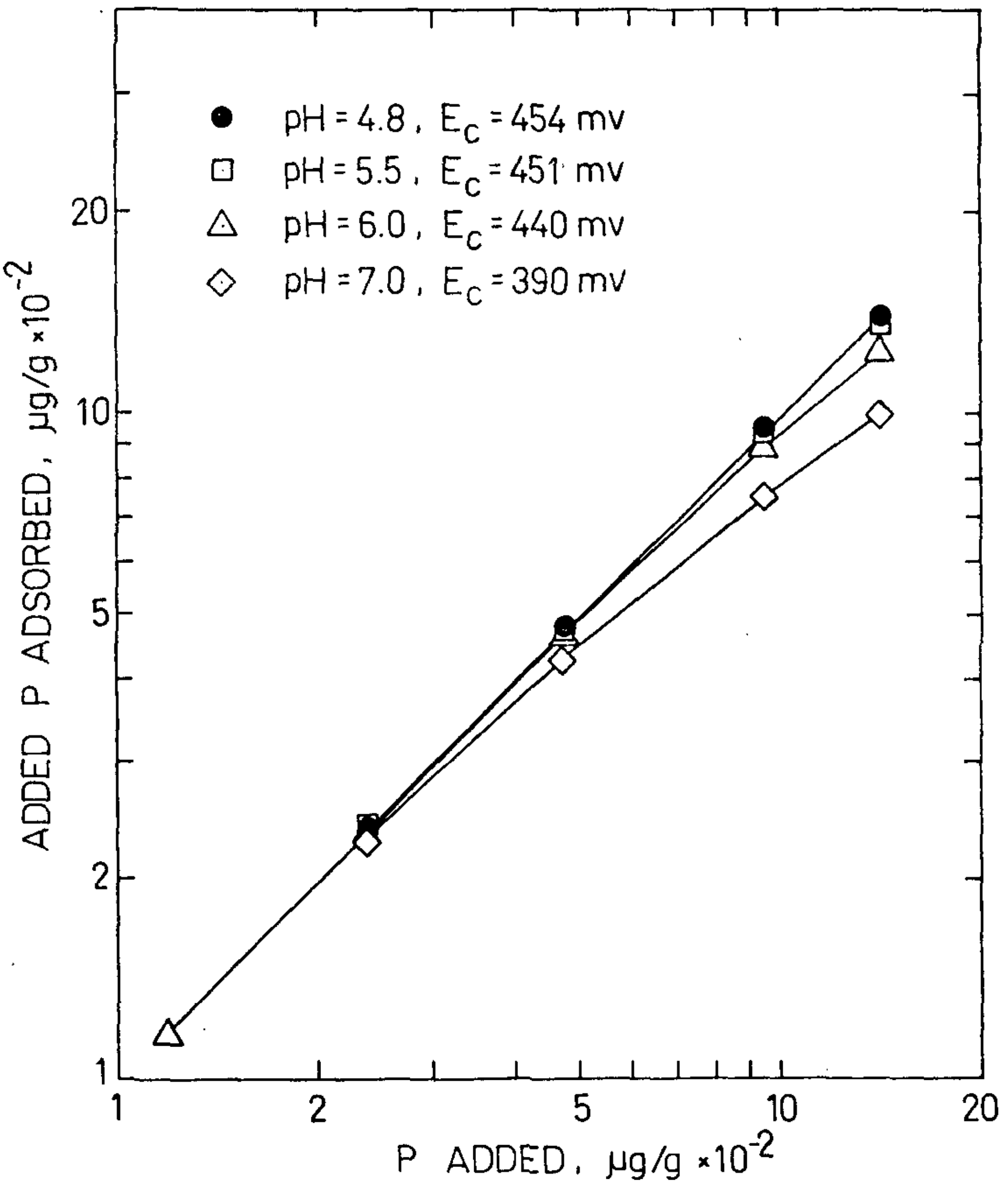


Figure 16. Effect of pH on Phosphate Adsorption by Lake Wyola Sediment at 20°C.

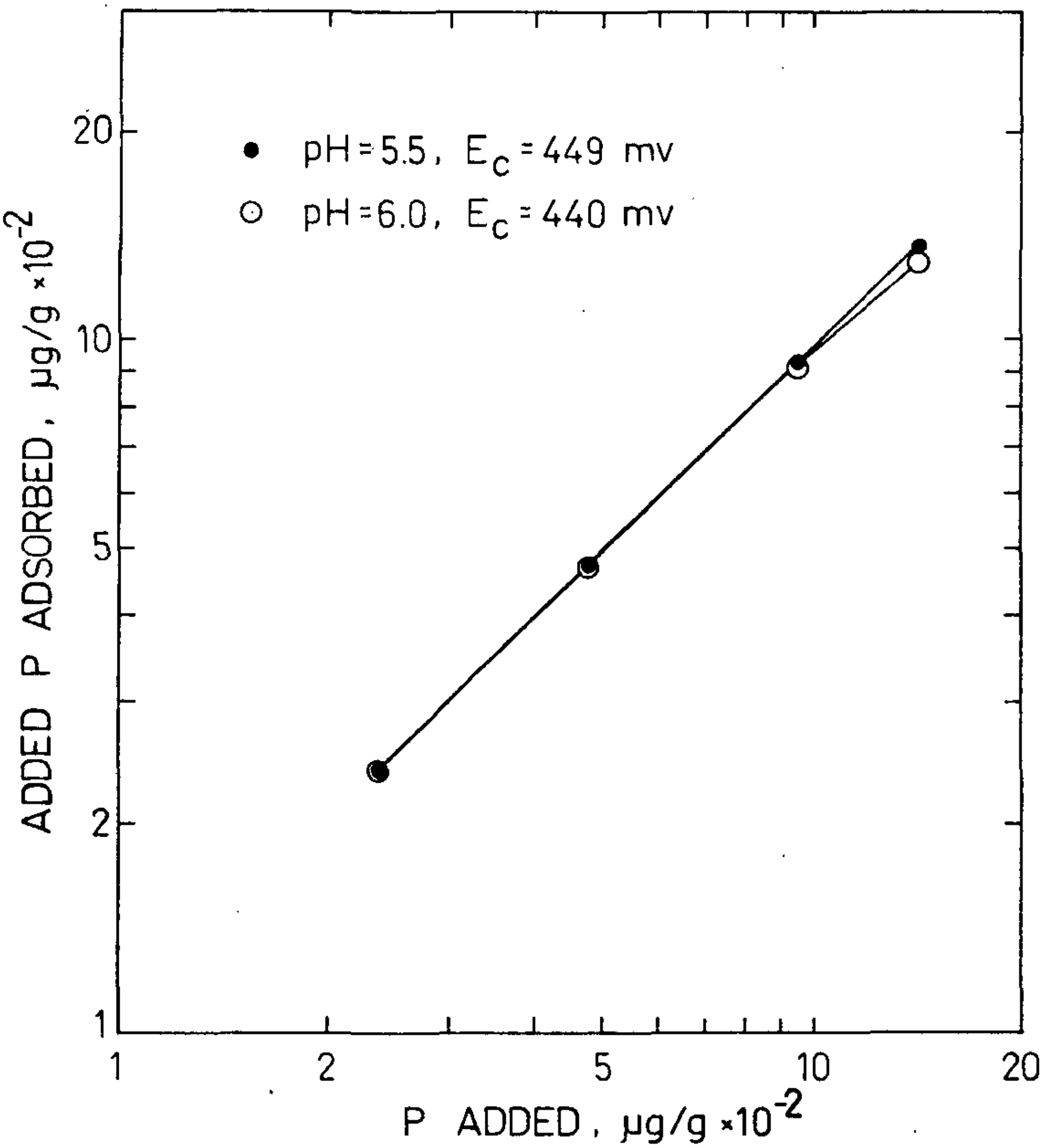


Figure 17. Effect of pH on Phosphate Adsorption by Lake Wyola Sediment at 11°C.

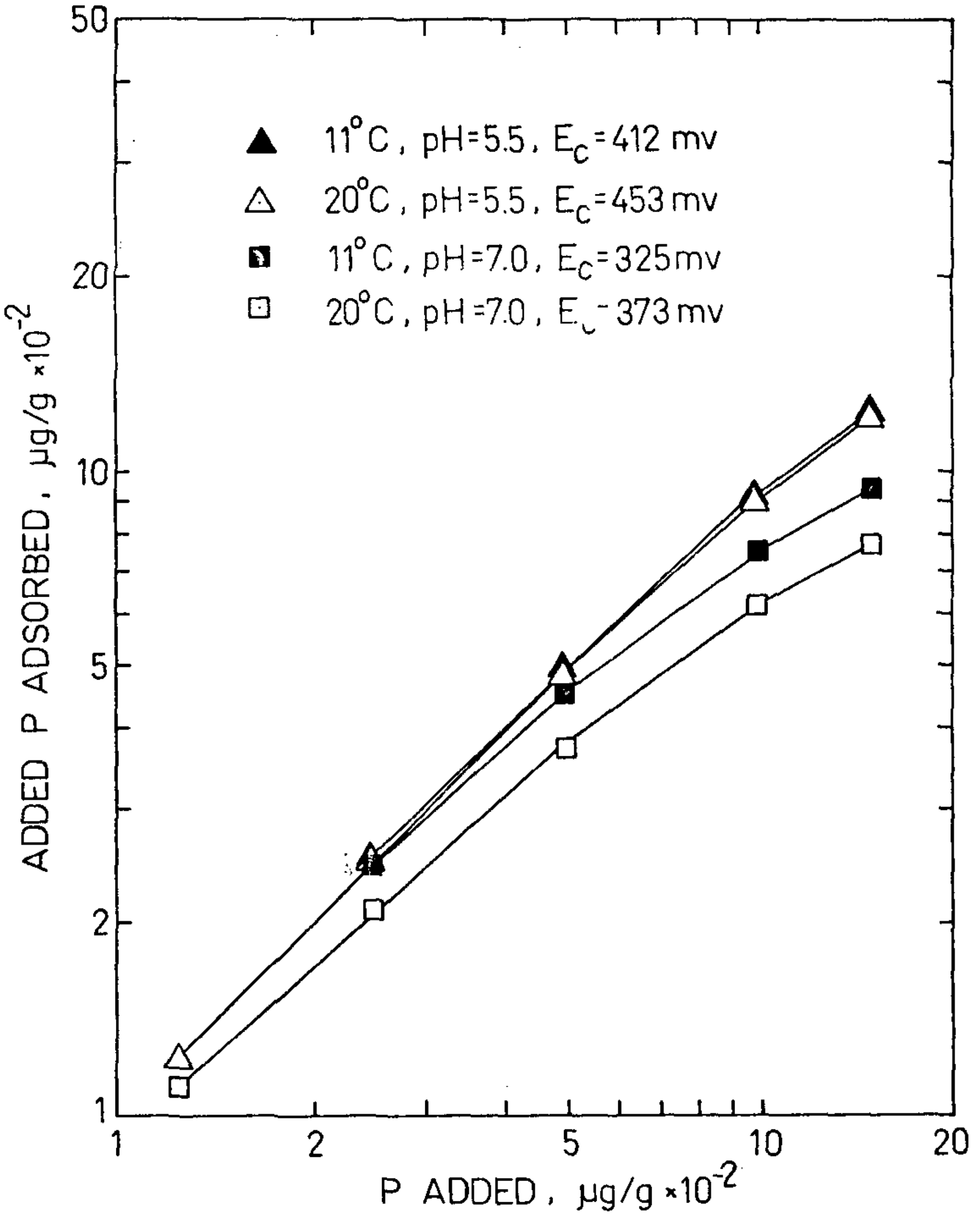


Figure 18. Effect of Temperature on Phosphate Adsorption by Lake Warner Sediment.

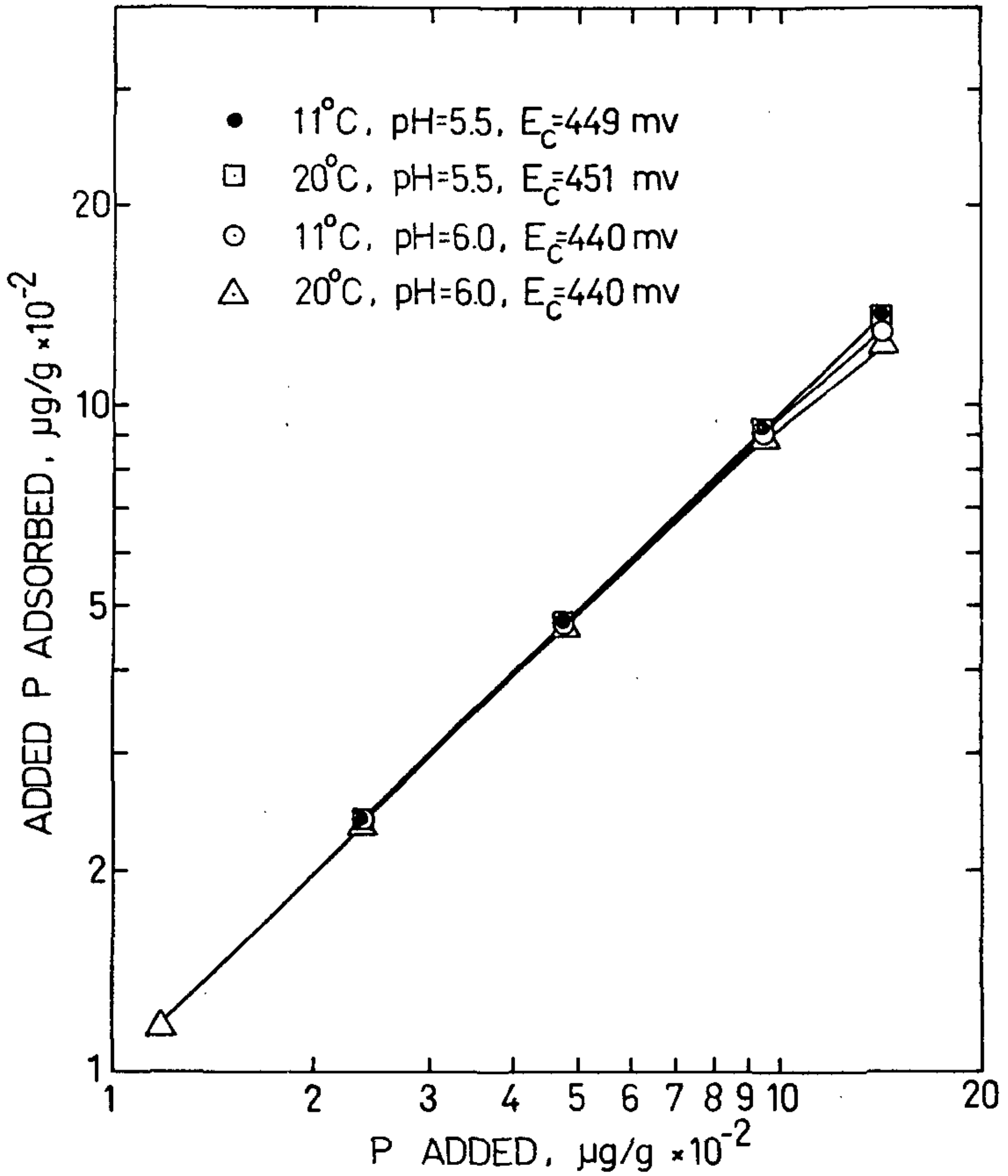


Figure 19. Effect of Temperature on Phosphate Adsorption by Lake Wyola Sediment.

adsorption capacity at a lower temperature than at a higher temperature. The temperature effect was more pronounced for equilibrium solutions at higher pH than at lower pH (Figures 18-19).

Phosphate Adsorption Under Low Redox Potential Conditions. The phosphate adsorption capacities of the Lake Warner and the Lake Wyola sediments under low redox potential conditions were studied at a temperature of 20°C and pH of 4.8. The pH in this case was that existed in the sediment-water mixtures when glucose was added to reduce the redox potential of the mixture. At the beginning of the experiment, the pH of the sediment-water mixtures were 6.7 and 5.8 for the Lake Warner and the Lake Wyola sediments, respectively. The reduced pH was possibly caused by the accumulation of organic acids, H^+ and CO_2 as a result of the decomposition of the added glucose by microorganisms in a closed anaerobic system.

For the Lake Warner sediment, the drop of pH from an initial value of 6.7 to a final stable value of 4.8 occurred within 48 hours after glucose was added to the sediment-water mixture and deaeration with pure nitrogen gas was in order (Table 6). This final pH was noticed to persist for the next 23 days until the experiment was ended. The fact that the pH did not change in the presence of active bacterial metabolism indicated that certain buffer system (or, systems) must have existed in the sediment-water mixture. The nature of the buffer system(s) is not known and warrants further studies. It probably involved the by-products of bacterial decomposition of both the added and the native organic matters. In this regard, the dissolved CO_2

Table 6. Establishment of Phosphate Adsorption Equilibrium for Lake Warner Sediment Under Anaerobic Condition

Experiment	Equilibration Time, hours	pH	E_c, mV	Soluble Ortho-phosphate, ppm-P
Run 1	0	6.7	-	4.81
	24	6.2	-142	0.94
	48	4.8	-210	2.72
	242	4.8	-221	3.23
	264	4.8	-198	3.23
	288	4.8	-210	3.16
	336	4.8	-259	3.04
	384	4.8	-260	3.28
	480	4.8	-200	2.72
	600	4.8	-264	3.00
Run 2	0	6.7	-	4.81
	308	4.8	-240	3.25
	332	4.8	-240	2.82
	356	4.8	-245	3.03
	374	4.8	-244	2.67

gas and the organic acids and their conjugate bases were the most probable influencing factors. Because of this buffering capacity, a pH of 4.8 is possibly the lowest pH which the surface layer of the Lake Warner sediment can reach. It is interesting to note that the final pH of the Lake Wyola sediment-water mixture was also 4.8 (Table 7). A similar buffer system (or systems) could have also existed in this sediment under anaerobic conditions. In the literature, the stability of pH was also shown to exist in the pore waters of marine sediments. Ben-Yaakov (1973) proposed that the pH of the pore waters of recent anoxic marine sediments was controlled by the by-products of organic decomposition, sulfate reduction, precipitation of sulfides and calcium carbonate.

A. Establishment of Phosphate Adsorption Equilibrium. During the equilibrium phosphate adsorption studies, parallel sets of samples were run to determine the time required for the adsorption to reach equilibrium. The results are shown in Tables 6 and 7 and in Figures 20 and 21. Data points in these tables and figures were the analytical results of the sample mixtures in separate containers. Separate containers had to be used for these experiments because tests showed that if a single container was used, sample withdrawal would introduce sufficient air to upset the whole system sealed in the container. That is, the redox potential would rise gradually after one sample withdrawal and would not return to its original value for a long period of time, or never would.

Table 7. Establishment of Phosphate Adsorption Equilibrium for Lake Wyola Sediment Under Anaerobic Condition

Equilibration Time, hours	pH	E_c, mv	Soluble Ortho-phosphate, ppm-P
0	5.8	-	4.61
600	4.8	-220	0.180
624	4.8	-230	0.166
672	4.8	-180	0.130
720	4.8	-178	0.142
768	4.8	-130	0.150
816	4.8	-110	0.144
887	4.8	-192	0.141

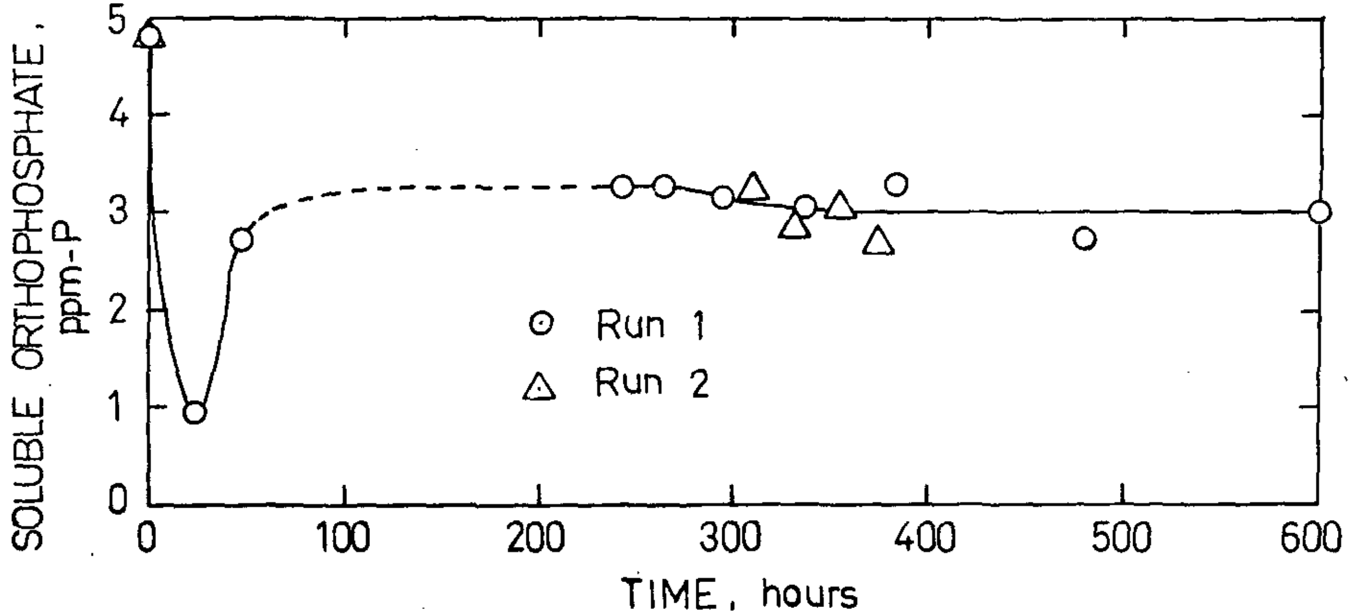


Figure 20. Establishment of Phosphate Adsorption Equilibrium for Lake Warner Sediment under Anaerobic Condition.

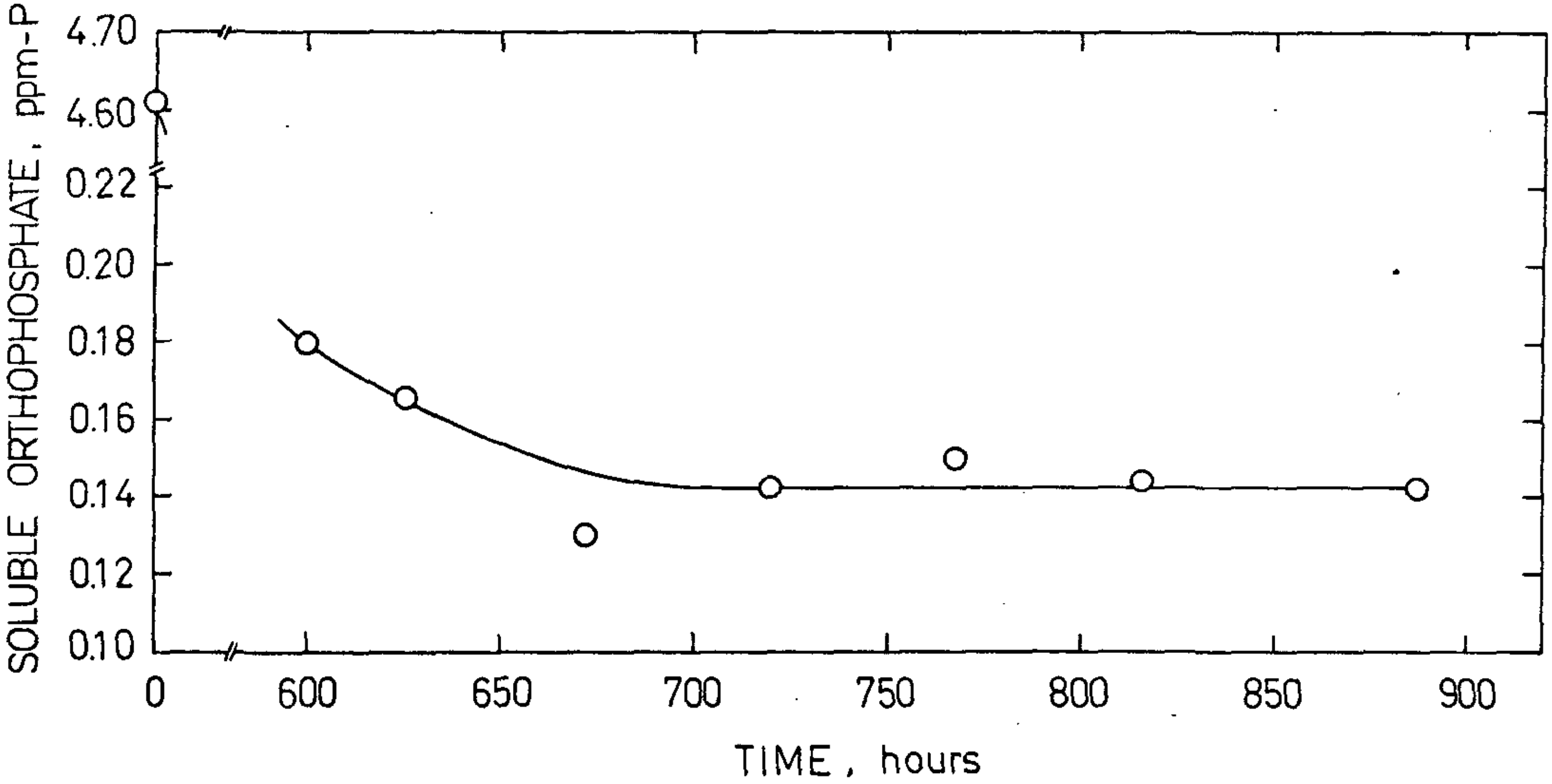


Figure 21. Establishment of Phosphate Adsorption Equilibrium for Lake Wyola Sediment under Anaerobic Condition.

For the Lake Warner sediments, the initial phosphate concentration in the mixtures was 4.81 ppm-P. After 24 hours of equilibration, the phosphate concentration in solution was 0.94 ppm-P, while after 48 hours of equilibration, the phosphate concentration increased to 2.72 ppm-P. At the 24th hour, the redox potential was -142 mv, but at the 48th hour, it dropped to -210 mv. This indicates that there was an initial rapid uptake of the added phosphate when the redox potentials of the mixtures were still high. But, with time, the redox potentials dropped and the initially adsorbed phosphate released back to solution. The release of phosphate might have continued after 48 hours, then finally it came to a stable level and an equilibrium was gradually reached. From Figure 20, it seemed that a period of at least 350 hours was required for reaching the equilibrium. To determine whether the results were reproducible, two experimental runs were started on separate dates. The results (Run 1 and Run 2 in Table 6 and Figure 20) showed that they could be reproduced.

For the Lake Wyola sediment, the data in Table 7 and Figure 21 indicated that the equilibrium could be reached after about 700 hours of equilibration.

B. Equilibrium Adsorption Studies. Triplicate samples were run for the phosphate equilibrium adsorption studies under low redox potential conditions. The redox potential in each sample was followed closely with time to detect any changes. Figures 22 and 23 show the changes of redox potentials with time for the Lake Warner and Lake Wyola sediments, respectivel The fluctuations of the redox potentials seemed to follow the same pattern for both sediment samples. Following the addition of glucose

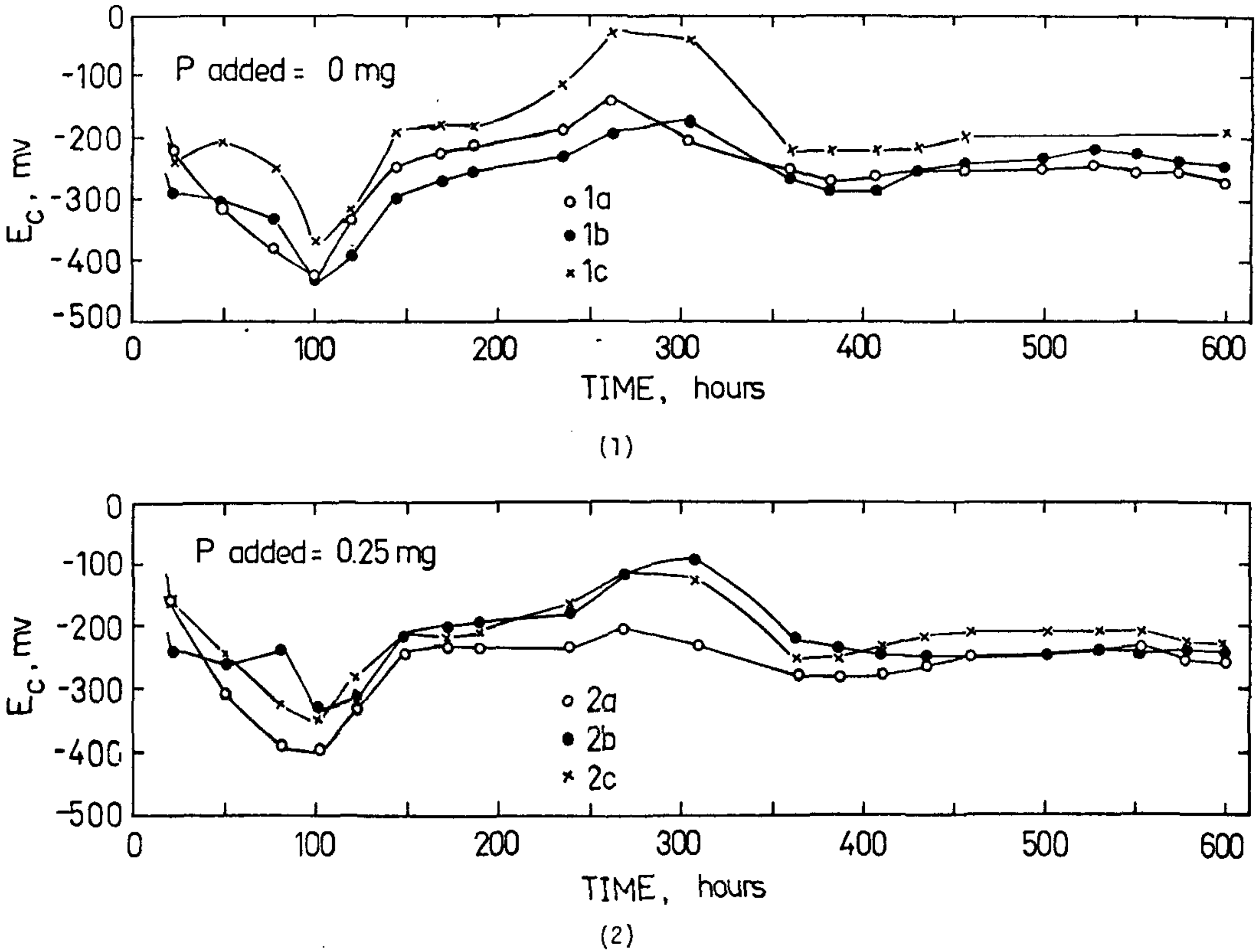
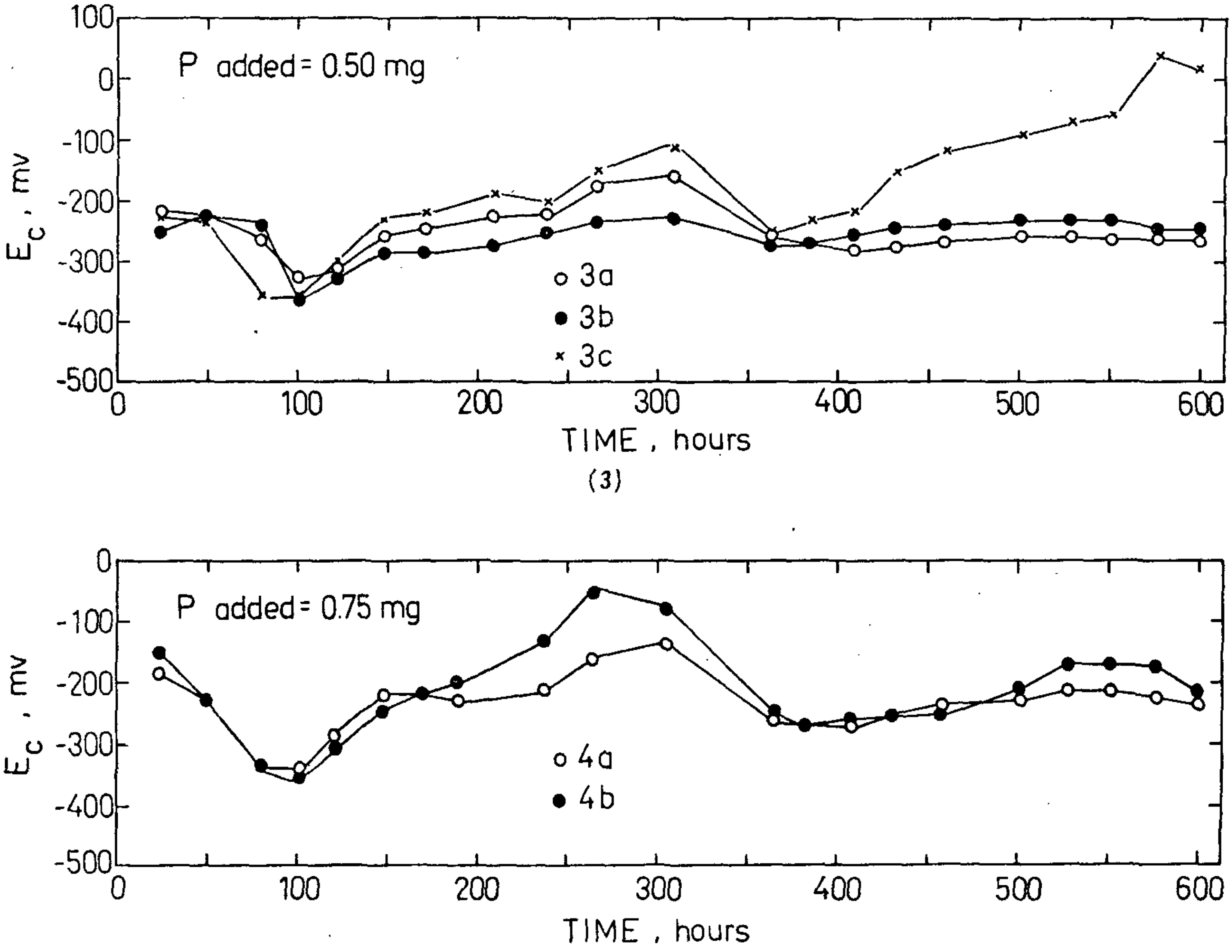


Figure 22. Change of Redox Potential with Time for Lake Warner Sediment under Anaerobic Condition.



(3)

(4)

Fiaure 22, continued

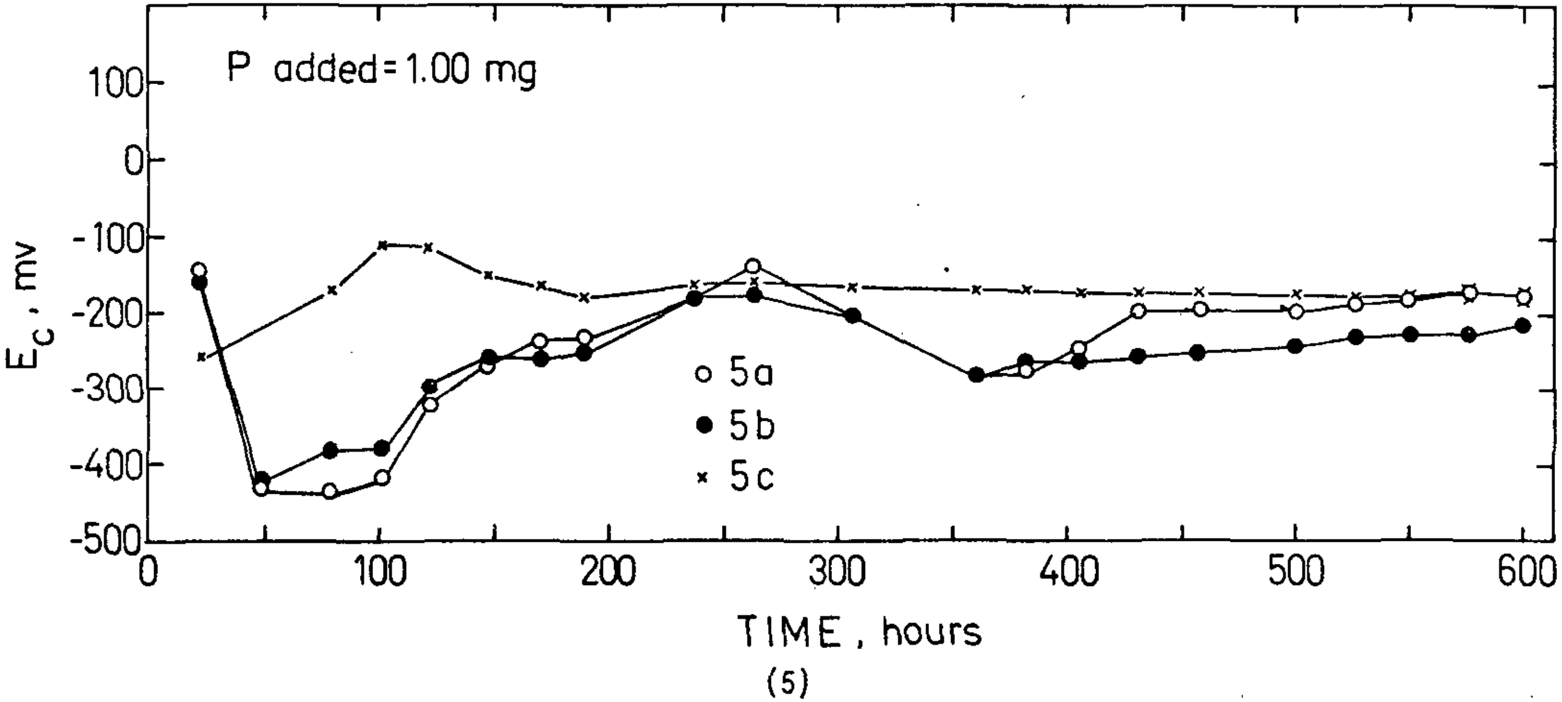
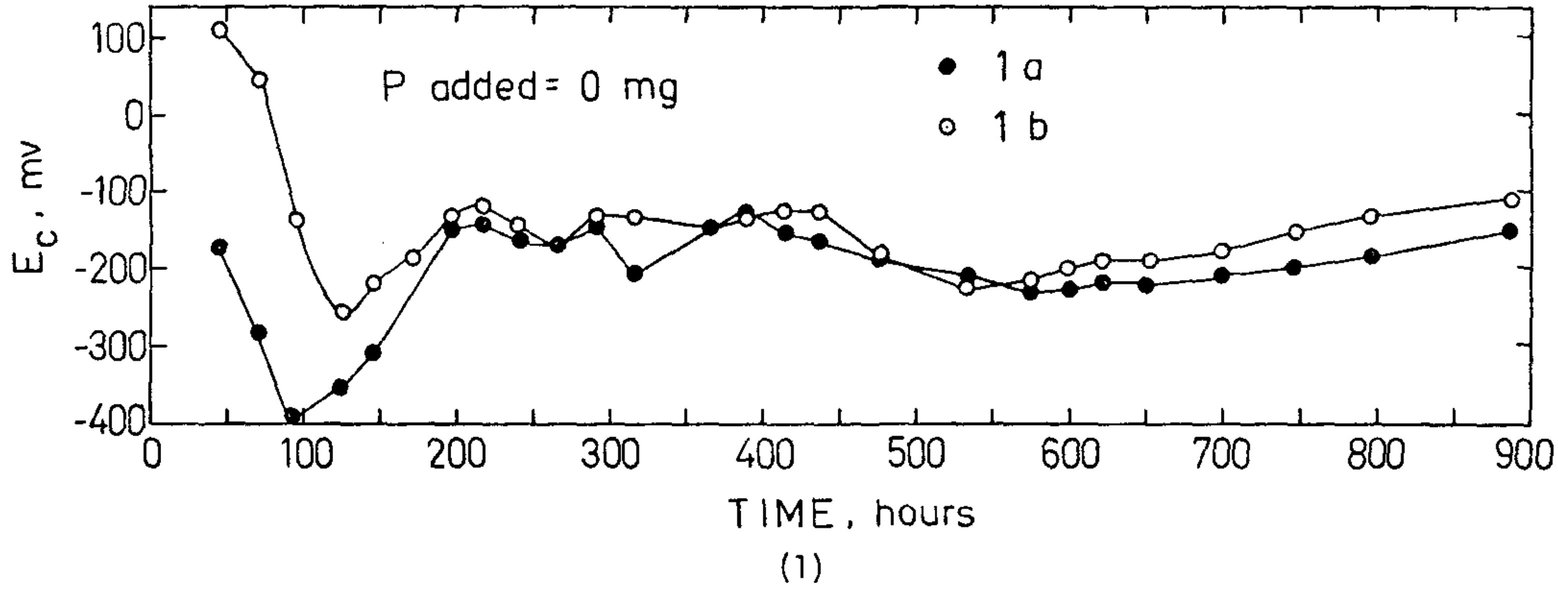


Figure 22, continued



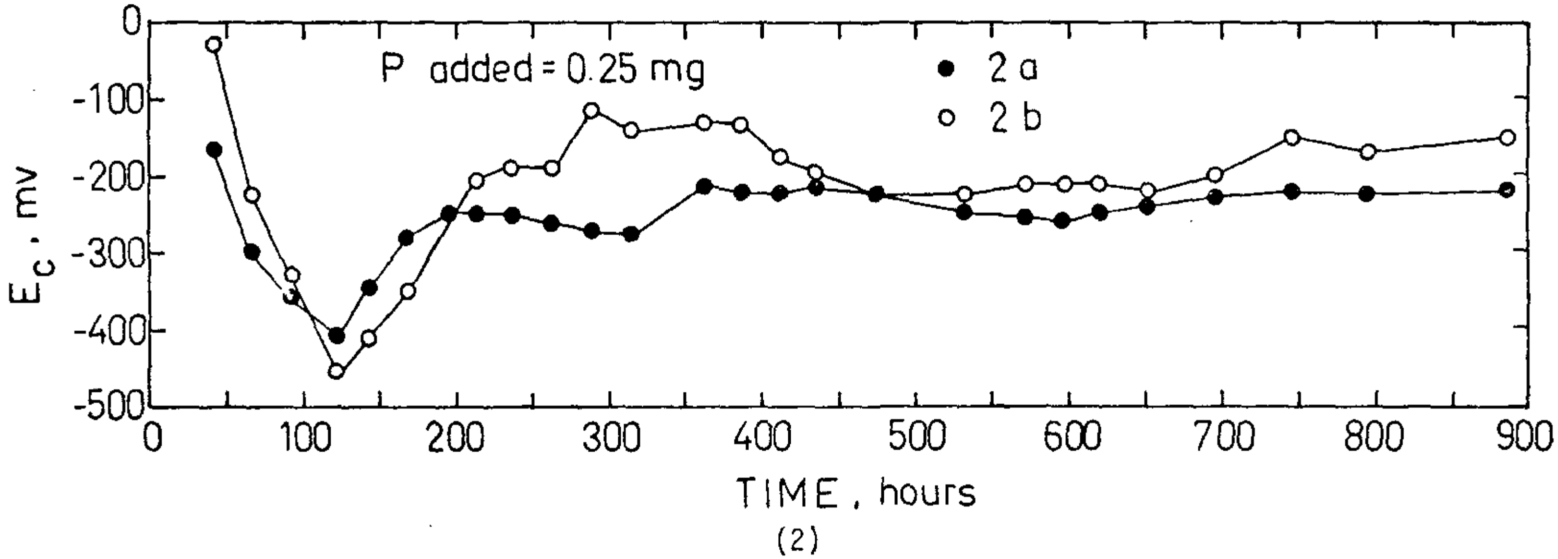
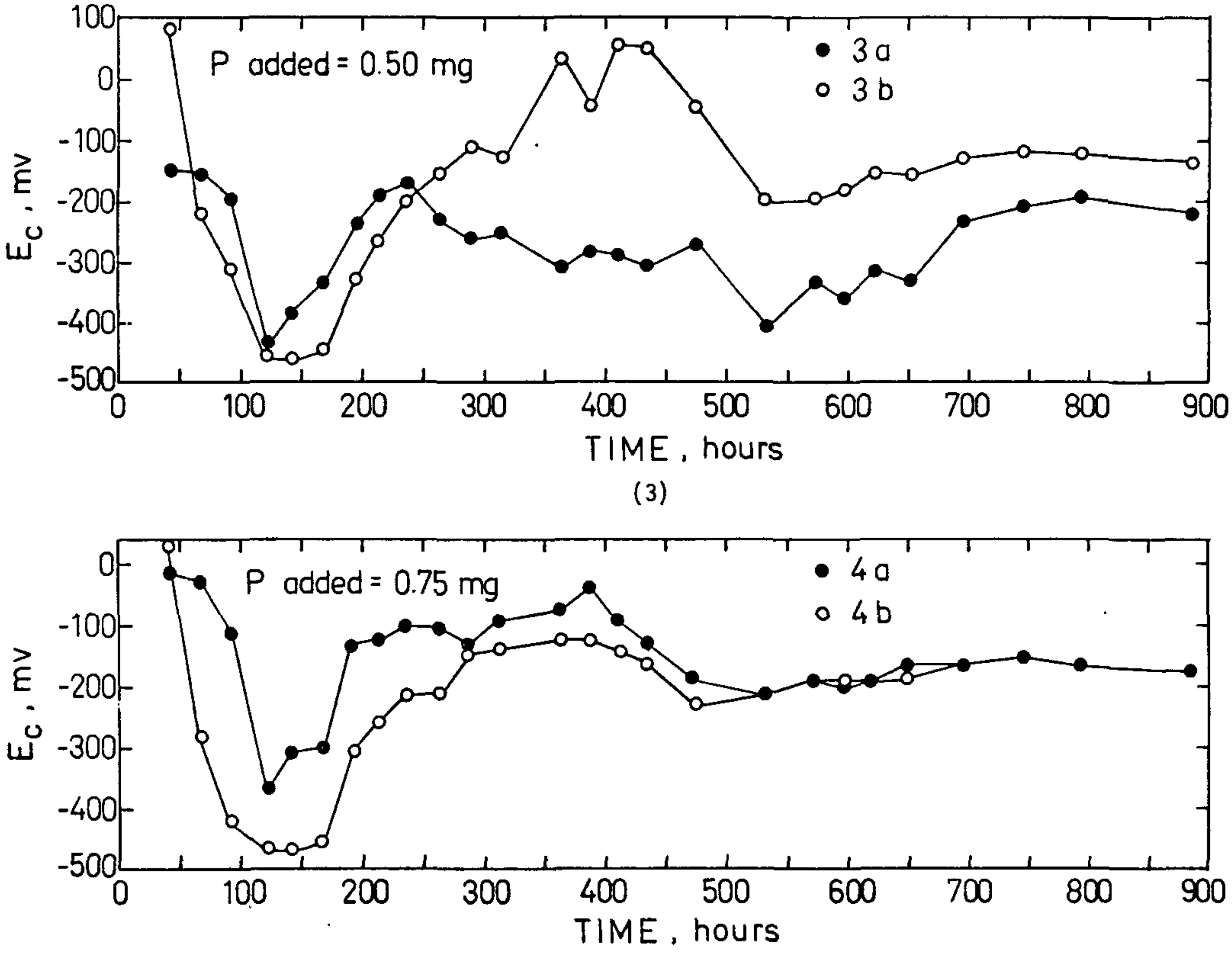


Figure 23. Change of Redox Potential with Time for Lake Wyola Sediment under Anaerobic Condition.



(3)

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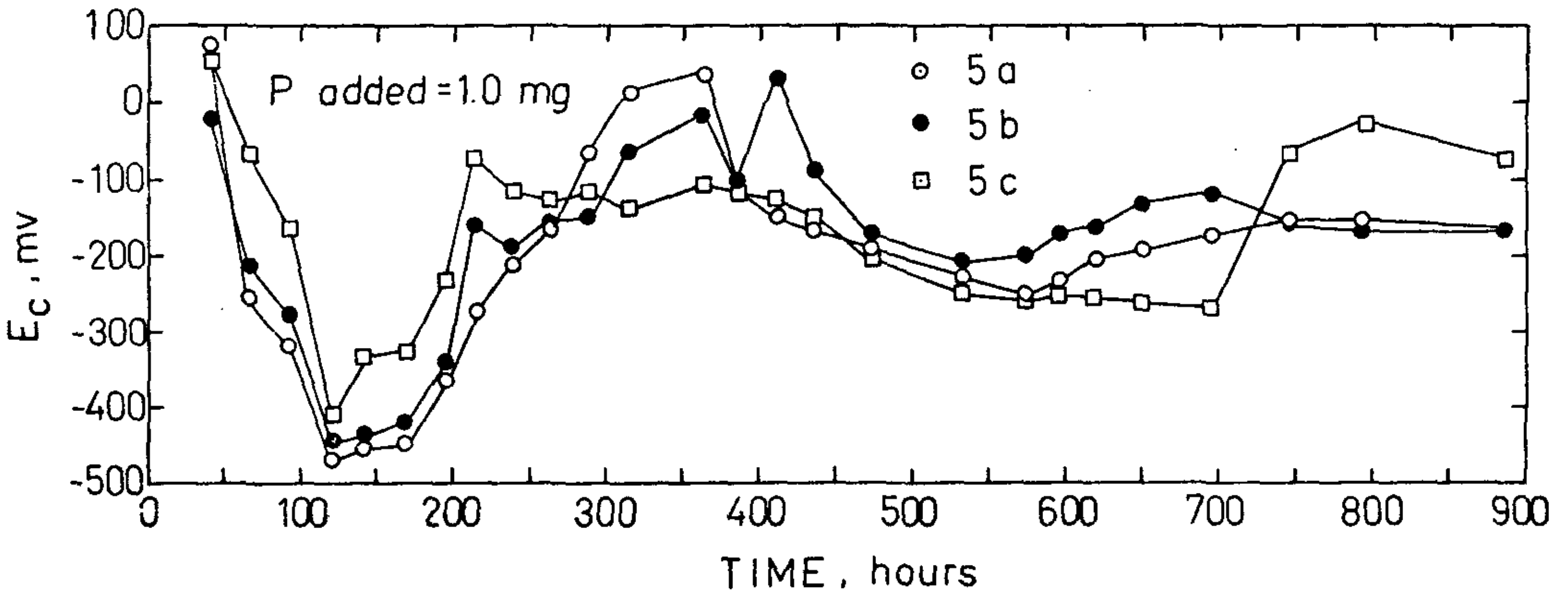
Figure 23, continued



(5)

Figure 23, continued.

and the deaeration with nitrogen gas, the redox potentials dropped quickly. Once reached the lowest point, in four and five days for the Lake Warner and Lake Wyola sediments, respectively, the redox potentials started to rise up again. The potentials fluctuated in the next ten days or so, until finally they reached more or less stable values.

The reduction of the redox potentials in these samples was induced by the microorganisms native to the sediments. The added glucose served as an energy source for the microorganisms. Being a reducing agent, glucose, upon its decomposition, released free electrons to reduce the oxidants in the sediments:

$$C_6H_{12}O_6 + 6\ H_2O \rightarrow 6\ CO_2(g) + 24\ H^+ + 24\ e^- \qquad (19)$$

This caused a rapid decrease in the redox potential of the sediment-water mixture. Once the added glucose was depleted, however, the microorganisms underwent endogeneous respiration and started to die off. Meanwhile, the oxidants that might have existed in the interior of the sediment particles were released to the exterior and raised the redox potentials to higher values. After a long period of adjustment, the systems finally settled for stable redox potential values.

An inspection of the E_c vs. time curves show that the fluctuation of the redox potential was smaller for the Lake Warner sediment than for the Lake Wyola sediment. This might indicate that the Lake Warner sediment was better poised than the Lake Wyola sediment.

As discussed in the previous section, the adsorption of added phosphate under low redox potentials could reach equilibrium in about

350 hours and 700 hours for the Lake Warner and Lake Wyola sediments, respectively. The curves in Figures 22 and 23 showed that the redox potentials also reached stable values in about 350 hours and 700 hours for these two sediments, respectively. Apparently, these latter observations confirm the former findings about the adsorption equilibrium, as shown in Figures 20 and 21.

Tables 8 and 9 are the summaries of the results for the equilibrium adsorption studies. The equilibration periods were 600 hours and 887 hours for the Lake Warner and Lake Wyola sediments, respectively. At the beginning of the experiments, triplicate samples were prepared. During the experiment, however, the salt bridges of some of the samples for the Lake Wyola sediment broke. As a result, the redox potential in these samples could not be measured. Therefore, these samples were discarded. The redox potential values (E_c) in these tables are the final redox potentials in the samples.

For each sediment and for the same amount of phosphate added initially, the equilibrium concentration of the soluble orthophosphate varied. This was probably due to the inhomogeneity of the sediment samples used for the adsorption studies and to the analytical errors. The difference in equilibrium phosphate concentrations seems to relate to the difference in redox potentials. Generally, the equilibrium phosphate concentration was higher corresponding to a lower redox potential. The data also showed that the Lake Warner sediment was more redox potential sensitive than the Lake Wyola sediment. For example, in samples with no phosphate added initially, both sediments released phosphorus to the solution under anaerobic conditions.

Table 8. Results for Equilibrium Adsorption of Inorganic Phosphate by Lake Warner Sediment Under Anaerobic Condition at 20^{o}C and pH 4.8

		Concentration in Final Solution			
Sample Number	Phosphate Added, mg-P	Soluble Ortho-phosphate, ppm-P	Soluble Total Phosphorus, ppm-P	Soluble Total Iron ppm-Fe	E_c, mv
1a	0	0.925	0.985	49.8	-274
1b	0	0.915	0.950	51.3	-245
1c	0	0.825	0.870	42.8	-195
2a	0.25	1.86	1.92	51.3	-260
2b	0.25	1.78	1.85	49.8	-250
2c	0.25	1.60	1.67	46.3	-230
3a	0.50	2.86	3.04	49.8	-269
3b	0.50	2.75	2.78	49.8	-244
3c	0.50	1.17	1.20	35.0	+8
4a	0.75	3.86	4.00	48.8	-233
4b	0.75	3.82	3.66	46.8	-216
4c	0.75	3.22	3.18	39.8	-
5a	1.00	5.26	5.22	44.3	-217
5b	1.00	5.26	5.42	44.8	-178
5c	1.00	4.46	4.54	43.0	-175

Table 9. Results for Equilibrium Adsorption of Inorganic Phosphate by Lake Wyola Sediment Under Anaerobic Condition at 20°C and pH 4.8

		Concentration in Final Solution			
Sample Number	Phosphate Added, mg-P	Soluble Ortho-phosphate, ppm-P	Soluble Total Phosphorus, ppm-P	Soluble Total Iron ppm-Fe	E_c, mv
1a	0	0.018	0.027	37.0	-150
1b	0	0.018	0.027	35.0	-110
2a	0.25	0.063	0.068	35.0	-220
2b	0.25	0.055	0.055	35.3	-150
3a	0.50	0.141	0.141	35.0	-220
3b	0.50	0.150	0.185	30.5	-138
4a	0.75	0.295	0.280	33.5	-180
4b	0.75	0.315	0.337	32.0	-178
5a	1.00	0.566	0.560	34.8	-167
5b	1.00	0.560	0.560	30.5	-165
5c	1.00	0.450	0.430	27.0	-75

For the Lake Warner sediment, an increase of redox potential from -274 to -245 mv, or an increase of 29 mv, caused a corresponding decrease of the equilibrium phosphate concentration from 0.925 to 0.915 ppm, or a decrease of 0.010 ppm. However, for the Lake Wyola sediment, an increase of the redox potential from -150 to -110 mv, or an increase of 40 mv, caused no change in the equilibrium phosphate concentration.

The concentrationsof the total phosphorus were very close to the concentrations of the orthophosphate for all samples. The total iron concentrations in the equilibrated solutions were high for both sediments, indicating that large quantities of iron were reduced and released to the solutions under the anaerobic conditions. The average amount of the iron released from the Lake Warner sediment was 5.04 mg/g which amounted to 13.5 percent of the total iron in one gram of that sediment. The average amount of the iron released from the Lake Wyola sediment was 3.67 mg/g which amounted to 25 percent of the total iron in one gram of the sediment. The amount of the iron released to solution was also related to the redox potential level in the solution: high iron concentrations corresponded to low redox potentials.

C. Effect of Redox Potential on Phosphate Adsorption. The average values of the data shown in Tables 8 and 9 are plotted in Figures 24 and 25, respectively, in a logarithmic scale. For the Lake Warner sediment, only the data points which have final redox potentials between -216 and -274 mv are selected for this plot. For the Lake Wyola sediment, the data points used for the plot have redox potential values in the range from -110 to -220 mv. For comparison, the curves shown in Figures 14 and 16 for adsorption studies under high redox potential conditions at 20°C and pH 4.8 are also shown in Figures 24 and 25.

In the logarithmic plotting, the amount of the P added is shown to relate to the adsorbed amount of the added P by a straight line. Comparison of the two curves in each figure shows that for both sediments, the amount of added phosphorus adsorbed was lower under low redox potential conditions. Redox potential seemingly had a greater effect on the Lake Warner sediment than on the Lake Wyola sediment.

Adsorption Isotherms. The equilibrium adsorption data discussed in the previous sections can be described by the Langmuir isotherms. The Langmuir equation (Adamson, 1960) has the form

$$\frac{C}{x/m} = \frac{1}{kb} + \frac{1}{b}\ C \qquad (20)$$

where C = the equilibrium concentration of phosphate, mg-P/1

x/m = the amount of phosphate adsorbed per unit weight of sediment, mg/g

b = adsorption maximum, mg/g

k = energy constant, $(\text{mg}/1)^{-1}$

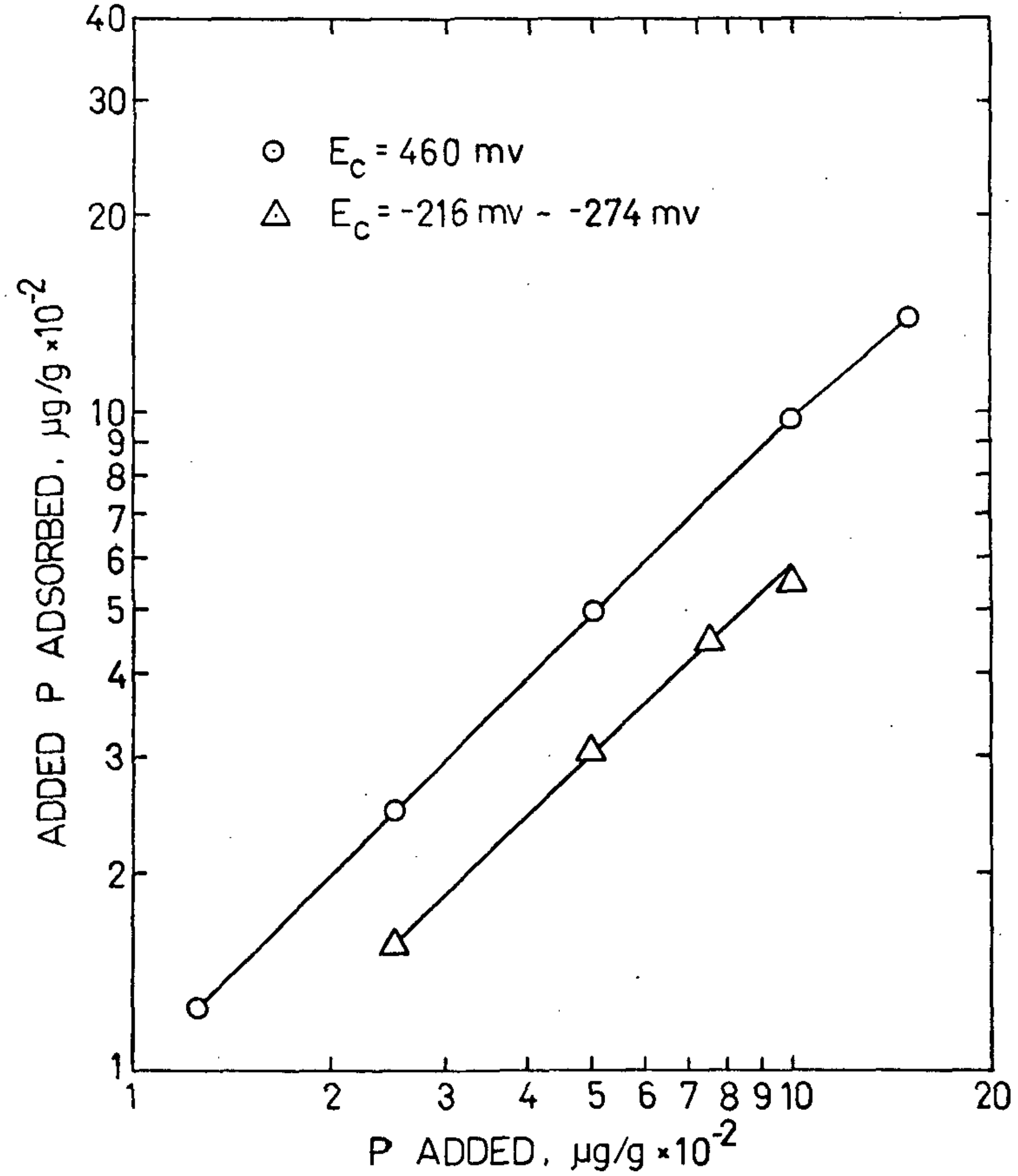


Figure 24. Effect of Redox Potential on Phosphate Adsorption by Lake Warner Sediment at 20°C and pH 4.8.

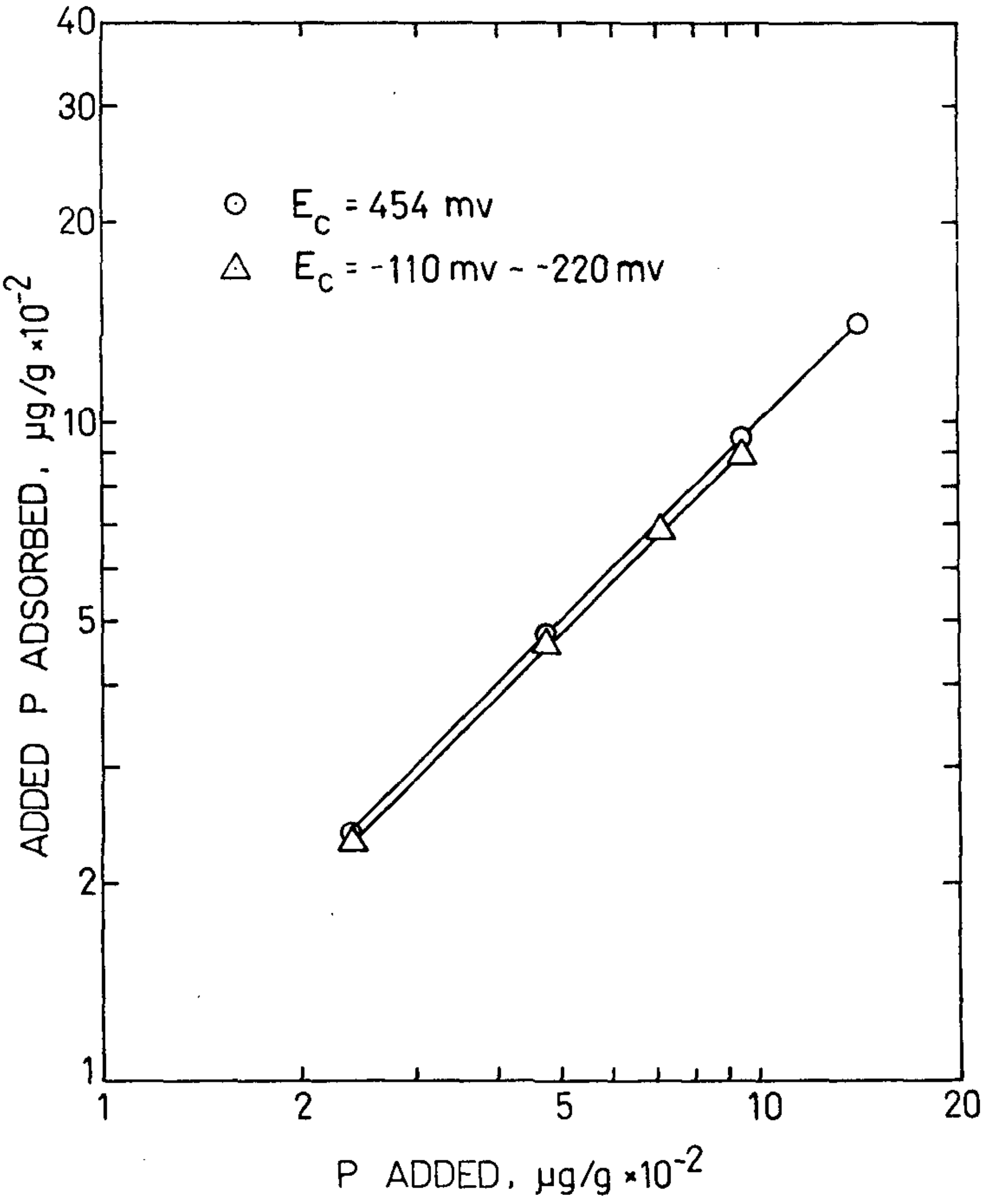


Figure 25. Effect of Redox Potential on Phosphate Adsorption by Lake Wyola Sediment at 20°C and pH 4.8.

The Langmuir plots are shown in Figures 26-38. The plots in these figures have been corrected for the surface phosphorus and the phosphorus in the interstitial water of the sediments. This correction was made by adding the value of ($P^{31}_{surface} + P^{31}_{solution}$) for each sediment, shown in Table 4, to the amounts of phosphorus adsorbed by the same sediment in the equilibrium adsorption experiments. The resulted x/m values were then used for the calculation of C/x/m. The data points shown by the symbol (x) in Figures 34-38 are the points that were not used for the calculation of adsorption maximums. These points correspond to the equilibrium phosphorus concentrations that were too low to be accurately measured by the analytical method used. The straight lines shown in these figures are the lines of best fit determined using the least square method. The slopes and the intercepts of these lines were used to calculate the adsorption maximums and the energy constants according to Equation (20).

The adsorption maximums and the energy constants have been calculated and are listed in Table 10. The adsorption maximums and the energy constants which have not been corrected for surface phosphorus and phosphorus in the interstitial water are also calculated and listed in Table 10 for comparison.

Since the amount of surface phosphorus was small in the Lake Wyola sediment, the surface phosphorus correction does not change the values of the adsorption maximums significantly. For the Lake Warner sediment, however, the values for the corrected and the uncorrected adsorption maximums differ appreciably. Generally, the adsorption

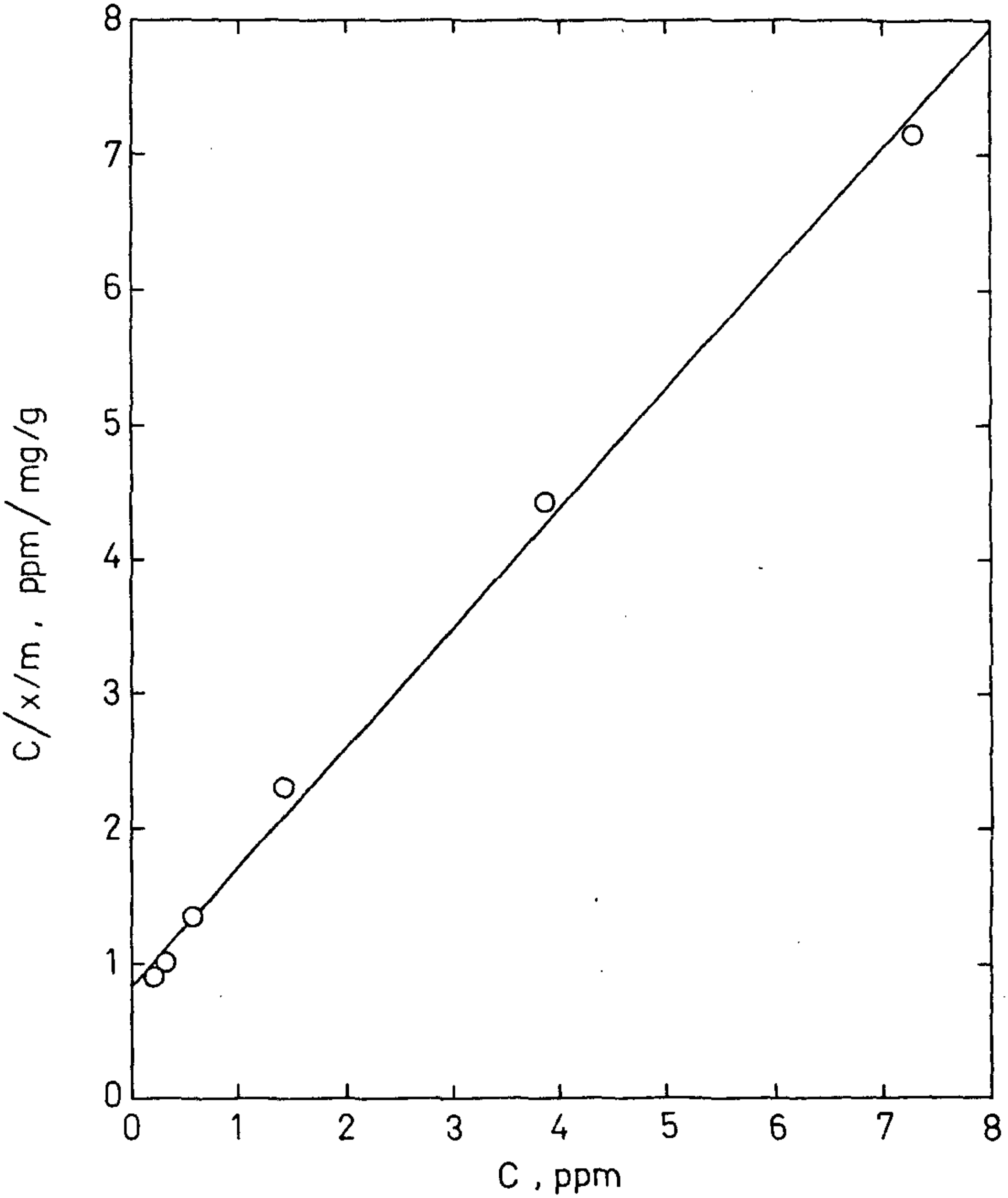


Figure 26. Langmuir Plot of Phosphate Adsorption by Lake Warner Sediment at 20°C, pH 7.0 and E_c 370 mv.

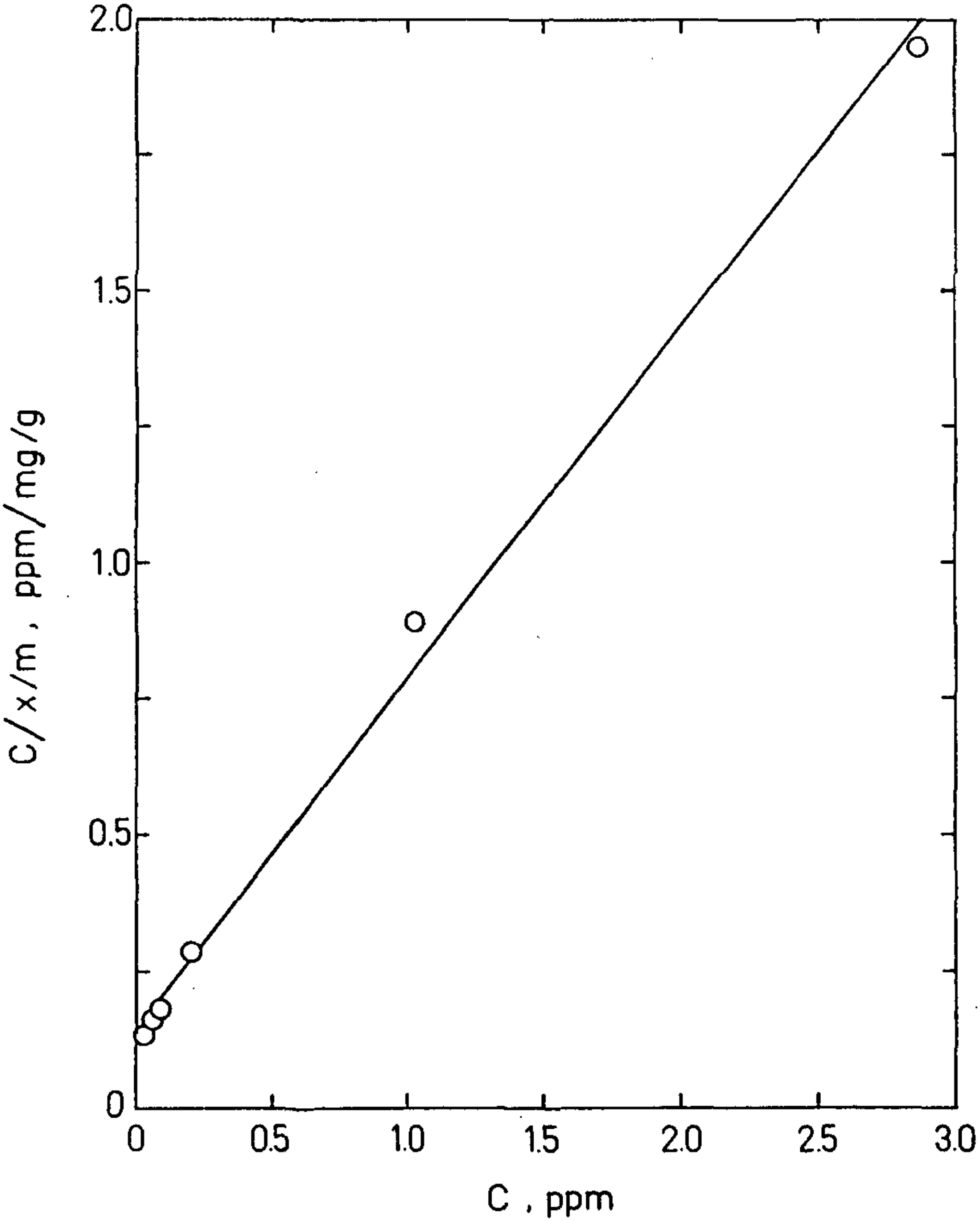


Figure 27. Langmuir Plot of Phosphate Adsorption by Lake Warner Sediment at 20°C, pH 5.5 and E_c 453 mv.

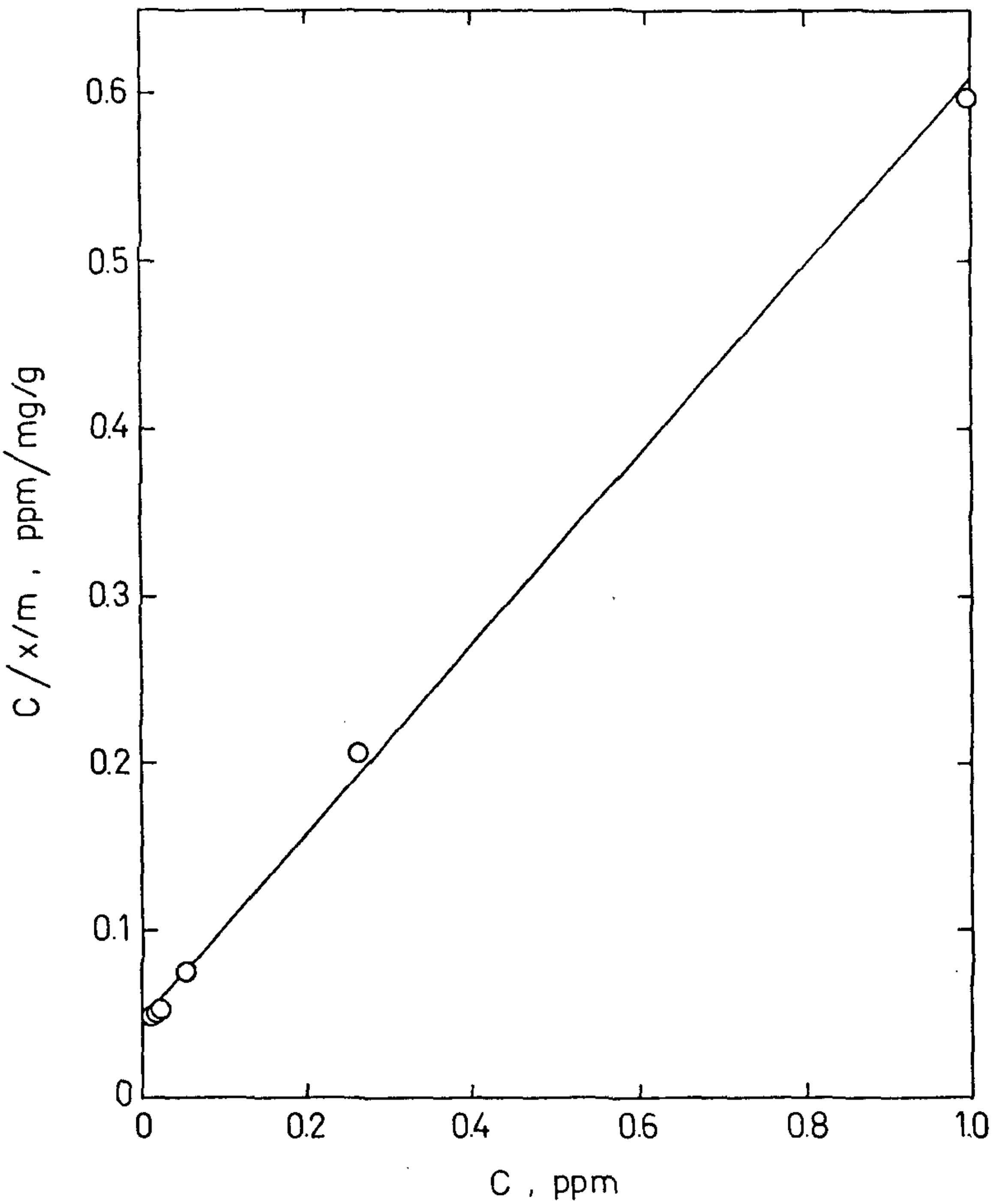


Figure 28. Langmuir Plot of Phosphate Adsorption by Lake Warner Sediment at 20°C, pH 4.8 and E_c 460 mv.

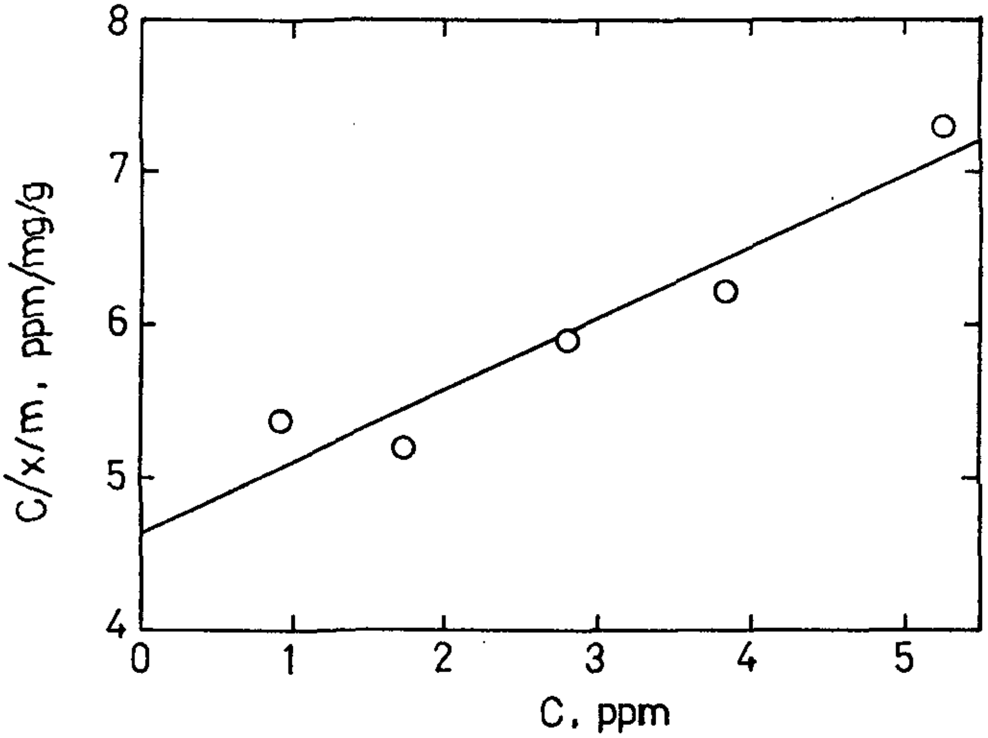


Figure 29. Langmuir Plot for Phosphate Adsorption by Lake Warner Sediment at 20°C, pH 4.8 and E_c -216 to -274 mv.

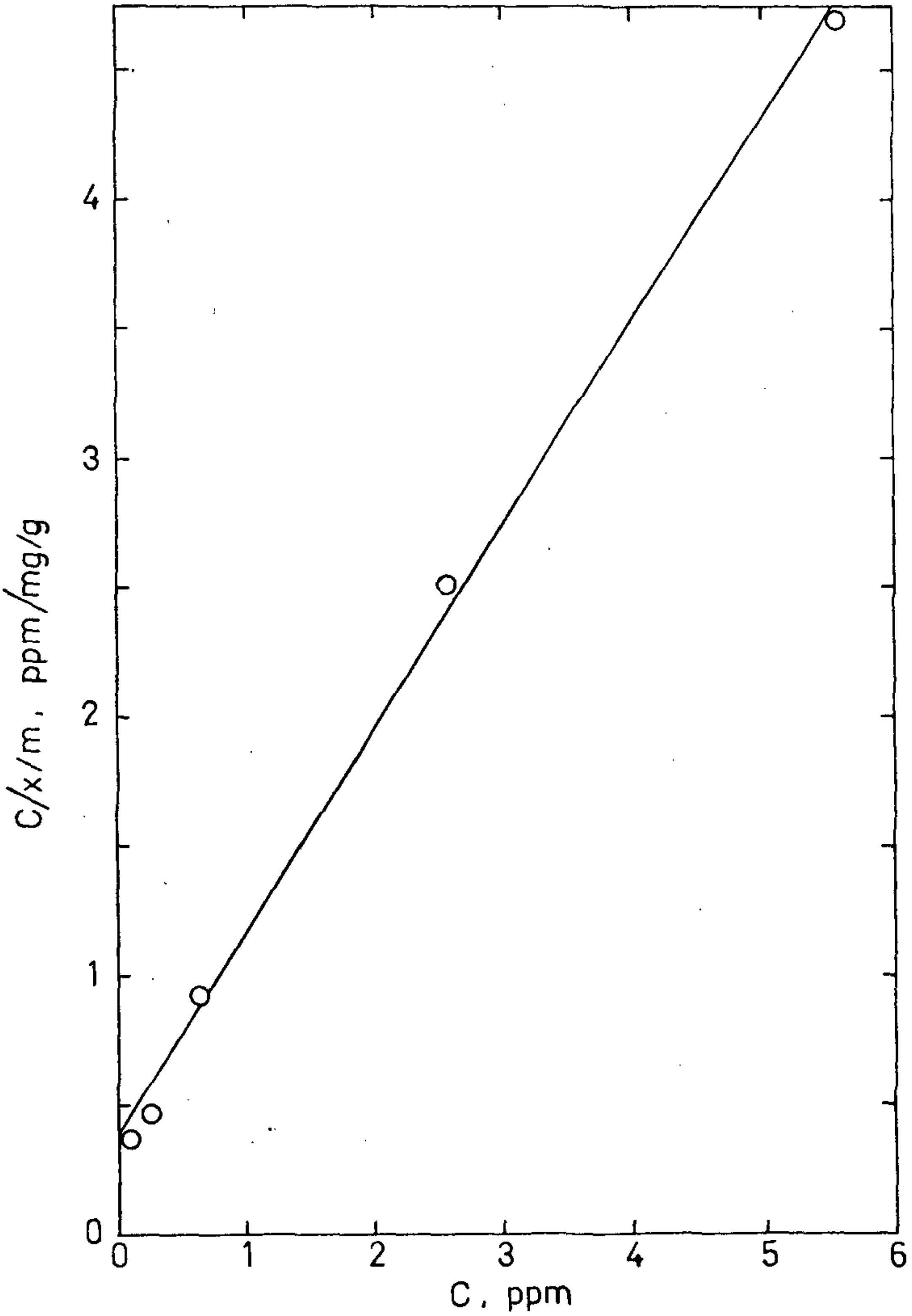


Figure 30. Langmuir Plot of Phosphate Adsorption by Lake Warner Sediment at 11°C, pH 7.0 and E_c 325 mv.

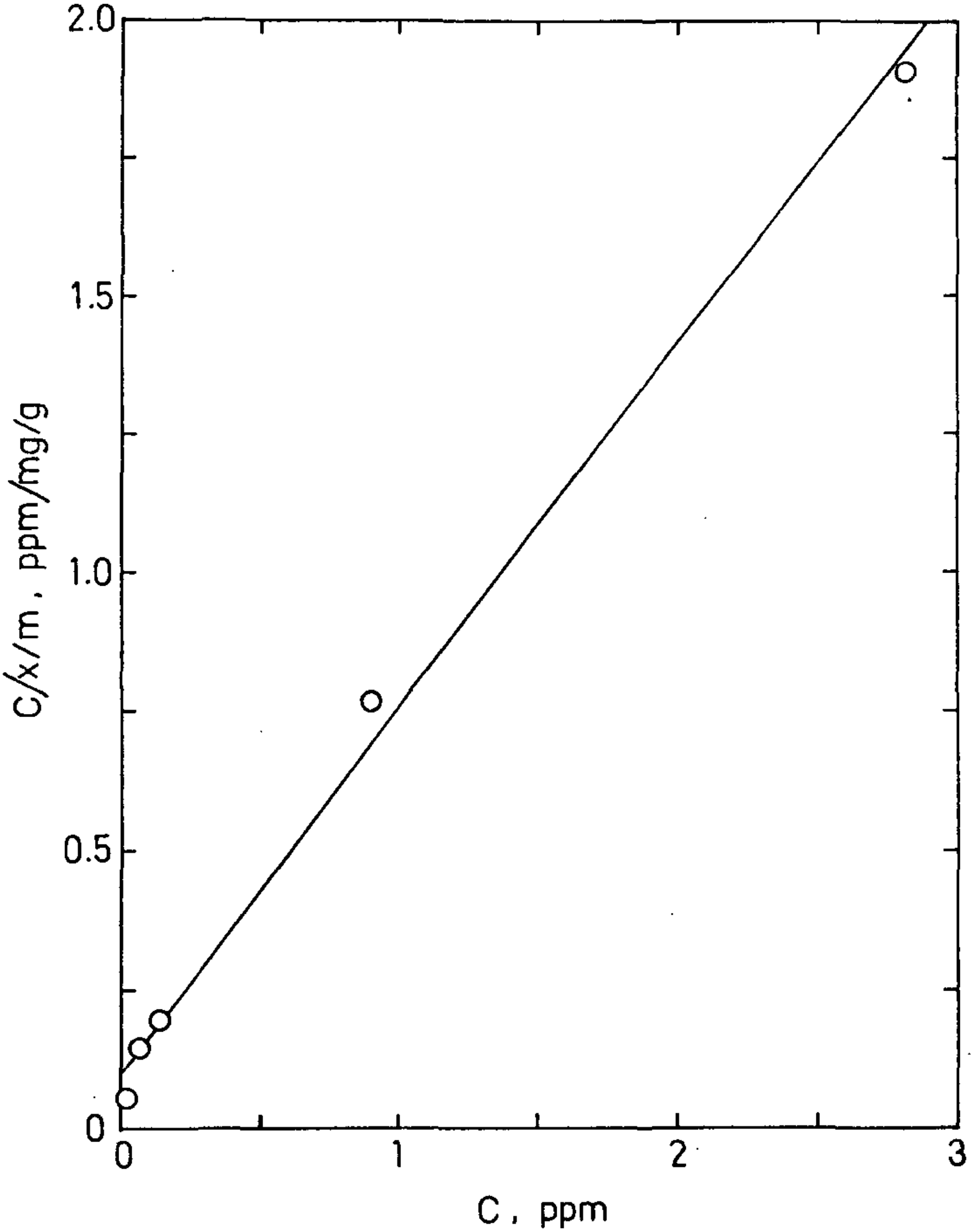


Figure 31. Langmuir Plot of Phosphate Adsorption by Lake Warner Sediment at 11°C, pH 5.5 and E_c 412 mv.

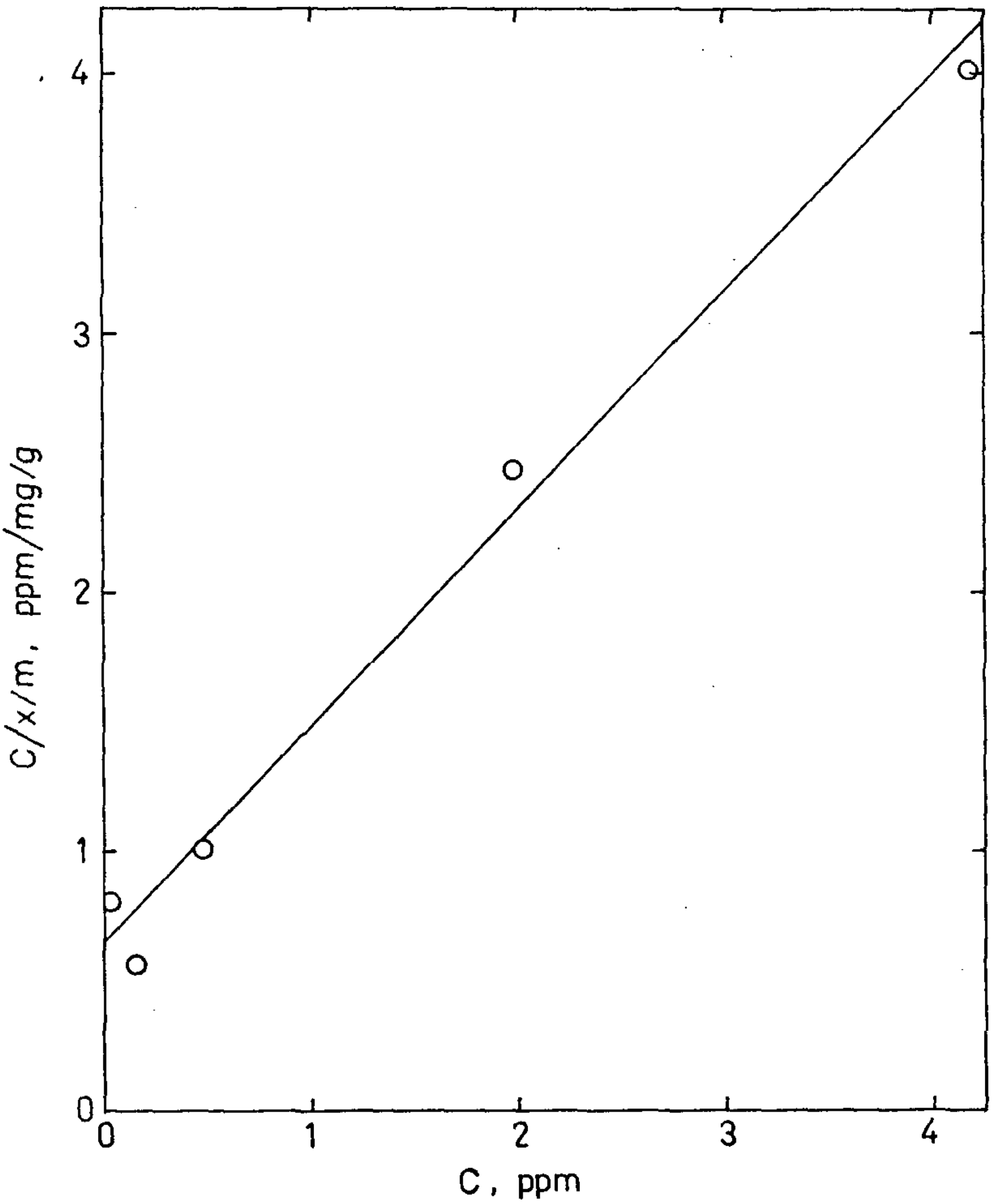


Figure 32. Langmuir Plot of Phosphate Adsorption by Lake Wyola Sediment at 20°C, pH 7.0 and E_c 390 mv.

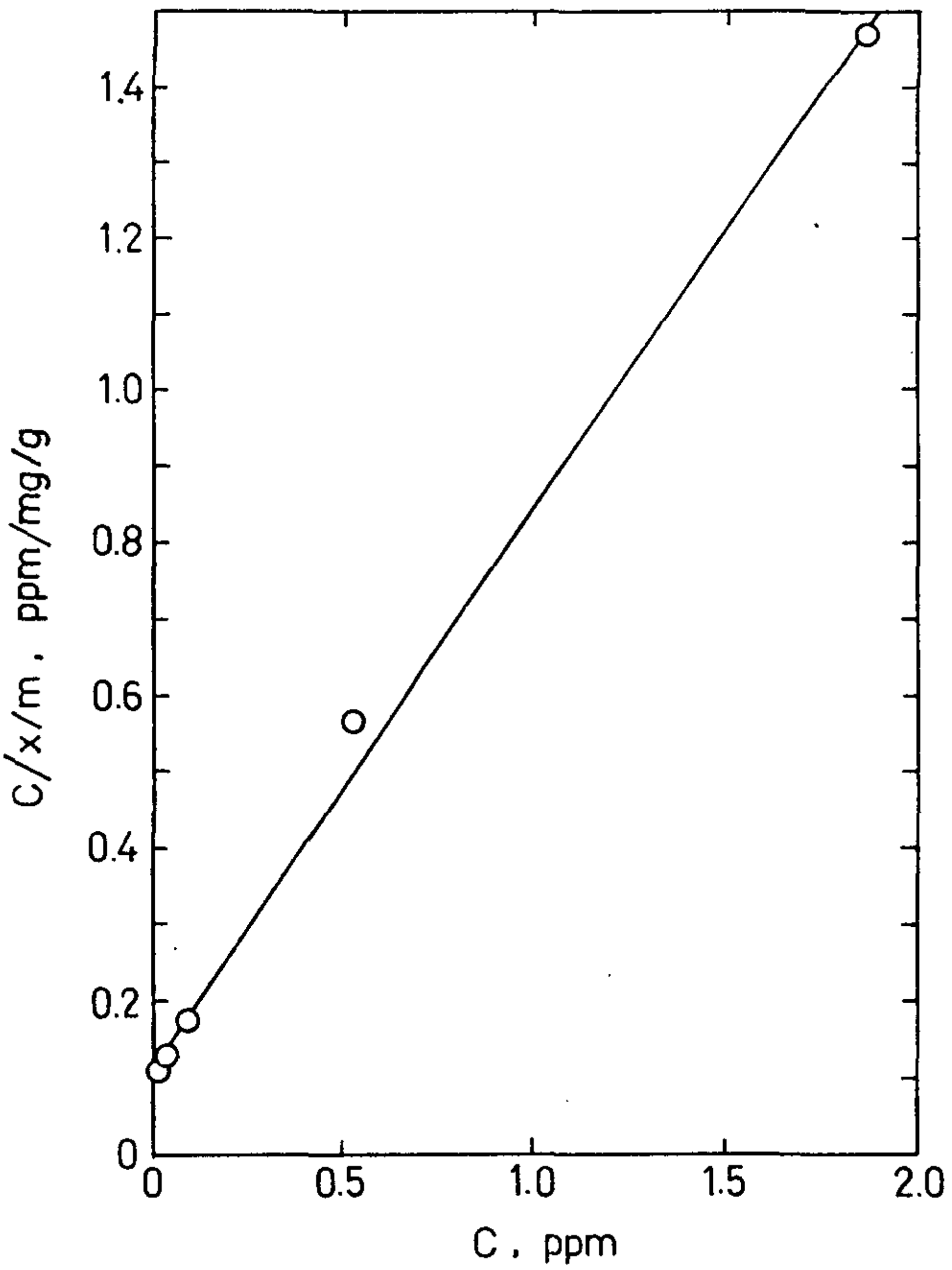


Figure 33. Langmuir Plot of Phosphate Adsorption by Lake Wyola Sediment at 20^{o}C, pH 6.0 and E_c 440 mv.

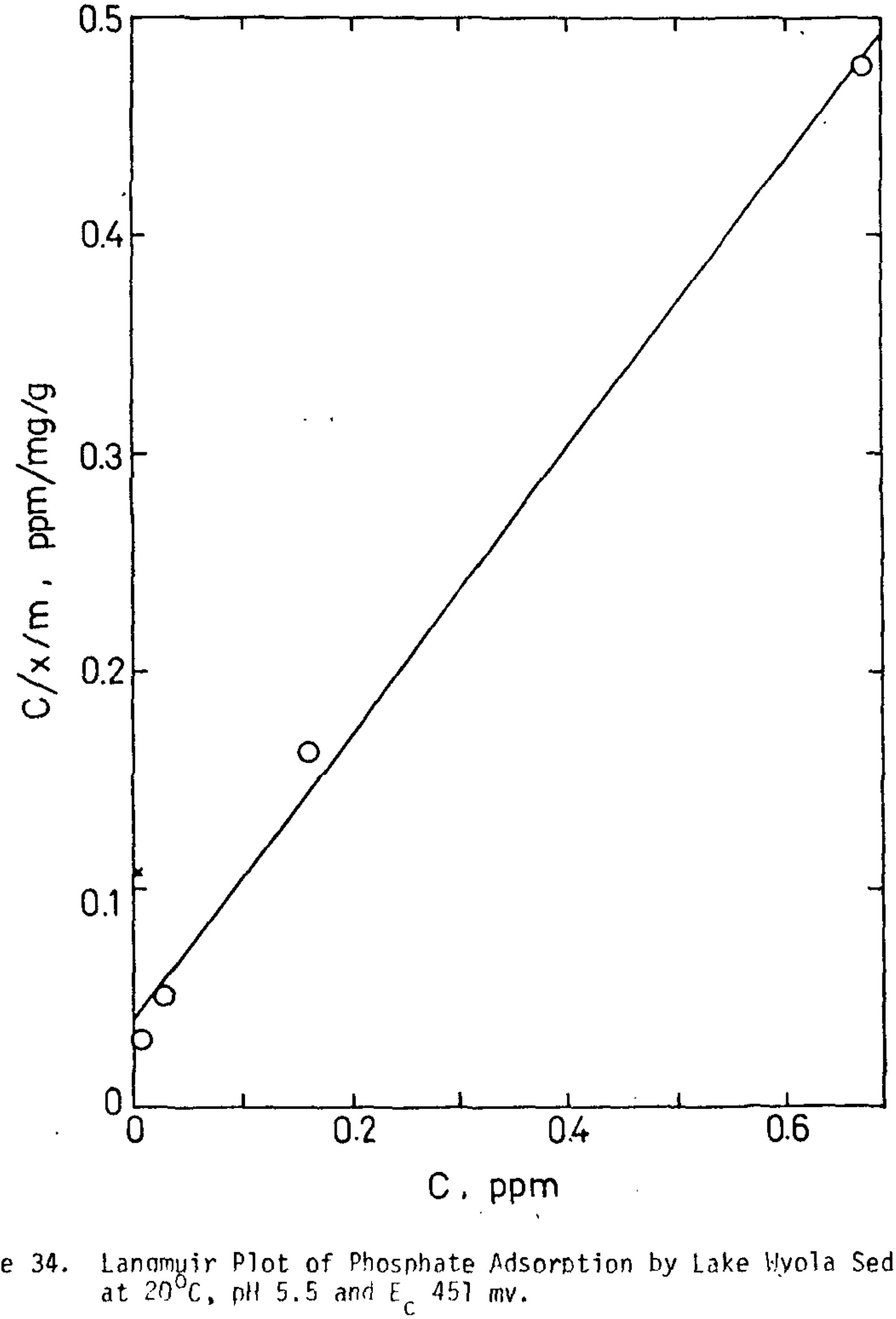


Figure 34. Langmuir Plot of Phosphate Adsorption by Lake Wyola Sediment at 20°C, pH 5.5 and E_c 451 mv.

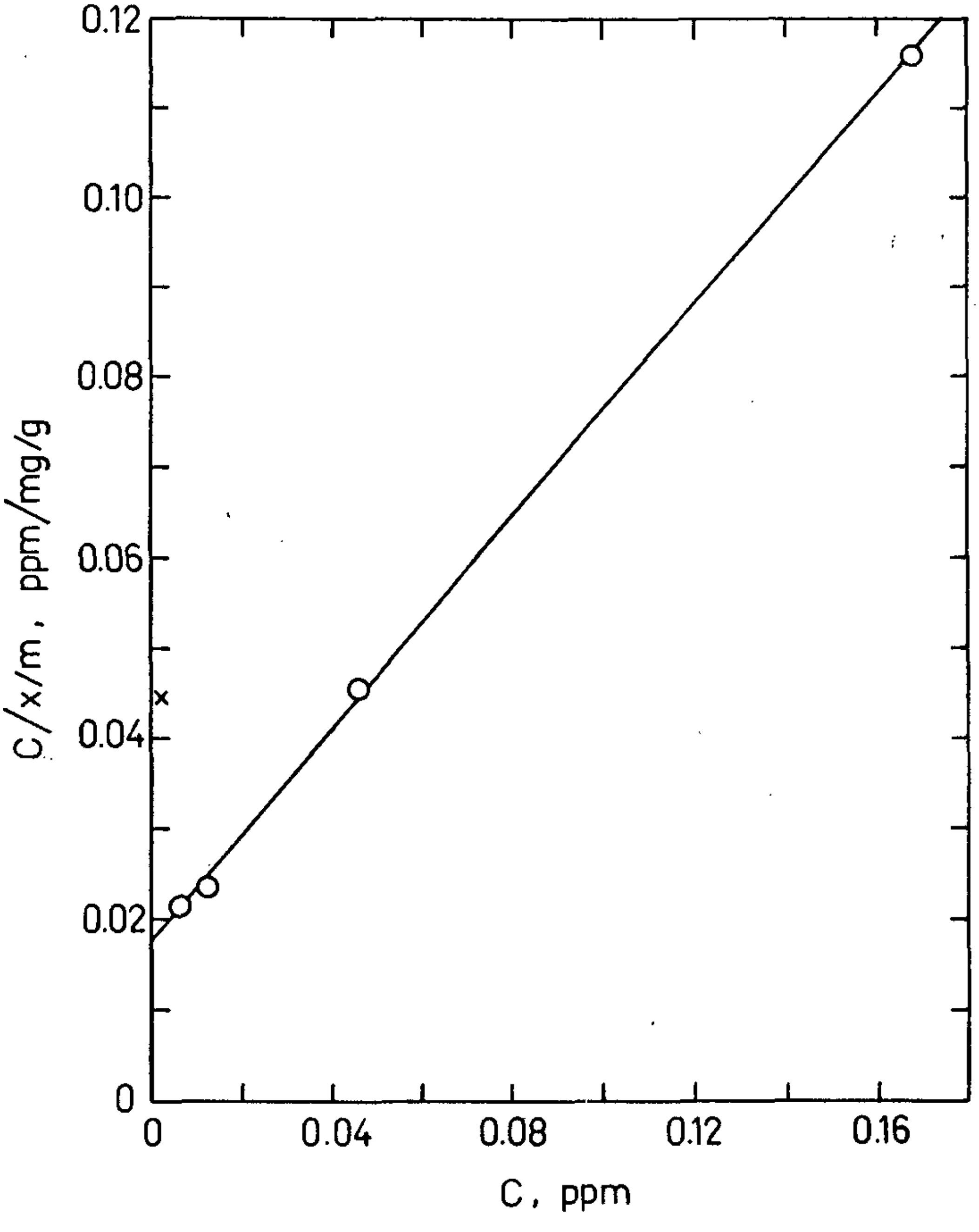


Figure 35. Langmuir Plot of Phosphate Adsorption by Lake Wyola Sediment at $20^{\circ}C$, pH 4.8 and E_c 454 mv.

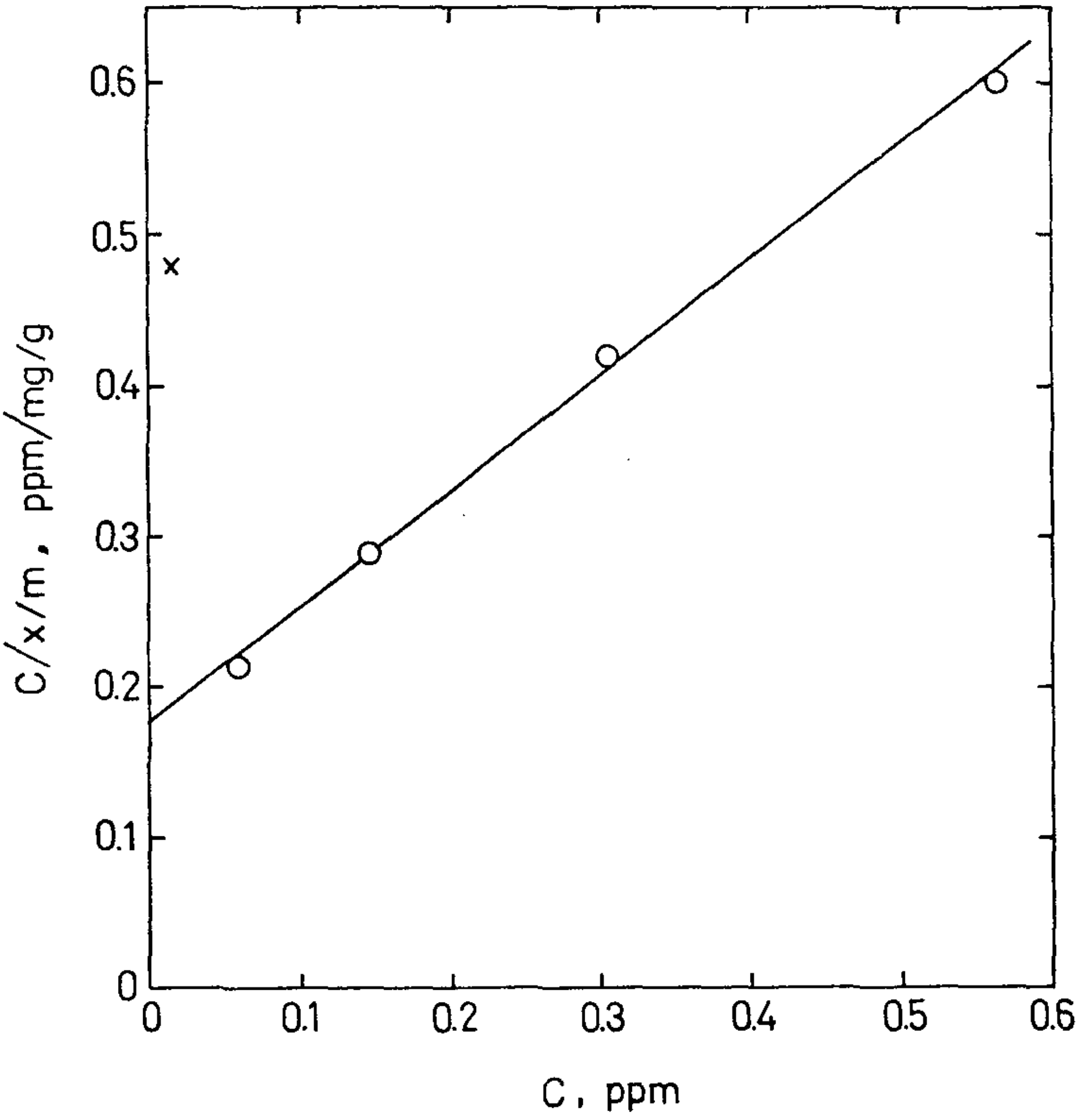


Figure 36. Langmuir Plot of Phosphate Adsorption by Lake Wyola Sediment at 20°C, pH 4.8 and E_c -110 to -220 mv.

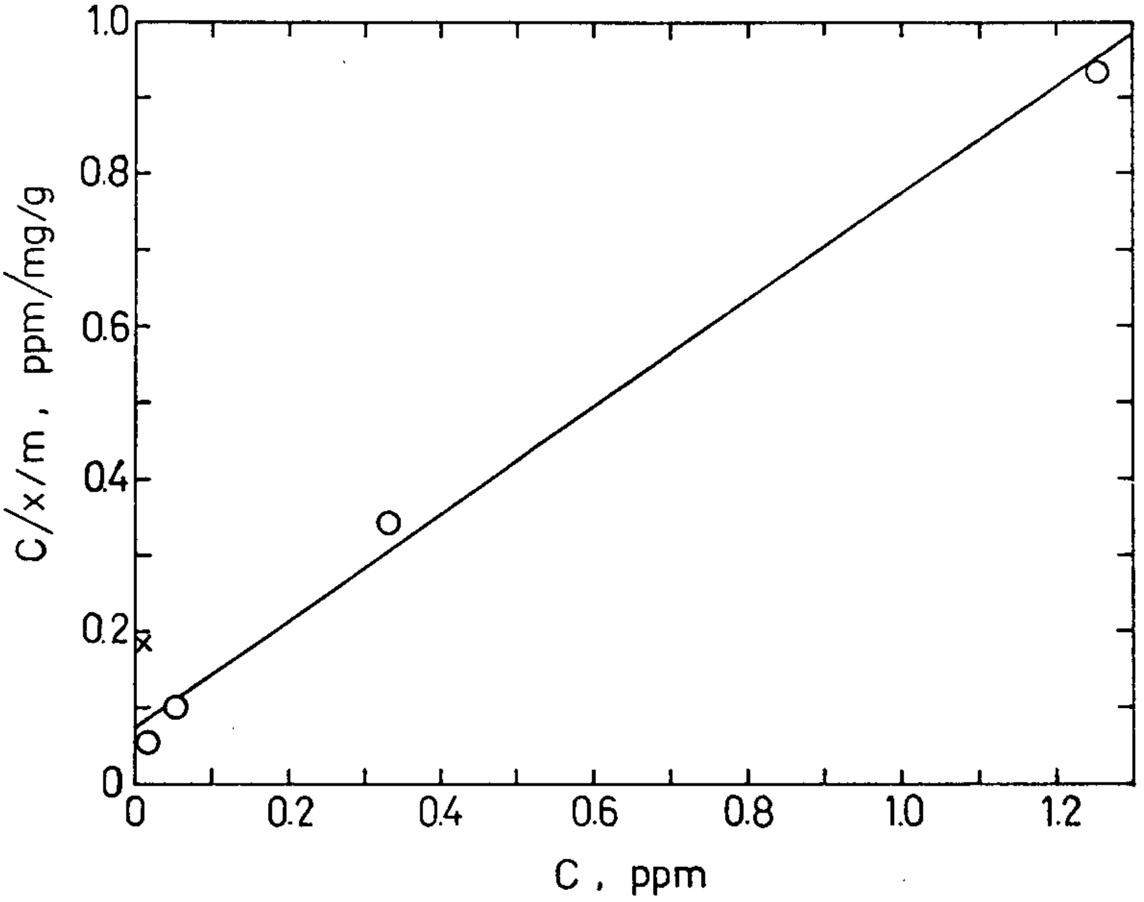


Figure 37. Langmuir Plot of Phosphate Adsorption by Lake Wyola Sediment at 11°C, pH 6.0 and E_c 440 mv.

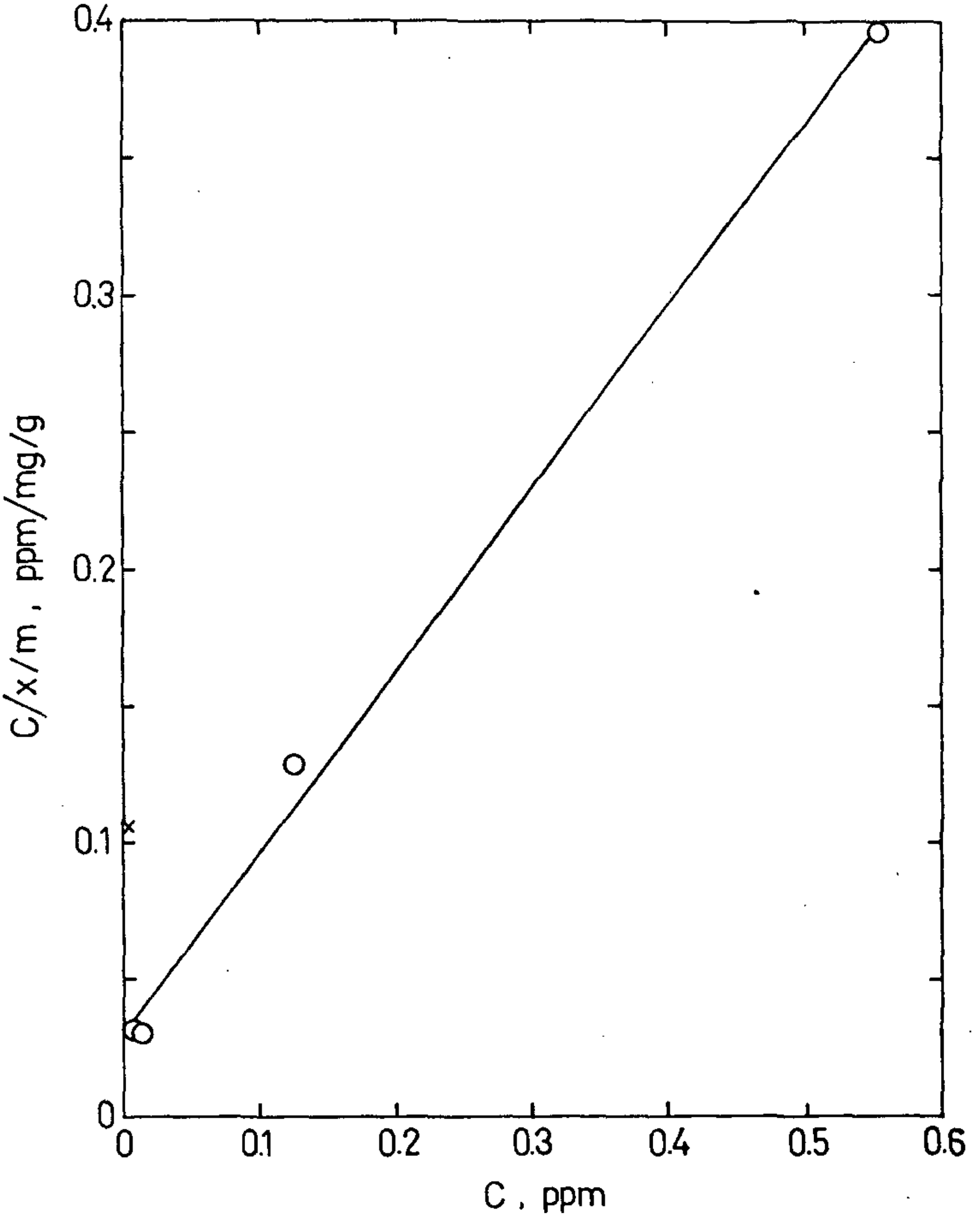


Figure 38. Langmuir Plot of Phosphate Adsorption by Lake Wyola Sediment at 11°C, pH 5.5 and E_c 449 mv.

Table 10. Langmuir Isotherm Constants

	Experimental Conditions			Langmuir Isotherm Constants*			
				Corrected for Surface P		Not Corrected for Surface P	
Sediment	Temperature, °C	pH	E_c, mv	b	k	b	k
Warner	20	7.0	373	1.126	1.08	1.120	0.29
	20	5.5	453	1.554	4.74	1.410	2.10
	20	4.8	460	1.782	12.63	1.115	9.67
	20	4.8	-216∿ -274	2.159	1.00	-	-
	11	7.0	325	1.265	2.19	1.065	1.06
	11	5.5	412	1.530	7.10	1.317	3.52
Wyola	20	7.0	390	1.210	1.27	1.155	1.25
	20	6.0	440	1.369	6.16	1.345	5.14
	20	5.5	451	1.504	17.63	1.468	15.81
	20	4.8	454	1.704	33.43	1.692	28.99
	20	4.8	-110∿ -220	1.304	4.37	1.330	3.55
	11	6.0	440	1.432	9.85	1.396	8.82
	11	5.5	449	1.511	22.41	1.476	20.13

*Value of b and k are in units of mg/g and $(mg/l)^{-1}$ respectively.

maximum increases with decrease in pH and with decrease in temperature. But, for the Lake Warner sediment, the adsorption maximum at 20°C and pH 5.5 was greater than the adsorption maximum at 11°C and pH 5.5. This might have been caused by an experimental error. The most probable cause was that the adsorption experiment for the 11°C and pH 5.5 condition was not carried long enough for the true equilibrium to reach.

For the Lake Wyola sediment at 20°C, pH 4.8 and under low redox potential conditions (E_c = -110 to -220 mv), the adsorption maximum was 1.304 which is smaller than the adsorption maximum at 20°C, pH 4.8 and under a high redox potential condition (E_c = +454 mv). This is what is expected, as under low redox potential conditions, the sediment released large quantities of iron which has affinity for phosphorus. As a result, the phosphorus adsorption capacity of the sediment was reduced. What seems unusual, however, is the adsorption maximum for the Lake Warner sediment at 20°C, pH 4.8 and low redox potential conditions (E_c = -216 to -274 mv). As shown in Table 10, the calculated adsorption maximum under this low redox potential condition is greater than that at a higher redox potential condition (E_c = +460 mv). The sensitivity of this sediment to redox potential and the wide range of redox potential values among the samples might have resulted this apparent error. But, another possibility is that although the data points seem to fit the Langmuir isotherm, the calculated adsorption maximum might not have its true physical meaning in a reduced sediment where biological activity prevail.

In Table 10, the values of the calculated energy constant, k, are shown to increase as pH decreases, as temperature decreases and as redox potential increases. The energy constant is related to the energy of adsorption, ΔH, by the following relationship (Weber, 1972; Adamson, 1960):

$$K \alpha e^{-\Delta H/RT} \tag{24}$$

where R is the gas constant and T is the absolute temperature. The energy of adsorption is defined as the change in heat content of a system during adsorption. As shown previously, the amounts of phosphate adsorbed by the sediments studied increased with decreasing temperature. This suggested that the phosphate adsorption by the sediments studied was an exothermic reaction, and the values of ΔH for the adsorption were negative. Therefore, at constant temperature, a high energy constant corresponded to a high (negative) energy of adsorption. The observed increase in values of the energy constant with decreasing pH at constant temperature suggested that as pH decreased more adsorption reaction occurred, resulting in an increase in the (negative) energy of adsorption. This is consistant with the observed adsorption maxima at different pH values. Similarly, the decrease of k values with decreasing redox potential at constant temperatures indicated that the (negative) energy of adsorption decreased with the decrease in redox potential in the sediment-water mixtures. Correspondingly, the amount of adsorption was less under low redox potential conditions than under high redox potential conditions.

The isotherms for the adsorption of inorganic phosphate on the two lake sediments studied are shown, along with the data points, in Figures 39-45. These isotherms were derived by using equation (20) and the Langmuir isotherm constants (calculated with surface phosphorus correction) shown in Table 10.

The Langmuir adsorption equation and the constants shown in Table 10 can be used for the derivation of mathematic models which describe the phosphate transport phenomena between lake sediments and the overlying waters. Several such models have been suggested by DiGiano (1970). Since, as shown in Table 10, the Langmuir isotherm constants vary from lake to lake, the values derived herein can only be used for the specific lakes studied. Since these constants also change under different pH, temperature and redox potential conditions even for the same lake, these latter factors should also be considered in the derivation of the mathematic models.

Release of Inorganic Phosphate and Iron from Lake Sediments. As determined previously, both sediments studied contained some native inorganic phosphates. During the equilibrium adsorption studies, it was found that some of these phosphates released to the solutions and the quantities released depended on the experimental conditions. Similarly, some of the iron in the sediment also released to the solutions when the sediments were equilibrated with water. Table 11 shows the amounts of the inorganic phosphate and the iron released from the sediments after the equilibration periods for both sediments studied under different

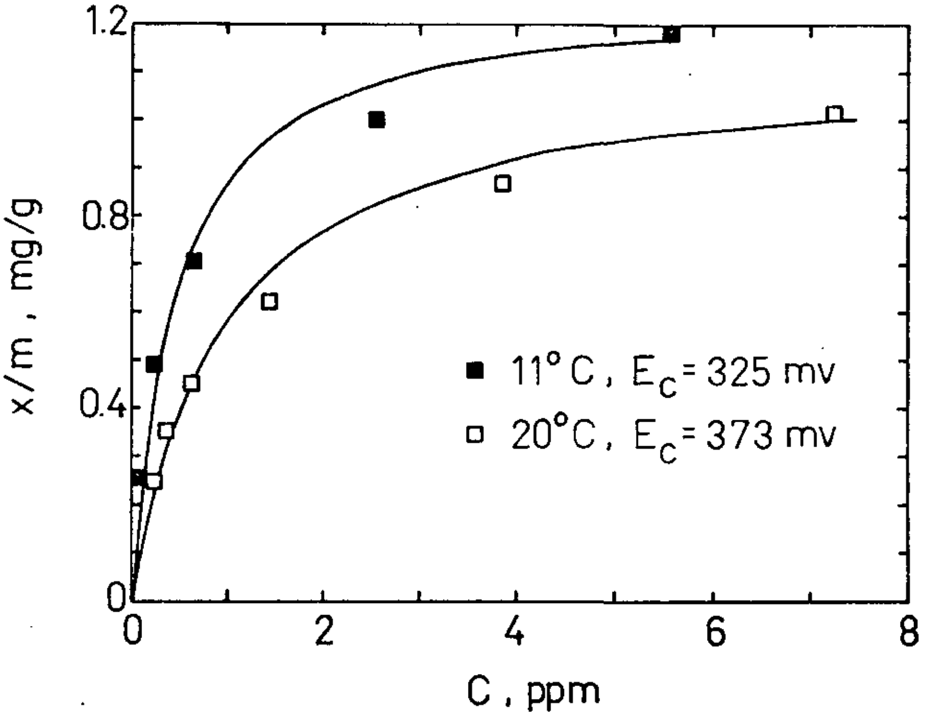


Figure 39. Isotherms for Adsorption of Phosphate on Lake Warner Sediment at pH 7.0.

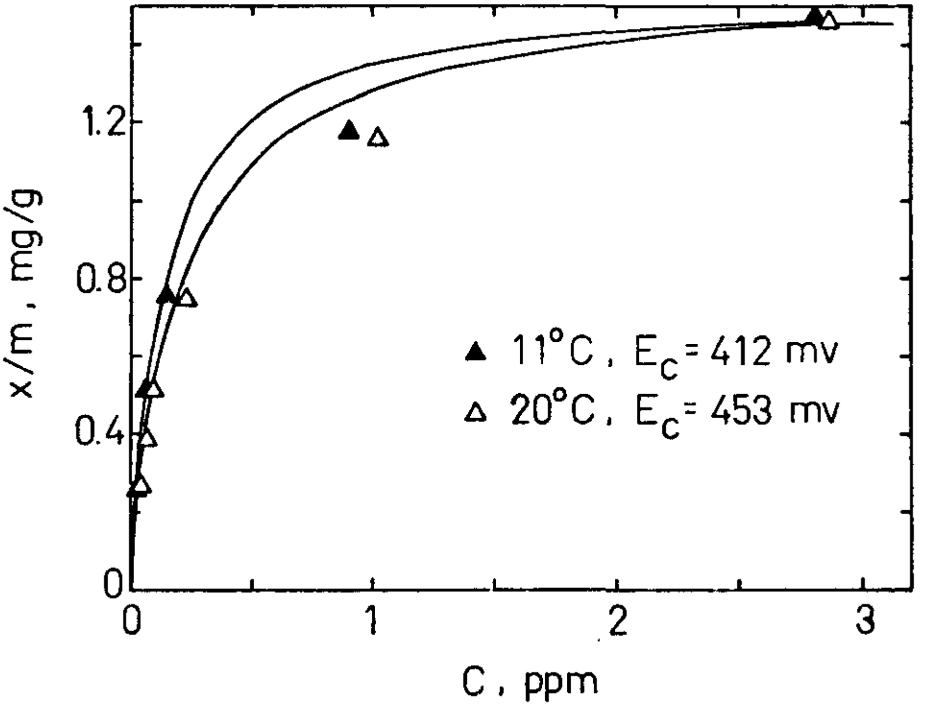


Figure 40. Isotherms for Adsorption of Phosphate on Lake Warner Sediment at pH 5.5.

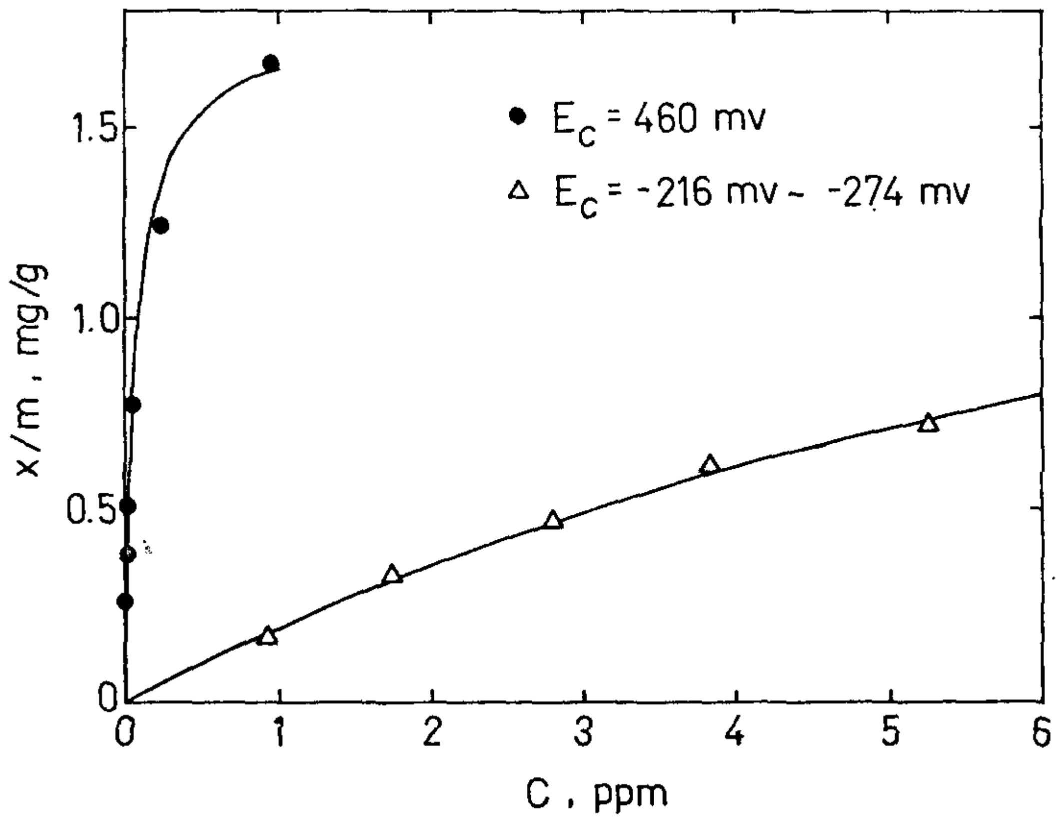


Figure 41. Isotherms for Adsorption of Phosphate on Lake Warner Sediment at 20°C and pH 4.8.

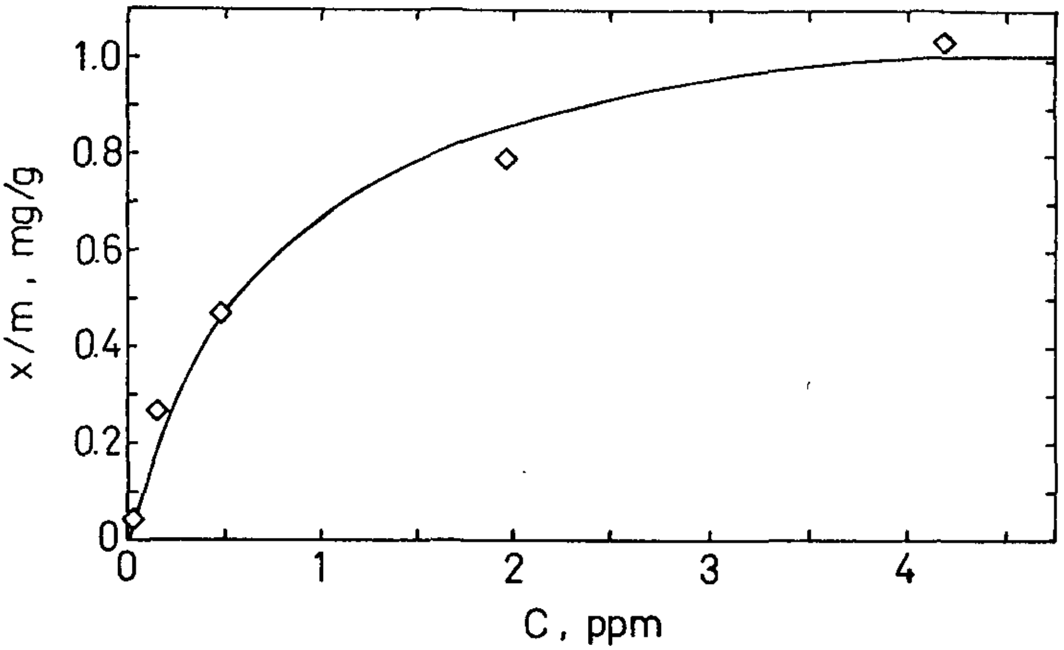


Figure 42. Isotherm for Adsorption of Phosphate on Lake Wyola Sediment at 20^{0}C, pH 7.0 and E_c 390 mv.

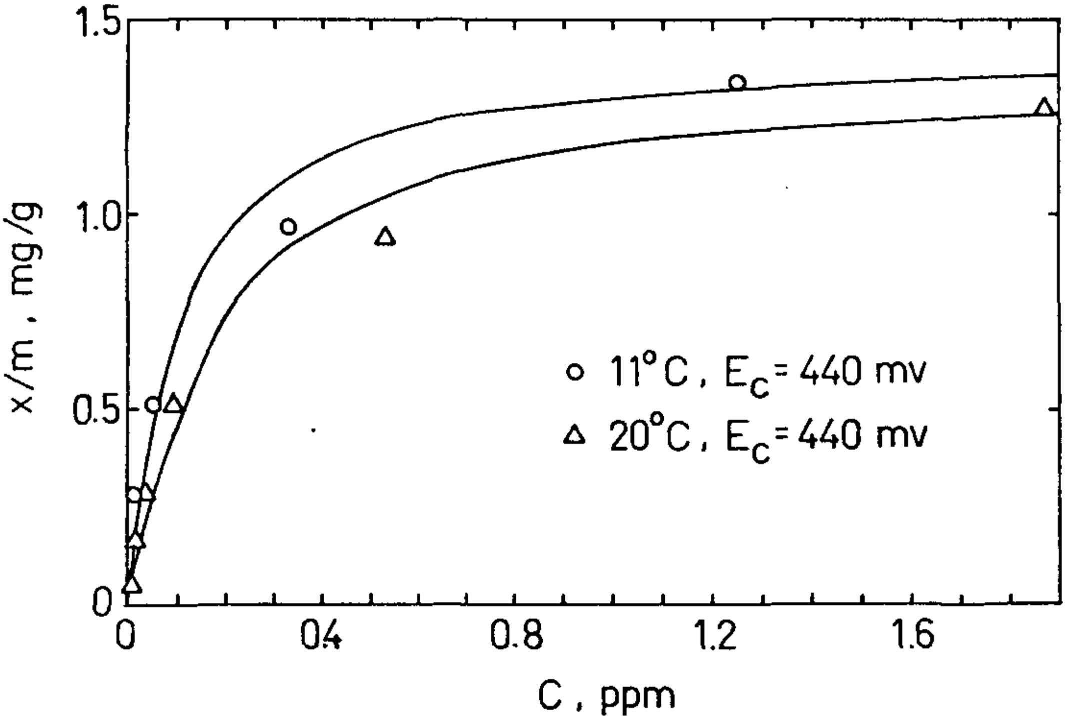


Figure 43. Isotherms for Adsorption of Phosphate on Lake Wyola Sediment at pH 6.0.

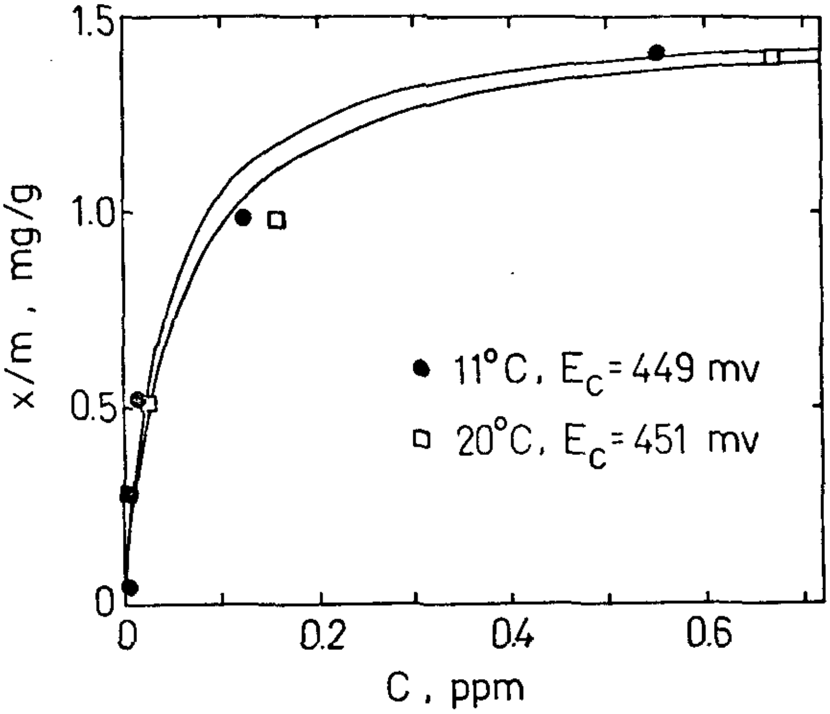


Figure 44. Isotherms for Adsorption of Phosphate on Lake Wyola Sediment at pH 5.5.

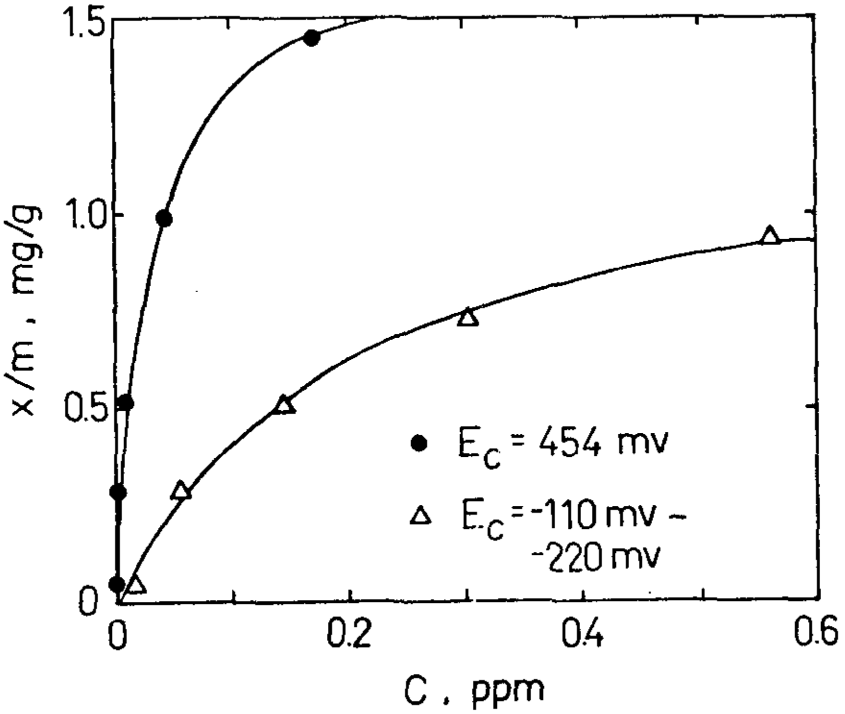


Figure 45. Isotherms for Adsorption of Phosphate on Lake Wyola Sediment at pH 4.8.

Table 11. Release of Inorganic Phosphate and Iron from Lake Sediments

Sediment	Experimental Conditions			Orthophosphate Released at Equilibrium,	Total Iron Released at Equilibrium,
	Temperature, ^{o}C	pH	E_c, mv	μg-P/g	mg/g
Warner	20	7.0	373	22.6	0.047
	20	5.5	453	3.8	0.002
	20	4.8	460	1.3	0.004
	20	4.8	-245∿ -274	95.7	5.26
	11	7.0	325	9.9	0.017
	11	5.5	412	1.7	0.003
Wyola	20	7.0	390	3.5	0.100
	20	6.0	440	1.1	0.021
	20	5.5	451	0.5	0.004
	20	4.8	454	0.2	0.002
	20	4.8	-110∿ -150	1.9	3.70
	11	6.0	440	0.8	0.010
	11	5.5	449	0.5	0.008

experimental conditions. These values are the averages of the values shown in Tables 8 and 9 of this chapter and in Tables C-1 to C-11 of Appendix C, for samples that had no initial phosphate additions.

The values in Table 11 indicate that the amounts of the native inorganic phosphate released from the sediments were greater at higher pH, higher temperature and lower redox potential. The effect of these factors on the release of phosphate to the solution was greater for the Lake Warner sediment than for the Lake Wyola sediment, indicating that changes in environmental conditions would affect the phosphate status more in the former than in the latter. Similarly, the release of iron was also affected by pH, temperature and redox potential, the release being greater at higher pH, higher temperature and lower redox potential. The relationships observed here are similar to the ones reported by Spear (1970) in his sediment phosphorus release studies.

Phosphate-Sorbing Components Studies

Equilibrium Adsorption of Inorganic Phosphate by Oxalate Extracted Sediments. The data for the equilibrium adsorption of inorganic phosphate by the oxalate extracted lake sediments are shown in Figures 46 and 47 and in Table 12. For comparison, the adsorption data for the unextracted original sediments studied under the same pH and temperature conditions are also shown. The data points all have been corrected for the native phosphorus released during the equilibration period. Although the samples were treated with a same procedure during the adsorption studies, the oxalate extracted samples resulted in lower redox potentials than the

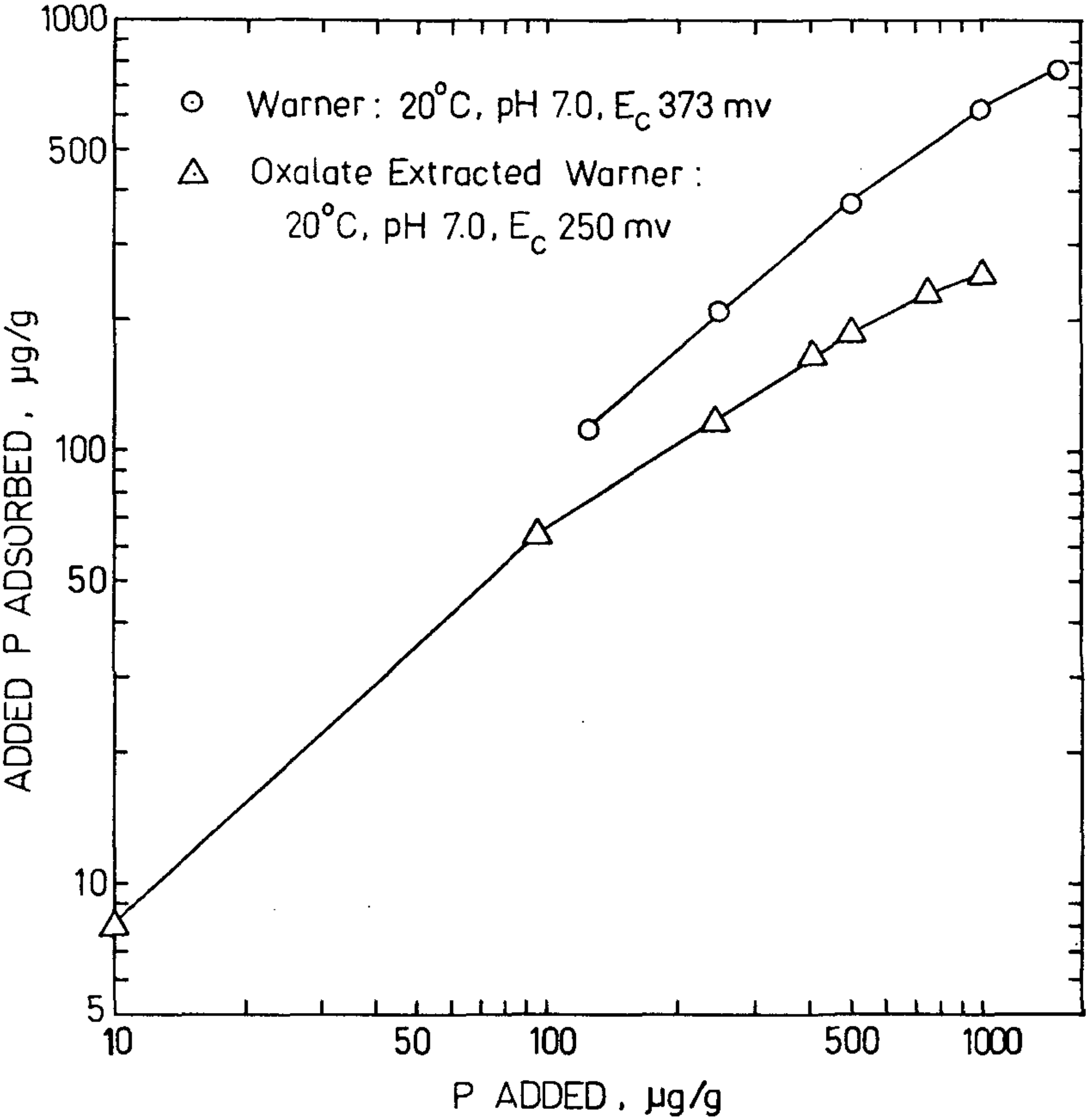


Figure 46. Comparison of Inorganic Phosphate Adsorption by Oxalate Extracted and Original Lake Warner Sediment.

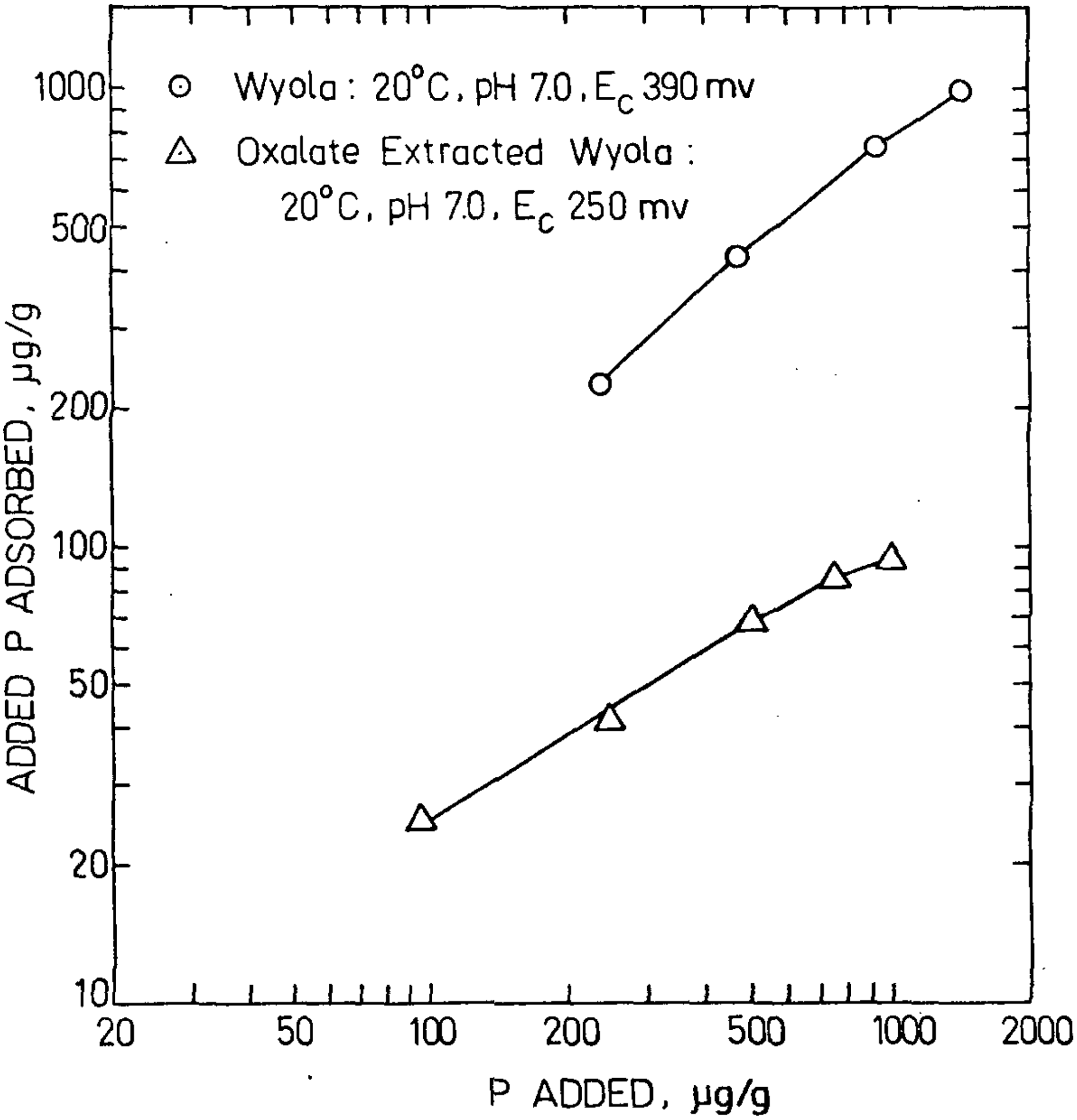


Figure 47. Comparison of Inorganic Phosphate Adsorption by Oxalate Extracted and Original Lake Wyola Sediment.

Table 12. Comparison of Inorganic Phosphate Adsorption by Original and Oxalate Extracted Sediments[a]

Sediment	P added, µg/g	P Adsorbed			
		Original		Oxlate Extracted	
		µg/g	%	µg/g	%
Warner[b]	250	210	84.0	120*	48.0
	500	375	75.0	172	34.4
	750	500*	66.7	230	30.7
	1000	625	62.5	253	25.3
Wyola[c]	250	240*	96.0	44*	17.6
	500	445*	89.0	68	13.6
	750	625*	83.4	85	11.3
	1000	780*	78.0	93	9.3

[a] Experiments were run at pH 7.0, Temperature 20°C.

[b] Percent of total Fe, Al and P removed by oxalate extraction were 28, 9, and 72 percent, respectively.

[c] Percent of total Fe, Al and P removed by oxalate extraction were 36, 27 and 55 percent, respectively.

[*] Values interpolated from the curves in Figure 46 or Figure 47.

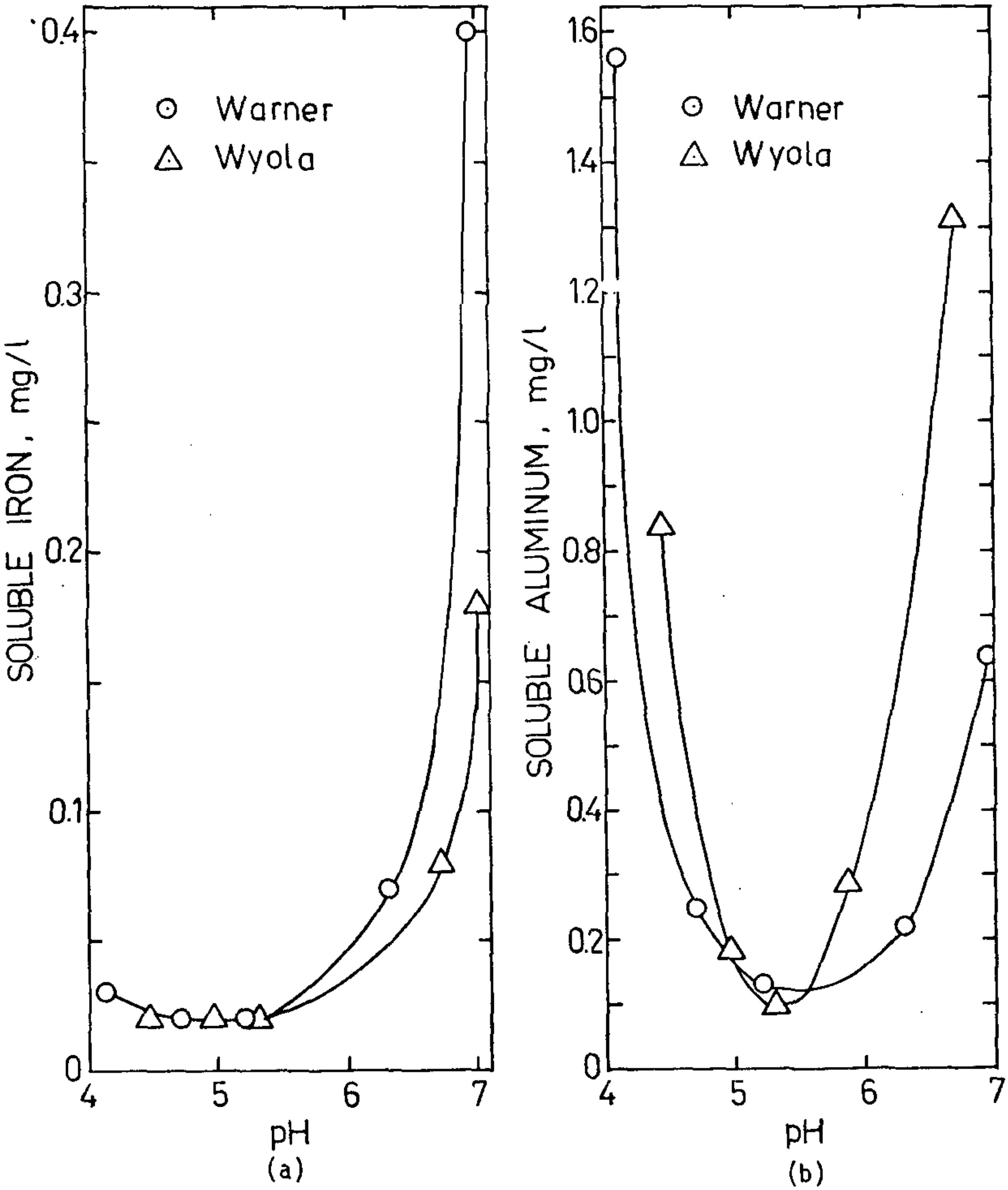
unextracted sediments. The residuals of the chemicals used for the extraction might have the capacity of reducing the potentials of the samples to the observed values.

Oxalate extraction reduced the phosphate adsorption capacities of both Lake Warner and Lake Wyola sediments. As shown in Table 2, oxalate extraction extracted a portion of the total iron and aluminum from both sediments. The oxalate extractable iron and aluminum in sediments are amorphous in nature. Table 12 shows that the oxalate extractable iron and aluminum have greater phosphate sorption capacity than the unextractable iron and aluminum. For the Lake Warner sediment, oxalate extraction removed 28 percent of the total iron and 9 percent of the total aluminum. This resulted in a more than 50 percent reduction in the phosphate adsorption capacity when the phosphorus added initially was more than 500 μg/g. For the Lake Wyola sediment, the effect of removing the amorphous iron and aluminum was even greater. Removing 36 percent and 27 percent of the total iron and aluminum, respectively, resulted in a reduction of phosphorus adsorption capacity of 5.5- to 8.4-fold when the initially added phosphorus was from 250 μg/g to 1000 μg/g.

The results reported herein are in agreement with those reported by Shukla et al. (1971) for the Wisconsin lakes. From these results, however, one could not tell the relative importance of iron and aluminum in the adsorption of phosphate.

Effect of pH on the Dissolution of Phosphorus, Iron and Aluminum from Lake Sediments. pH was found to affect the phosphate adsorption capacity of lake sediment. In the range of pH studied (pH 4.8-7.0), the phosphate adsorption capacities of both the Lake Warner and the Lake Wyola sediments were found to increase with decreasing pH. Since it was found previously that both iron and aluminum were involved in the phosphate adsorption by lake sediments, it was decided to investigate the effect of pH on the dissolution of phosphorus, iron and aluminum from the sediments, in the hope that the adsorption mechanism could be determined. The results are shown in Figures 48 and 49.

Figure 48(a) shows that the amounts of the iron released from both sediments were minimal at pH 4.5 to 5.5, and increased at both higher and lower pH values, the increase being greater at higher pH than at lower pH. The release of aluminum had a minimum at a pH value near 5.5 for both sediments and increased at both higher and lower pH values (Figure 48(b)). Along with the release of iron and aluminum, phosphorus was also released (Figure 49). The amount of phosphorus release increased steadily from pH 4 to pH 7. Comparing the curves shown in these figures, one could easily conceive that although at pH values greater than 5.5 the release of both iron and aluminum might be responsible for the release of phosphorus, at pH values lower than 5.5 the release of aluminum alone did not cause a corresponding release of phosphorus. It is therefore concluded that aluminum release was not responsible for the release of phosphorus from the sediments when the pH in the sediments was less than 5.5. But it is not clear from these data whether the release of phosphorus was also not related to the release of aluminum at pH values greater than 5.5.



(a)

(b)

Figure 48. Effect of pH on the Dissolution of Iron and Aluminum from Lake Sediments at 20°C.

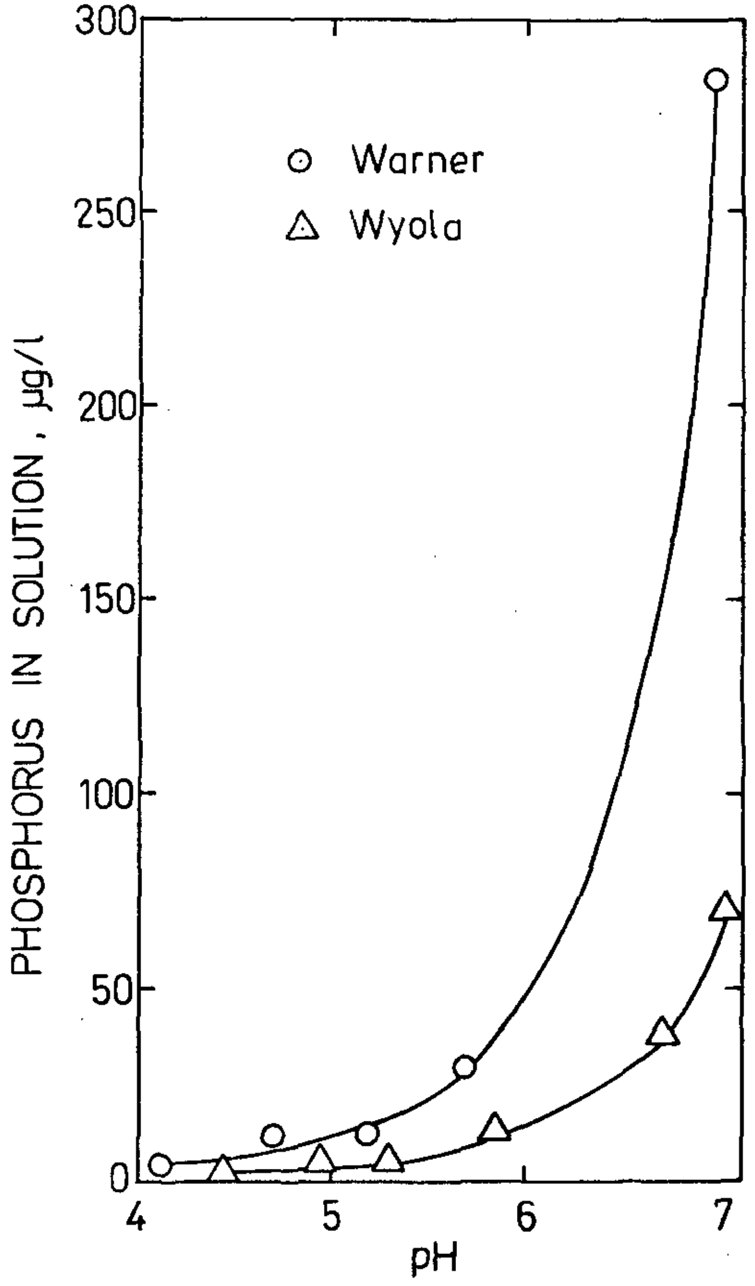


Figure 49. Effect of pH on Phosphorus Release from Lake Sediments at 20°C.

It is very interesting to note that the shapes of the release curves for both iron and aluminum are very similar to the solubility curves for $FePO_4$ and $AlPO_4$ respectively (see Committee Report, 1970). This may imply that the relationships between phosphorus and iron and aluminum in these sediments followed closely the chemistry of $FePO_4$ and $AlPO_4$. Since, in the previous studies of this thesis, it was shown that amorphous iron and aluminum were the major phosphorus adsorbing components in these sediments, it is not surprising that the above relationships are possible.

The existence of such relationships, however, does not have to mean that the removal of the added phosphate was through chemical precipitation of the phosphate by the iron and aluminum released from the sediment. As a matter of fact, as shown previously, the reactions between phosphate and the sediments studied were exothermic in nature. Since adsorption reactions are normally exothermic (Weber, 1972), it is very possible that the removal of phosphate by lake sediments was actually an adsorption reaction. In order to explain the observed fact about the relationships between phosphate and iron and aluminum, the following mechanisms are hypothesized: (1) initially, when phosphate was added to a sediment-water mixture, it was rapidly adsorbed to the sediment particles. The surfaces of the amorphous forms of iron and aluminum in the sediment served as the major adsorption sites although the surfaces of other sediment constituents such as clays, silts, microorganisms and organic matters could all serve as adsorption sites, (2) the phosphate adsorbed on the surfaces of the amorphous iron and/or aluminum gradually exchange with the OH^- or H_2O groups in the hydroxometal complexes and formed $FePO_4$ and/or $AlPO_4$.

Inorganic Phosphate Fractionation of Sediments after Equilibrium Adsorption. In order to further investigate the relative importance of iron and aluminum in sorbing added inorganic phosphate, selected samples from the equilibrium studies were fractionated according to a modified Chang and Jackson procedure (Petersen and Corey, 1966). The results are summarized in Tables 13 and 14. The results for the inorganic phosphate fractionation of the original sediments are also included in these tables as references.

The results indicate that of all the phosphorus newly adsorbed to the sediments, only little amounts were loosely bound. Calcium had very low additional capacity to adsorb the added phosphate. For the Lake Warner sediment, the increase in reductant soluble phosphate was very small with the added phosphate. For the Lake Wyola sediment, the amount of reductant soluble phosphate reduced a little, possibly due to the dissolution of some of the iron oxides with the corresponding release of the occluded phosphorus. But, the reason why this did not happen to the Lake Warner sediment is not known.

The major components that were responsible for the retention of added phosphate were iron and aluminum. The distribution of the adsorbed phosphate between iron and aluminum depended on the type of sediment and on pH. For the Lake Warner sediment that had been equilibrated with phosphate solution at pH 4.8 and 20^{o}C, the adsorbed phosphate is shown to distribute almost evenly between iron and aluminum, with the latter retained a slightly less amount of the phosphate than the former. For the same sediment that had been equilibrated with phosphate solution

Table 13. Fractionation of Inorganic Phosphates of Lake Warner Sediments[a]

Phosphate Fraction	Original Sediment	Sediment Equilibrated with P at 20°C and pH 4.8	Difference	Sediment Equilibrated with P at 10°C and pH 7.0	Difference
(1)	(2)[b]	(3)[c]	(4) = (3) - (2)	(5)[a]	(6) = (5) - (2)
Loosely Bound P	0.00	0.03	0.03	0.04	0.04
Aluminum Phosphate	0.42	0.94	0.52	0.77	0.35
Iron Phosphate	0.47	1.08	0.61	1.04	0.57
Reductant Soluble Phosphate	0.24	0.30	0.06	0.31	0.07
Calcium Phosphate	0.19	0.21	0.02	0.26	0.07
Sum	1.32	2.56	1.24	2.42	1.10
Total Inorganic P Present	2.19	3.16		2.93	
P Unrecovered	0.87	0.60		0.51	

[a] All figures have the unit mg-P/g oven-dried sediment.

[b] Average from analyses of duplicate fractionations.

[c] Average from analyses of triplicate fractionations, except iron phosphate which is the value of a single fractionation and calcium phosphate which is an average of two fractionation.

Table 14. Fractionation of Inorganic Phosphates of Lake Wyola Sediments[a]

Phosphate Fraction	Original Sediment	Sediment Equilibrated with P at 20°C and pH 4.8	Difference	Sediment Equilibrated with P at 20°C and pH 7.0	Difference
(1)	(2)	(3)	(4) = (3) - (2)	(5)	(6) = (5) - (2)
Loosely Bound P	0.00	0.01	0.01	0.02	0.02
Aluminum Phosphate	0.20	0.50	0.30	0.37	0.17
Iron Phosphate	0.09	0.13[b]	0.04	0.33	0.24
Reductant Soluble Phosphate	0.14	0.10	-0.04	0.12	-0.02
Calcium Phosphate	0.03	0.03	0	0.04	0.01
Sum	0.46	0.77	0.31	0.88	0.42
Total Inorganic P Present	1.10	2.09		1.89	
P Unrecovered	0.64	1.32		1.01	

[a] All figures have the unit mg-P/g of oven-dried sediment and are the average of duplicate fractionations except as noted.

[b] Value from a single fractionation.

at pH 7.0 and 10^{o}C, on the other hand, the difference between the Al-PO$_4$ and Fe-PO$_4$ increased, but still, the amount of Al-PO$_4$ was smaller than the amount of Fe-PO$_4$.

For the Lake Wyola sediment that had been equilibrated with phosphate solution at pH 4.8 and 20^{o}C, the adsorbed phosphate was retained more by aluminum than by iron. For the same sediment that had been equilibrated with phosphate solution at pH 7.0 and 20^{o}C, the phosphate retaining ability of aluminum reduced while that of iron increased, although the amount of the total aluminum phosphate in the sediment was still greater than the amount of the total iron phosphate.

In recent years, many studies have shown that iron was the major phosphorus adsorbing component in lake sediments, although some authors also found that aluminum was more important than iron in adsorbing added phosphorus (see CHAPTER II). From this study, it is found that both iron and aluminum are important for the adsorption of added phosphate in lake sediments. Their relative importance actually depends on the characteristics of the individual sediments and the environmental conditions they are in. No general conclusions can be applied to all lake sediments.

CHAPTER VI

CONCLUSIONS

From the above studies, the following conclusions can be drawn:

1. The chemical characteristics of the sediments from Lake Warner and Lake Wyola were quite different. While the two sediments were both noncalcareous, the Lake Warner sediment contained more minerals than the Lake Wyola sediment. The former also contained more phosphorus than the latter. This latter fact was related to the different trophic states of the two lakes: Lake Warner was a eutrophic lake and Lake Wyola was a mesotrophic lake.
2. The isotopic exchange method that has been used for the determination of the surface phosphorus in soils was found to be applicable to lake sediments. Using the method, it was found that the Lake Warner sediment contained a greater amount of surface exchangeable phosphorus than the Lake Wyola sediment. This suggested that the sediment in Lake Warner could release P to the overlying water more easily than the sediment in Lake Wyola.
3. The rate of phosphate adsorption by lake sediments was rapid initially and decreased with time. The initial rate was higher at lower pH and at lower temperature. The overall

reaction involved in the phosphate adsorption could have consisted of an initial rapid surface adsorption and a subsequent slower reaction which could be explained by a number of mechanisms including diffusion, crystallization and dissolution/precipitation.

4. The phosphate adsorption capacities of both sediments were affected by pH, temperature and redox potential. The adsorption capacities increased with decreasing pH, decreasing temperature and increasing redox potential. These factors affected the adsorption capacity of the Lake Warner sediment more than they affected the adsorption capacity of the Lake Wyola sediment.
5. Data from the adsorption studies under low redox potential conditions (E_c in the range -216 mv to -274 mv and in the range -110 mv to -220 mv for the Lake Warner and the Lake Wyola sediments, respectively) indicated that the Lake Warner sediment was more sensitive to redox potential than the Lake Wyola sediment. The close relationship between redox potential and the phosphate adsorption capacity of the sediments suggested that redox potential could be a valuable parameter for sediment phosphate adsorption studies.
6. When glucose was used to lower the redox potentials in the lake sediment-water mixtures, the mixtures showed a buffer capacity that resisted the change of pH to lower than 4.8. The buffer system(s) involved might have consisted of the by-

products of biological decomposition of the glucose and the sediment constituents.

7. *The equilibrium phosphate adsorption data for both sediments* could be described by the Langmuir isotherm in the range of phosphate concentration, pH and temperature studied. The adsorption maximums were calculated with and without the surface phosphorus correction. The adsorption maximums were higher at *lower pH and lower temperatures. Langmuir isotherm could also be used to describe the* phosphate adsorption data for sediments under low redox potential conditions (E_c = - 216 mv to -274 mv and -110 mv to -220 mv for the Lake Warner and the Lake Wyola sediments, respectively). For the Lake Wyola sediment, the calculated adsorption maximum for the low redox potential condition was lower than that for the high redox potential condition. But, for the Lake Warner sediment, the reverse was true. Since the Lake Warner sediment was sensitive to the change in redox potential, it is possible that the wide range of redox potential values in which the data points were subjected to had caused some experimental error.
8. The Langmuir adsorption equation and the Langmuir constants derived herein can be used for the derivation of mathematic models which describe the phosphate transport phenomenon between lake sediments and the overlying waters.

9. Oxalate extraction removed a portion of the total iron and aluminum from both sediments. This reduced the phosphate adsorption capacities of the sediments from both lakes appreciably, especially the Lake Wyola sediment. Since it was the amorphous forms of the iron and aluminum that were removed from the sediments, the amorphous iron and aluminum must be the major phosphate-sorbing components in these two sources of sediments.

10. The dissolution of phosphorus, iron and aluminum from the two sediments were pH dependent. Minimal iron was released from the sediments at pH 4.5 to 5.5, and minimal aluminum was released at pH near 5.5. Release of aluminum below pH 5.5 caused no corresponding release of phosphorus from the sediments. This indicated that below pH 5.5, iron could hold back the phosphorus despite the fact that large quantities of aluminum was released. The dissolution curves of iron and aluminum for both sediments were very similar to the solubility curves of FePO and $AlPO_4$, suggesting that the relationships between phosphorus and iron and aluminum in these sediments followed closely the chemistry of $FePO_4$ and $AlPO_4$.

11. Data for the fractionation of the inorganic phosphate in the sediments that had been equilibrated with phosphate solutions showed that for the Lake Warner sediment the adsorbed phosphate was equally distributed between iron and aluminum. This indicated

that in this sediment both iron and aluminum were important for phosphate fixation. For the Lake Wyola sediment at a pH of 4.8 and 20°C, aluminum played a more important role in the fixation of the added phosphate. But as the pH increased to 7.0, the distribution of phosphate became almost equal between iron and aluminum. The relative importance of sediment iron and aluminum in the fixation of the added phosphate was therefore dependent upon the nature of the sediment and the environmental conditions prevailing in the sediment.

12. From the above studies, it seems that for the control of the release of phosphorus from lake sediments, aluminum, especially in amorphous forms, should be an effective agent. The phosphate adsorption data for the Lake Wyola sediment equilibrated under low redox potential conditions indicated that the aluminum in the sediment could hold back the phosphorus on the sediment even when large quantities of iron was released. But, for more effective control of the release of phosphorus from lake sediments, the pH of the sediment should be somehow controlled to a value below 5.5. The technique of using aluminum, iron or calcium for removing phosphate from wastewaters has been well-established. The idea of using these metals for the control of phosphorus in lakes has been proposed by previous authors. In an experiment using

aluminum sulfate for the precipitation of phosphate from the water of a eutrophic lake in Sweden, Jernelöv (1970) found that by adding about 50 gms of granulated aluminum sulfate per cubic meter of the lake volume, the phosphorus concentration in the lake water was greatly reduced. The added advantage with the addition of aluminum sulfate was that the oxygen content of the bottom water became higher during winter ice-cover period. Besides, no release of phosphate from the sediments was observed even under anaerobic conditions.

Lee (1973) proposed an inlake treatment of the water from diffuse sources such as urban storm water drainage, agricultural runoff and ground water, using iron or aluminum for the precipitation of phosphate. Because of the sensitivity to redox potential, iron apparently is not so effective as aluminum for the control of phosphorus release from lake sediments. Although simple in principle for the precipitation of phosphate with aluminum, in actual application of this precipitation technique to a lake many factors should be considered. Among these are the optimal dosage of the aluminum compound to be added to the lake that would both remove the phosphorus in the water and minimize the release of the phosphorus entrapped in the sediment under low redox potential conditions, the season of application, the depth of chemical application and the degree of mixing required to ensure maximal removal, and, most of all, since a lake is a living environment, to minimize the disturbance of the balance of its ecology, one should always fully assess the impact of the addition of the chemical on the aquatic life before the technique is adopted.

CHAPTER VII

RECOMMENDATIONS

1. That equilibrium adsorption studies be conducted using sediments from other locations of the two lakes to determine whether sediments from different locations in the same lake differ in their phosphate adsorption capacities.
2. That the adsorption studies under low redox condition be extended to other pH, temperature and redox potential values using the apparatus devised by Patrick (1966) for close control of pH and redox potential to the desired values.
3. That a detailed study of the applicability of the Langmuir equation to the equilibrium adsorption of phosphate by lake sediments under low redox conditions be conducted.
4. That experiments be conducted to assess the relative importance of sediment iron and aluminum in the fixation of added phosphate by extracting part of the aluminum from the sediment using fluoride and then perform the equilibrium adsorption study. For proper pH and redox potential controls, the apparatus devised by Patrick (1966) could again be used.
5. That the biological effect on the phosphate fixation by the sediments be studied using suitable biocides. (Tests have showed that biccides such as β-propiolactone and tetracycline interfere with the adsorption of phosphate by the sediments and should not be used.)

6. That the nature of the redox potential in the sediments be determined.
7. That the effects of other factors such as size distribution, clay content and organic matter content on the equilibrium adsorption of phosphate by lake sediments be determined.
8. That more quantitative phosphate adsorption data be gathered from other lakes of different characteristics so that a generalization can be made regarding the phosphate adsorption capacities of lake sediments.

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APPENDIX A

Isobutanol Extraction Method for Phosphorus Determination

A. Orthophosphate Determination

All glassware are rinsed in 2N sulfuric acid, then stored under deionized water. The acid rinse is needed only when the glassware is initially prepared and after every ten or twelve runs.

Mixed reagent: 50 ml 5 N sulfuric acid

20 ml Ammonium Molybdate solution (15 gm Ammonium Molybdate in 500 ml dionized water) - store in plastic bottle at 4^{o}C.

10 ml Potassium Antimony Tartrate solution (0.34 gm in 500 ml deionized water).

1.08 gm Ascorbic Acid dissolved in 20 ml deionized water - prepare daily.

Mix the above constituents in the order given to make the mixed reagent. This reagent is to be prepared fresh each time; the unused portion is to be discarded.

Control Stock Solution: 5.3 ppb-P

Procedure:

1. Transfer 100 ml of each sample to a separatory funnel. Samples A and B are to be deionized water and control stock solution respectively.
2. Add 10 ml of the mixed reagent to each separatory funnel. Shake each funnel vigorously for one minute immediately after the reagent is added.

3. Add 20 ml isobutanol to each separatory funnel and shake the funnel vigorously for one minute immediately after the addition.
4. After all the isobutanol has been added to the funnels and shaking has been effected, shake each funnel once more in turn for one minute.
5. Separate the organic layer (top) from the water layer and discard the water layer. Transfer the organic layer directly to respective calorimeter tubes to which have been added each .8 ml 95 percent ethanol.
6. Swirl tubes to insure mixing of the butanol and ethanol and measure transmittance against the deionized sample at 690 millimicrons. Remember to use the red tube and filter for this measurement. Estimate measurement to 1 percent transmittance.

   (Source: Snow and DiGiano, 1973).

B. Total Phosphorus Determination

1. Add 1 ml of strong-acid solution (310 ml of concentrated H_2SO_4 diluted to 1 liter with distilled water) to a 50 ml sample in a 125 ml Erlenmeyer flask.
2. Add 0.4 gram of ammonium persulfate.
3. Boil gently on a pre-heated hot plate for approximately 30-40 minutes or until a final volume of about 10 ml is reached. Do not allow sample to go to dryness.
4. Add phenolphathalein and adjust sample to pink with 1N NaOH. Bring back to colorless with one drop of strong acid solution. Cool and dilute the sample to 100 ml. If sample is not clear at this point, filter.

5. Determine phosphorus according to the procedures outlined in (A) for orthophosphate.

   (Source: Methods for Chemical Analysis of Water and Wastes (EPA, 1971).)

APPENDIX B

Preparations for Counting Radioactivity Using Liquid Scintillation Technique

A. Determination of Optimal Combination of Sample, BioSolve and Scintillator System.

To a series of polyethlene vials, different volume combinations of the scintillator system and the BioSolv were first added, followed by one ml of a P^{32} solution. The contents of the vials were well mixed and counted for activities immediately using the Beckman LS-100 Liquid Scintillation System. The values of the activity counts were compared. The volume combination that gave the maximum number of counts per minutes for the same amount of added P^{32} was considered to be the optimal combination.
After a number of tryings, it was determined that the optimal combination was: 1 ml P^{32} sample solution + 1.65 ml BioSolv + 9 ml scintillator system (Figure B-1).

B. Preparation of Quench Calibration Curve.

Theprocedures for the preparation of a quench calibration curve for the Beckman LS-100 Liquid Scintillation System are as follows:

1. To a series of vials, add 0.025 ml of a P^{32} solution of known activity, followed by 9 ml of the scintillator system and from 0.1 ml to 1.7 ml of BioSolv.
2. To the vials add, in increasing amount from 0 to 1 ml, of distilled water to simulate the aqueous quench, and add, from 0 to several drops, of chloroform to simulate other types of quench.

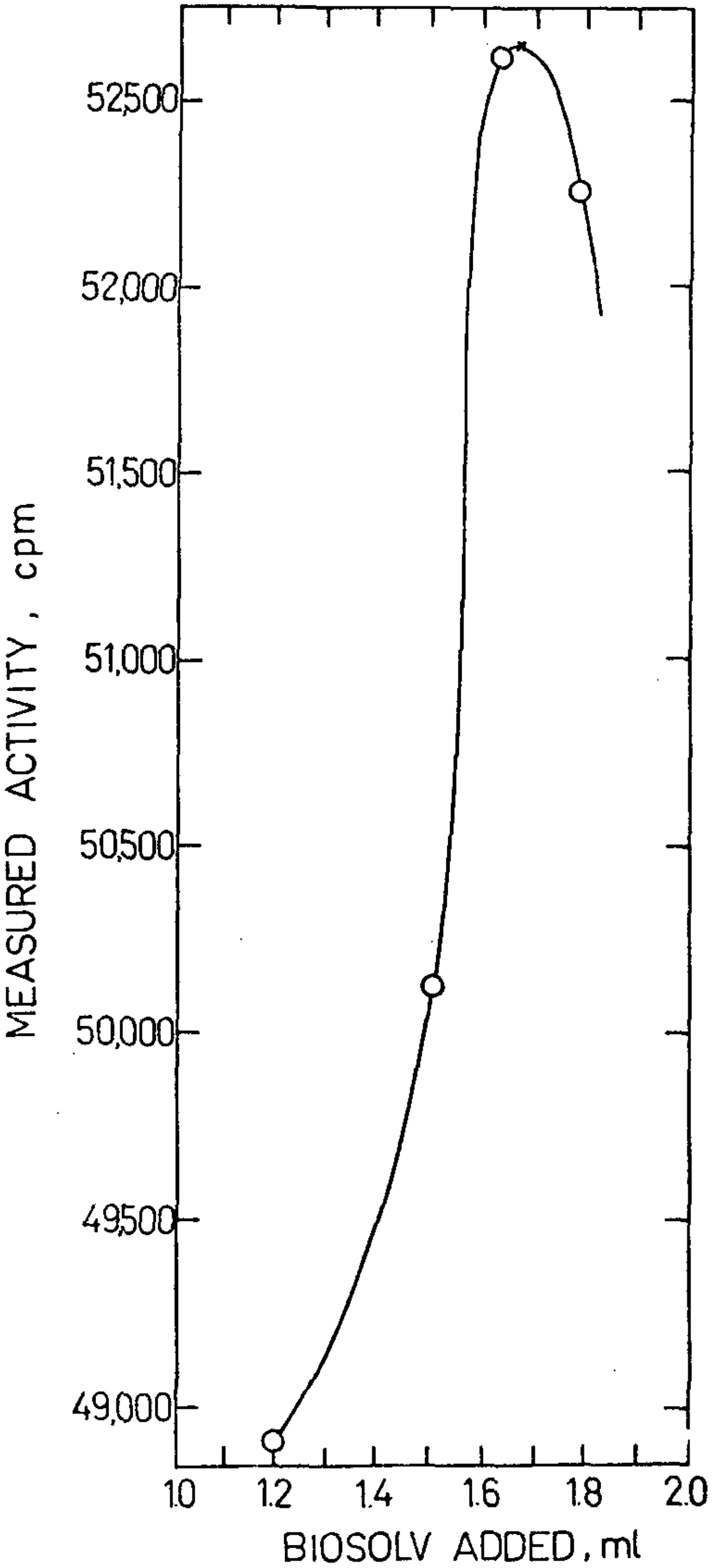

Figure B-1. Determination of Optimal Amount of BioSolv N Needed for 9 ml of Scintillator and 1 ml of Sample.

3. Mix the contents of the vials and count the activity using the Beckman LS-100 Liquid Scintillation System. Record the number of counts per minute and the External Standard Ratio for each sample.
4. Based on the known activity of the P^{32} solution added to each vial initially (i.e. the value of disintegrations per minute, DPM) and the actually measured counts per minute (CPM), the counting efficiency for the sample in each vial can be calculated by the following definition.

$$\text{Counting Efficiency} = \frac{\text{CPM}}{\text{DPM}} \tag{24}$$

5. Plot the counting efficiency against the corresponding External Standard Ratio for each sample. A curve best fitting all such points is the desired quench calibration curve (Figure 3).

C. Natural Decay and Background Corrections

Natural Decay. P^{32} has a half life of 14.29 days. Since the experiment for the surface phosphorus determination lasted 14 days, it was necessary to consider the loss of activity of P^{32} due to natural decay in all the calculations. The decay of a radioactive atom is a first order reaction and can be expressed by the following equation

$$N = N_o e^{-\lambda t} \tag{25}$$

where N_o = original number of atoms present (or, original DPM)

N = number of atoms remaining at time t (or, DPM at t)

λ = decay constant which is related to the half life, $t_{1/2}$, by equation

$$\lambda = 0.693/t_{1/2} \tag{26}$$

for P^{32},

$\lambda = 0.0485\ (\text{day}^{-1})$.

Background. In counting the radioactivity of a sample, some of the total counts are caused by the background radiations which are produced by cosmic radiation, natural radioactivity in the building, etc.. The background count must be subtracted from the gross count of a sample to give the net activity of the sample. For determining the background count, 1 ml of distilled water was used to replace the 1 ml of the P^{32} sample to be added to the vials for activity counting. The background radiation was determined at the beginning and at the end of each sample counting period. The average of the two counts was considered the background count at that particular period.

APPENDIX C Results for Equilibrium Adsorption of Inorganic Phosphate by Lake Sediments under Aerobic Condition

Table C-1. Results for Equilibrium Adsorption of Inorganic Phosphate by Lake Warner Sediment Under Aerobic Condition at 20°C and pH 7.0

		Concentration in Final Solution			
Sample Number	P Added mg	Soluble Orthophosphate, ppm-P	Soluble Total Phosphorus, ppm-P	Soluble Total Iron, ppm-Fe	E_c, mv
1a	0	0.220	0.232	0.45	
1b	0	0.228			370
1c	0	0.206			
2a	0.25	0.355	0.348	0.44	
2b	0.25	0.365			360
2c	0.25	0.348			
3a	0.50	0.600	0.565	0.44	
3b	0.50	0.600			370
3c	0.50	0.620			
4a	1.00	1.50	1.45	0.58	
4b	1.00	1.38			380
4c	1.00	1.39			
5a	2.00	3.84	3.84	0.60	
5b	2.00	3.84			380
5c	2.0	3.85			
6a	3.00	7.24	7.40	0.50	
6b	3.00	7.24			380
6c	3.00	7.24			

Table C-2. Results for Equilibrium Adsorption of Inorganic Phosphate by Lake Warner Sediment Under Aerobic Condition at 20°C and pH 5.5

		Concentration in Final Solution			
Sample Number	P Added, mg	Soluble Orthophosphate, ppm-P	Soluble Total Phosphorus, ppm-P	Soluble Total Iron ppm-Fe	E_c, mv
1a	0	0.036	0.037	0.02	452
1b	0	0.036			
1c	0	0.038			
2a	0.25	0.062	0.063	0.04	
2b	0.25	0.057			453
2c	0.25	0.060			
3a	0.50	0.083	0.088	0.03	
3b	0.50	0.083			456
3c	0.50	0.083			
4a	1.0	0.202	0.216	0.04	
4b	1.0	0.202			453
4c	1.0	0.204			
5a	2.0	1.075	1.080	0.04	
5b	2.0	0.960			452
5c	2.0	1.055			
6a	3.0	2.91	3.05	0.02	
6b	3.0	2.79			453
6c	3.0	2.91			

Table C-3. Results for Equilibrium Adsorption of Inorganic Phosphate by Lake Warner Sediment *Under Aerobic Condition at 20^{0}C and pH 4.8*

Sample Number	P added, mg	Concentration in Final Solution: Soluble Ortho-phosphate, ppm-P	Soluble Total Phosphorus, ppm-P	Soluble Total Iron, ppm-Fe	E_c, mv
1a	0	0.014	0.018	0.04	455
1b	0	0.014			
1c	0	0.012			
2a	0.25	0.019	0.019	0.04	455
2b	0.25	0.022			
2c	0.25	0.020			
3a	0.50	0.029	0.034	0.03	465
3b	0.50	0.029			
3c	0.50	0.026			
4a	1.00	0.059	0.059	0.03	-
4b	1.00	0.054			
4c	1.00	0.058			
5a	2.00	0.260	0.270	0.04	461
5b	2.00	0.264			
5c	2.00	0.263			
6a	3.00	0.985	1.008	0.04	464
6b	3.00	1.012			
6c	3.00	0.995			

Table C-4. Results for Equilibrium Adsorption of Inorganic Phosphate by Lake Warner Sediment Under Aerobic Condition at 11°C and pH 7.0

Sample Number	P added, mg	Concentration in Final Solution Soluble Ortho-phosphate, ppm-P	Soluble Total Phosphorus, ppm-P	Soluble Total Iron, ppm-Fe	E_c, mv
1a	0	0.079	0.085	0.16	
1b	0	0.113			333
2a	0.50	0.224	0.259	0.28	327
2b	0.50	0.231			
3a	1.00	0.645	0.640	0.28	
3b	1.00	0.620			332
4a	2.00	2.515	2.59	0.44	325
4b	2.00	2.600			
5a	3.00	5.70	5.94	0.40	310
5b	3.00	5.46			

Table C-5. Results for Equilibrium Adsorption of Inorganic Phosphate by Lake Warner Sediment Under Aerobic Condition at 11°C and pH 5.5

Sample Number	P added, mg	Concentration in Final Solution: Soluble Ortho-phosphate, ppm-P	Soluble Total Phosphorus, ppm-P	Soluble Total Iron, ppm-Fe	E_c, mv
1a	0	0.016	0.025	0.03	415
1b	0	0.015			
2a	0.50	0.053	0.064	0.03	410
2b	0.50	0.053			
3a	1.00	0.146	0.162	0.03	
3b	1.00	0.146			415
4a	2.00	0.854	0.860	0.04	405
4b	2.00	0.940			
5a	3.00	2.72	2.81	0.04	415
5b	3.00	2.90			

Table C-6. Results for Equilibrium Adsorption of *Inorganic Phosphate by Lake Wyola Sediment* Under Aerobic Condition at 20°C and pH 7.0

		Concentration in Final Solution			
Sample Number	P added, mg	Soluble Orthophosphate, ppm-P	Soluble Total Phosphorus, ppm-P	Soluble Total Iron, ppm-Fe	E_c, mv
1a	0	0.022	0.150	0.98	390
1b	0	0.046			
2a	0.50	0.154	0.244	0.88	-
2b	0.50	0.150			
3a	1.00	0.473	0.563	0.88	-
4a	2.00	2.02	2.14	1.06	-
4b	2.00	1.91			
5a	3.00	4.32	4.62	1.16	-
5b	3.00	4.04			

Table C-7. Results for Equilibrium Adsorption of Inorganic Phosphate by Lake Wyola Sediment Under Aerobic Condition at 20°C and pH 6.0

		Concentration in Final Solution			
Sample Number	P added, mg	Soluble Orthophosphate, ppm-P	Soluble Total Phosphorus, ppm-P	Soluble Total Iron, ppm-Fe	E_c, mv
1a	0	0.012	0.012	0.20	440
1b	0	0.010			
1c	0	0.011			
2a	0.25	0.018	0.020	0.18	
2b	0.25	0.019			440
2c	0.25	0.018			
3a	0.50	0.034	0.040	0.16	
3b	0.50	0.036			442
3c	0.50	0.036			
4a	1.00	0.094	0.100	0.16	
4b	1.00	0.095			442
4c	1.00	0.085			
5a	2.00	0.534	0.576	0.20	
5b	2.00	0.508			440
5c	2.00	0.552			
6a	3.00	1.875	1.885	0.26	
6b	3.00	1.850			441
6c	3.00	1.905			

Table C-8. Results for Equilibrium Adsorption of Inorganic Phosphate by Lake Wyola Sediment Under Aerobic Condition at 20°C and pH 5.5

Sample Number	P added, mg	Concentration in Final Solution: Soluble Ortho-phosphate, ppm-P	Soluble Total Phosphorus, ppm-P	Soluble Total Iron, ppm-Fe	E_c, mv
1a	0	0.006	0.011	0.04	456
1b	0	0.003			
2a	0.50	0.010	0.013	0.04	448
2b	0.50	0.008			
3a	1.00	0.027	0.044	0.02	448
4a	2.00	0.160	0.180	0.05	455
4b	2.00	0.160			
5a	3.00	0.670	0.620	0.07	450
5b	3.00	0.670			

Table C-9. Results for Equilibrium Adsorption of Inorganic Phosphate by Lake Wyola Sediment Under Aerobic Condition at 20°C and pH 4.8

Sample Number	P Added, mg	Concentration in Final Solution			E_c, mv
		Soluble Orthophosphate, ppm-P	Soluble Total Phosphorus, ppm-P	Soluble Total Iron, ppm-Fe	
1a	0	0.002	0.003	0.02	460
1b	0	0.002			
2a	0.50	0.006	0.008	0.02	440
2b	0.50	0.006			
3a	1.00	0.013	0.014	0.02	450
3b	1.00	0.010			
4a	2.00	0.044	0.045	0.02	460
4b	2.00	0.046			
5a	3.00	0.170	0.177	0.02	462
5b	3.00	0.165			

Table C-10. Results for Equilibrium Adsorption of Inorganic Phosphate by Lake Wyola Sediment Under Aerobic Condition at 11°C and pH 6.0

		Concentration in Final Solution			
Sample Number	P added, mg	Soluble Orthophosphate, ppm-P	Soluble Total Phosphorus, ppm-P	Soluble Total Iron, ppm-Fe	E_c, mv
1a	0	0.008	0.012	0.10	430
1b	0	0.008			
2a	0.50	0.017	0.020	0.16	453
2b	0.50	0.015			
3a	1.00	0.052	0.132	0.20	440
4a	2.00	0.342	0.332	0.20	440
4b	2.00	0.314			
5a	3.00	1.270	1.305	0.26	439
5b	3.00	1.235			

Table C-11. Results for Equilibrium Adsorption of Inorganic Phosphate by Lake Wyola Sediment Under Aerobic Condition at 11°C and pH 5.5

		Concentration in Final Solution			
Sample Number	P added, mg	Soluble Orthophosphate, ppm-P	Soluble Total Phosphorus, ppm-P	Soluble Total Iron ppm-Fe	E_c, mv
1a	0	0.005	0.008	0.08	443
1b	0	0.005			
2a	0.50	0.008	0.012	0.08	453
2b	0.50	0.009			
3a	1.00	0.016	0.020	0.08	452
4a	2.00	0.144	0.170	0.10	450
4b	2.00	0.106			
5a	3.00	0.570	0.570	0.12	450
5b	3.00	0.535			