PHOSPHORUS AND IRON CONTENT, REDOX POTENTIAL AND PHOSPHORUS FRACTIONATION OF LAKE SEDIMENT - WATER INTERFACES

Thesis for the Degree of M. S.
MICHIGAN STATE UNIVERSITY
DENNIS B. FENN
1970

PHOSPHORUS AND IRON CONTENT, REDOX POTENTIAL AND PHOSPHORUS FRACTIONATION OF LAKE SEDIMENT-WATER INTERFACES

By

Dennis B. Fenn

AN ABSTRACT OF A THESIS

Submitted to

Michigan State University
in partial fulfillment of the requirements
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Department of Crop and Soil Sciences

1970

ABSTRACT

PHOSPHORUS AND IRON CONTENT, REDOX POTENTIAL AND PHOSPHORUS FRACTIONATION OF LAKE SEDIMENT-WATER INTERFACES

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Six lakes of widely varying quality were sampled at 5 or 6 depths at 3 m intervals in June 1969, October 1969, and June 1970.

The first objective was to study the effects of a reducing environment upon the solubility of P. The second objective was to determine the forms in which P is stored when sorbed by the sediment and the degree to which it might be soluble under a reducing environment.

The sediment-water interface was analyzed for Eh, P and Fe immediately after sampling and after 30 days of anaerobic incubation. It was found that anaerobic incubation increased the level of P in solution. Regression analysis yielded the equation $P_I = 3.51 P_S + .09$ where P_S = P at sampling time and P_I = P after incubation, indicating that a 3.5 fold increase in P would be predicted during anaerobic incubation. In samples aerobically incubated for 30 days it was found that those originally low in P, below .445 ppm, also showed an increase in P during incubation. For those samples with more than .445 ppm P, aerobic incubation caused a decrease in P solubility.

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Redox potentials were shown to have a qualitative influence upon both P and Fe in the lake waters, but the data would not support the view that Eh quantitatively controls the levels of P and Fe in solution.

The P forms in the lake sediments were fractionated according to the revised method of Chang and Jackson. Al-P and Fe-P levels were much lower than in most mineral soils. Ca-P levels were similar to many Michigan soils but lower than expected in the marl lake bottoms. Reductant soluble-P predominated in the sediments, reaching a maximum average of 591.9 ppm in Fenton Lake. This is much higher than is found in most mineral soils. This fraction is assumed to be reductant soluble Fe-P according to Chang and Jackson. The levels of total P extracted are much too high to have been contributed simply by the deposition of eroded agricultural soil alone. Considerable P must have been fed into the lakes from sources such as municipal discharges, industrial effluents and septic drain fields of bordering homes. Sediments are capable of adsorbing considerable quantities of P and can serve as a buffer upon the level of P in solution. The fact that the predominant storage form of P is reductant soluble-P is important because this form can become readily soluble under the reducing conditions produced at the bottoms of many lakes.

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To JACQUE

This thesis is dedicated to my wonderful wife for without her support, understanding, compassion, inspiration, patience and active interest, this study would have been an impossibility.

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The author expresses sincere appreciation to his major professor, Dr. B. G. Ellis, for his interest, guidance and support during this study. His knowledge and interest in science has been a great inspiration.

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Thanks is expressed to my wife for her efforts in typing this manuscript.

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INTRODUCTION

The pollution of our environment, especially our lakes and streams, has come to the point where practically every body of water in America is showing signs of eutrification. The awakening public concern about this tragic occurrence and its potential effect on the human population has greatly increased the need to determine the chief factors involved in the degradation of our aquatic environment. Phosphorus (P) has been found to be a very limiting nutrient in the eutrification process. When P levels in solution are low, algal blooms and higher plant growth is restricted--the water remains pleasing for recreational and municipal uses. But as the input of P increases, water becomes choked with algae scum and weed growth and the fish population degrades to scavengers and undesirable species--the water is no longer of great value to man.

The huge amounts of P fertilizer applied to our agricultural lands and the potential erosion of our fertile topsoil each year has brought condemnation upon agriculture as a chief cause of the pollution of America's waterways. The research conducted up to the present time has not totally relieved this condemnation, but it has shown that an even more important source of pollution is our industrial plants and their discharges. However, the chief source of P in our waters has been determined to be the sewage effluents of our cities, many of whom still dump raw, untreated sewage into streams and rivers. Most present day sewage treatment plants do not have the capacity to adequately remove the levels

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of P that are in the sewage. The average person in this country discharges 3.5 lbs P/year. Of this amount, 1 lb is from waste and 2.5 lbs are from detergents. Detergents on the market today contain from 0 - 53% PO_4, and water softeners such as calgon contain up to 70% PO_4.

Pollution by P from agriculture is still very real. Although P is very immobile in the soil and ground water seepage into lakes and streams adds little total P, areas of intense irrigation have large volumes of runoff which may contain P concentrations of up to 0.08 ppm P which is sufficient to support an extensive algal bloom. Studies over many years have noted that as much as 82% of the P added as fertilizer may ultimately be lost by erosion on some soils (Taylor, 1967), but this is an extreme condition. Most agricultural land today is well protected against erosion by proper conservation practices, and the losses of P by erosion are much lower than in Taylor's study. Losses from cattle feedlots, especially in winter when runoff is increased due to the frozen ground, can be very large and very damaging to the water environment.

The objectives of this study were to: (1) study the effects of a reducing environment upon the solubility of P; (2) determine the forms that most P is stored in when sorbed by sediments; and, finally (3) study the influence of laboratory controlled redox potentials upon the solubility of P.

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LITERATURE REVIEW

Redox Potentials

The application of the concept of oxidation-reduction potentials to a soil system has been tried by numerous researchers; but they have met with, at best, only limited success. As will be seen below, contrasting conclusions have been reached by various workers as to usefulness of redox measurements as a valid analytical tool.

Jeffery (1961) found that he could differentiate between oxidized and reduced soils with Eh measurements, but the error was too great to yield precise information about the state of reduction of the waterlogged soil. He also felt that the large experimental error made it of little value to correct for pH change. He suggested that a more accurate estimation of the state of reduction of a soil could be obtained by determining the concentrations of the two oxidation states of iron in the soil. He developed the equation $Eh = 1.032 - 0.0601 \log C_{Fe} - 0.180pH$ (30 C) as being applicable to waterlogged soils.

In another paper, Jeffery (1961) expanded his equation and ran experiments in an effort to define oxidizing conditions, healthy reducing conditions, and extreme reducing conditions in quantitative terms. Using the above equation, he developed the term $r_h = Eh + 0.180pH$ and calculated the values $r_h > 1.34$ volts for oxidizing conditions, $r_h = 1.27 - 1.21$ volts for healthy reducing conditions and $r_h < 1.15$ volts for extreme reducing conditions.

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Ponnamperuma, Tianco, and Loy (1967) found, in a 17 week study, that the quantitative treatment of redox equilibria in a complex system such as a flooded soil was difficult because: (1) the highly dynamic nature of the flooded soil prevents the attainment of a stable, true equilibria; (2) uncertainty about which of a large number of possible redox systems is operating at a given time; (3) the lack of thermodynamic data on the transition substances present in the soils that undergo reversible oxidation-reduction; (4) complex formation which may alter redox equilibria between inorganic ions; and (5) the uncertainty about the true potential of a reduced soil--the soil potential or the potential of the soil solution. However, they were able to determine that the equation $Eh = 1.058 - 0.059 \log Fe - 0.177pH$ held for most of the 17 weeks of submergence. They proposed that the participation of the metastable compounds $Fe(OH)_3$ and $Fe_3(OH)_8$ in the equilibria was confirmed by their findings, indicating that the soil solution was the thermodynamically meaningful phase.

Yamane and Sato (1968) conducted a series of experiments to determine the best way to get reproducible values of redox potentials of submerged soils. They found that the area of the electrode was related to the measured Eh values. The smaller the area of the electrode, the slower was the soil Eh value reached. Therefore, they felt that platinum electrodes should be at least 100 mm^2 in area. Even with such large electrodes, it was necessary for the electrode to be in contact with the soil for longer than 6 hours and in most cases at least 24 hours to obtain reproducible results.

Bohn (1968) attempted to relate the emf of gold, graphite and platinum electrodes in soil suspensions to electrode potentials of redox couples in the soil but was unsuccessful. He found that E_{Au} and E_C did not respond to aeration of the suspension or to the presence of sucrose as a reducing agent. E_{pt} did respond to these conditions but did not correspond to the electrode potentials of the Mn^{+2} – Mn oxide, O_2 - H_2O, or H^+ - H_2 couples. He concluded that E_{pt} is a mixed potential whose major components are the O_2 - H_2O couple in aerated suspensions, but whose value is not related to the Nernstian distribution of oxidized and reduced species. Although E_{pt} is a qualitative measure of the oxidation, it has no quantitative meaning according to Bohn. He used a 1:10 soil-water suspension in his experiments; however, and at the low redox potentials measured, there was not enough total manganese in the soil to respond quantitatively to the potential as predicted by the Nernstian expression. This could also account for why no appreciable quantitative relationship was found.

In a review of the topic of redox potentials, Bohn (1970) notes that the limit of oxidizing conditions in an aqueous system is the oxidation of water to molecular oxygen (O_2) and that the limit of reducing conditions in an aqueous system is the reduction of hydrogen ion to molecular hydrogen (H_2). The redox potential or electron availability affects the oxidation states of H, C, N, O, S, Mn, Fe, Co, and Cu in aqueous systems. But for the oxidation-reduction limits upon the stability of water, the list could be extended to include the entire periodic table.

Bohn states that the reason redox measurements have been found wanting in soil systems is because the soil redox potential is often a nonequilibrium potential rather than an equilibrium potential upon which the Nernst equation is based. Natural systems rarely reach oxidation-reduction equilibrium because of the continual addition of oxidizable organic matter. Being a mixed potential, redox potential measurements are quantitatively unrelated to the Nernstian distribution of ion oxidation states. In oxidized systems, the low concentration of redox couples decreases the stability, reproducibility and general usefulness of redox potential measurements. In reduced systems, the higher concentrations of redox couples increase the stability and utility of redox measurements.

It is apparent that Bohn disagrees with the conclusions of Jeffery and Ponnamperuma that quantitative expressions can be applied to redox measurements in a soil system. They all agree, however, that certain ionic substances respond to oxidation and reduction potential changes. The debate remains in whether or not equilibrium is ever obtained between the redox couples and Eh.

Phosphorus and Reducing Conditions

Bartholomew (1931) found that flooding a soil caused a disappearance of soluble soil P and suggested that it may have been due to the reversion of soluble inorganic P to an organic form that is not available to plants. He noted an increase in water soluble organic P after three months of flooding which could have been produced by anaerobic bacterial action. The water used for irrigation was high in $Ca(HCO_3)_2$. The amounts of soluble Ca, Fe, and Al added annually by the irrigation water were sufficient to have caused the reversion of large amounts of soluble P.

Gasser (1956) noted that waterlogging soils caused an increase in acid soluble P. This increase could be attributed to the reduction of ferric phosphate to ferrous phosphate. Gasser proposed that in assessing the P status of rice soils, the ferric phosphate should be considered as an "available" form.

Hayes and Phillips (1958) reported that the redox potential had little or no effect upon the level of P in solution. They felt that the biological

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system was the controlling factor and that the inorganic chemical system was secondary in importance. After waterlogging a series of soil samples and administering antibiotics to quench the biological system, 10 out of 12 of the soil samples showed an increase in P under reducing conditions; but, in 4 out of the 10, the difference was less than 5%. They concluded that these results indicated the minor influence of the inorganic reducing system upon P levels in solution.

Shapiro (1958) showed that flooding caused an increase in soil P availability. He noted that applied P was utilized more efficiently under flooded conditions. These results held for soils high, moderate, and low in native P. His data showed that the increased P availability came from both the Fe-P and Al-P fractions but that the Fe-P fraction was affected to a much greater degree. He proposed that the small increase in Al-P availability was probably due to a chelation reaction. The large increase in Fe-P availability was due to the reducing conditions brought on by the addition of organic matter and flooding the soil.

Mandal (1964) tested the effects of starch and lime on the availability of P in a waterlogged soil and found that waterlogging a soil only slightly increased acetic acid soluble P with a slight decrease in Fe-P and no change in the Al- or Ca-P. When starch was added, however, a considerable increase in acid soluble P and a decrease in the Ca-P fraction occurred. He stated that the release of large amounts of CO_2 formed during starch decomposition may have caused tricalcium phosphate to convert to more soluble di- and mono- calcium phosphates. The addition of lime caused a decrease in Fe- and Al-P, especially Fe-P. Ca-P was increased appreciably, the effect seeming to be a conversion from Fe-P to Ca-P upon liming.

Mandal suggested that in acid soils having most of their inorganic phosphorous in the ferric form, liming followed in a few days by the addition

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of organic matter will result in an increase in P under waterlogged conditions.

He further found that even after 105 days of waterlogging, the Al-P fraction remained unchanged. The Ca-P fraction showed results similar to the Al, except in very high organic matter soils where CO_2 evolution was high enough to be important. His data did not support the view that the increased availability of soil P upon waterlogging is largely due to the reduction of ferric phosphates. The available data suggested that the reduction of ferric phosphates did not occur to any great extent or that if it did proceed, a reversion reaction with Fe^{+3} in the soil occurred at almost an equal rate.

Patrick (1964) found that extractible ferric and ferrous forms of Fe were very sensitive to changes in redox potential of the soil. Ferric Fe predominated at potentials above +200 millivolts, and extractible Fe was mostly ferrous below +200 millivolts. At the same time, he found that extractible P increased over threefold between redox potentials +200 and -200 millivolts. The sharp break in the phosphate release curve at +200 millivolts, the same point at which ferric Fe began to be reduced, indicates that the conversion of P to an extractible form is dependent upon the reduction of ferric compounds in the soil.

Broeshart, Haunold, and Fried (1965) noted that flooding significantly increased the availability of soil P in rice soils in which free $CaCO_3$ is absent. The reduced availability of phosphates under upland conditions was not enough to account for the reduced growth of rice under upland conditions in their opinion, however. They also found that the availability of fertilizer P was similar under reduced or oxidized conditions but that the efficiency of use was greater under flooded conditions.

Williams and Simpson (1965), in conducting experiments on cultivation and waterlogging, found that waterlogging for 1 - 2 days produced anaerobic conditions that caused a decrease in P availability and an increase in the sorption capacity. This reduced P availability applied both to soil P and applied P. They concluded that the decrease in P availability upon waterlogging was due to the effects of certain reactions during the waterlogging treatment. Reducible metals such as Mn could have interfered; the nature of the sorption sites may have been altered due to Fe reduction causing P to be more tightly bound; or, some of the P sorbed could have been occluded by reprecipitation of Fe upon restoration of aerobic conditions. They felt that the increases in soil P availability upon waterlogging as noted by several researchers, must be due to the presence of easily reducible ferric phosphate. In soils low in ferric phosphates, a decrease in P availability should be noted.

Chiang (1968) noted that soils rich in organic matter showed rapid lowering of Eh and increased formation of organic acids and gases. Disintegration of soil aggregates and lowered Eh values caused an increase in P solubility. These effects were more significant in Fe rich soils. H_2, H_2S and the organic acids, especially HOAc, increased P solubility in Fe and Al rich soils. CO_2 increased Ca-P solubility.

Chakravarti and Ghoshal (1968) mixed two acid soils with 50% dried grass and each of the following treatments: (1) Fe-P; (2) Al-P; or (3) Fe- and Al-P. Then they waterlogged and incubated the samples at room temperature for 53 days. The amount of P released was found to be greatest in the Fe phosphate treatment followed by Fe and Al phosphate treatment, Al phosphate, and the control in decreasing order.

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Patrick and Mahapatra (1968) and Mahapatra and Patrick (1969) showed that the greatest change in a P fraction between a soil under flooded conditions and under aerobic conditions occurs in the reductant soluble fraction. When placed under waterlogged conditions the reductant soluble fraction was greatly decreased, indicating that the ferric oxide coating on the P had been reduced to a soluble ferrous oxide and the P released to the solution. The mechanism of P release in a flooded soil may be explained by: (1) reduction of ferric phosphate to soluble ferrous phosphate; (2) release of occluded P by reduction of ferric oxide coating; (3) displacement of P from Fe- and Al-P by organic anions; (4) hydrolysis of Fe- and Al-P; and (5) anion (phosphate) exchange between clay and organic anions. They warn, however, that resorption processes and refixation by unreduced ferric Fe processes can occur and waterlogging will not always increase available P.

Furukawa and Kawaguchi (1969) submerged paddy soil samples for two weeks at 40 C and obtained up to a 21% decrease in organic P. This decrease correlated well with the increase of easily soluble P (Bray No. 2) and was attributed to the mineralization of organic P. This increased mineralization was thought to be due to the enhanced solubility of the Fe or Al salts of inositol hexaphosphoric acid, the predominant organic P constituent, by reducing conditions or pH rise, and rapid hydrolysis accompanying submergence.

Terman, Allen, and Engelstad (1970) conducted greenhouse pot experiments with flooded rice on a soil which was low in available P for upland crops. Marked yield responses by rice to applied P were obtained, but maximum yields were obtained at much lower rates of applied P than was true for most upland crops. Response to applied P decreased with liming of the soil and with increasing levels of acid soluble soil P. Granular, water soluble sources were most effective. The P in Fe-P was more available than that in Al-P in the flooded soil. Both forms were more available in fines than as granules and in colloidal form rather than as fine crystals.

Sediments and Phosphorus

Hayes and Phillips (1958) proposed that there is a single pool of P belonging to lake water and solids which is distributed between them in a dynamic equilibrium or steady state. This dynamic equilibrium might be represented as:

$$\begin{array}{l}\text{P in aqueous phase, a small}\\ \text{fraction of the whole}\end{array} \leftrightarrows \begin{array}{l}\text{P in solid phase, a large}\\ \text{fraction of the whole,}\end{array}$$

with a constant value for each phase but a continuous exchange between them. The level of productivity, the state of oxidation and reduction, and the presence of green plants and bacteria all work together to produce the observed equilibrium.

Hayes and Phillips concluded that bacteria are decisive and can, to a considerable degree, suppress the classical inorganic mechanism of oxidation-reduction that has been proposed by many as the controlling factor in P release and availability.

Pomeroy, Smith, and Grant (1965) found that the exchange of P between water and sediment was a combination of a sorption reaction and a biologically controlled exchange. Their observations supported the view that sediments act to buffer the P content of water. They estimated the daily exchange across an undisturbed sediment boundary to be 1 μmole PO_4/m^2. For sediments being stirred by wave action, the exchange is greater. In their opinion, this rate of release from the sediments is sufficient to support a continuous growth of plankton and that it is a continuous and rapid release tha

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release that is not responsive to certain P limits within the water.

Harter (1968) noted that lake sediment possessed a tremendous capacity to adsorb P from solution. He added P to a sediment sample (1:50 soil-water ratio) and allowed equilibrium to be reached. He then extracted the sediment with 0.5N NH_4F to extract Fe-P and found that about half the freshly adsorbed P could be recovered in this way. He also discovered that the NH_4F extraction contained a considerable amount of labile or loosely bound P and that this labile P could also be removed by successive water extractions. His conclusions were that the sediment could sorb much of the P in this labile form and that it can be re-released in a few hours, days, or weeks for use by plants and algae. Hence, large influxes of P may be intercepted and stored for use over a period of time.

Frink (1969) found that many of the sediment characteristics were highly correlated with depth of water. P increases in solution as depth increases. A correlation coefficient of 0.68 existed between depth of water and total P in solution. In his fractionation of the sediment, he found that Al-P, reductant soluble P, and Fe-P all increased with depth and had correlation coefficients of 0.80, 0.85, and 0.90 respectively. The Ca-P fraction decreased with depth, however, and had a correlation of 0.52. Frink found that Ca-P correlated with the coarser sediments. The lake samples showed a particle size gradation of coarse (sandy) to fine (silt, clay, organic matter) from the bank to the center of the lake. This accounts for the decrease in Ca-P with depth. Most of the changes in physical characteristics are attributed to particle size sorting during transport and deposition within the lake. He noted a shift of stored phosphates from Al-P and Fe-P to Ca-P when sediments from acid soils were deposited in neutral lakes.

MATERIALS AND METHODS

Sediment Sampling

The necessity of obtaining a relatively undisturbed sample of the sediment-water interface that would be suitable for analysis posed some interesting problems. It had to be accomplished without introducing air into the sample or the redox readings would be invalid. After reviewing the literature on sampling methods and personally contacting several agencies involved in water quality research, it was decided that a small sampler developed at the Gull Lake research station would best suit our purposes. A schematic drawing of the sampler is shown in Figure 1.

The irrigation valve allows water to flow through as the sampler is dropped. This helps keep the sampler upright and also insures that the water picked up comes from the mud-water interface and not some other point nearer the surface. This valve seals when the sampler is lifted toward the surface. This prevents mixing and also forms a suction that holds the sample in the tube as the apparatus is hoisted to the surface. The sampler is small enough that the entire operation can be performed from a canoe. Once at the surface, the sampler is placed onto a number 13 stopper which has been mounted on a bolt in the bottom of a galvanized bucket. This stopper will go inside the sampler head and lodge in polyethylene tube. Then the sampler is disassembled leaving only the sample in the polyethylene tube mounted on the stopper. The tube is carefully

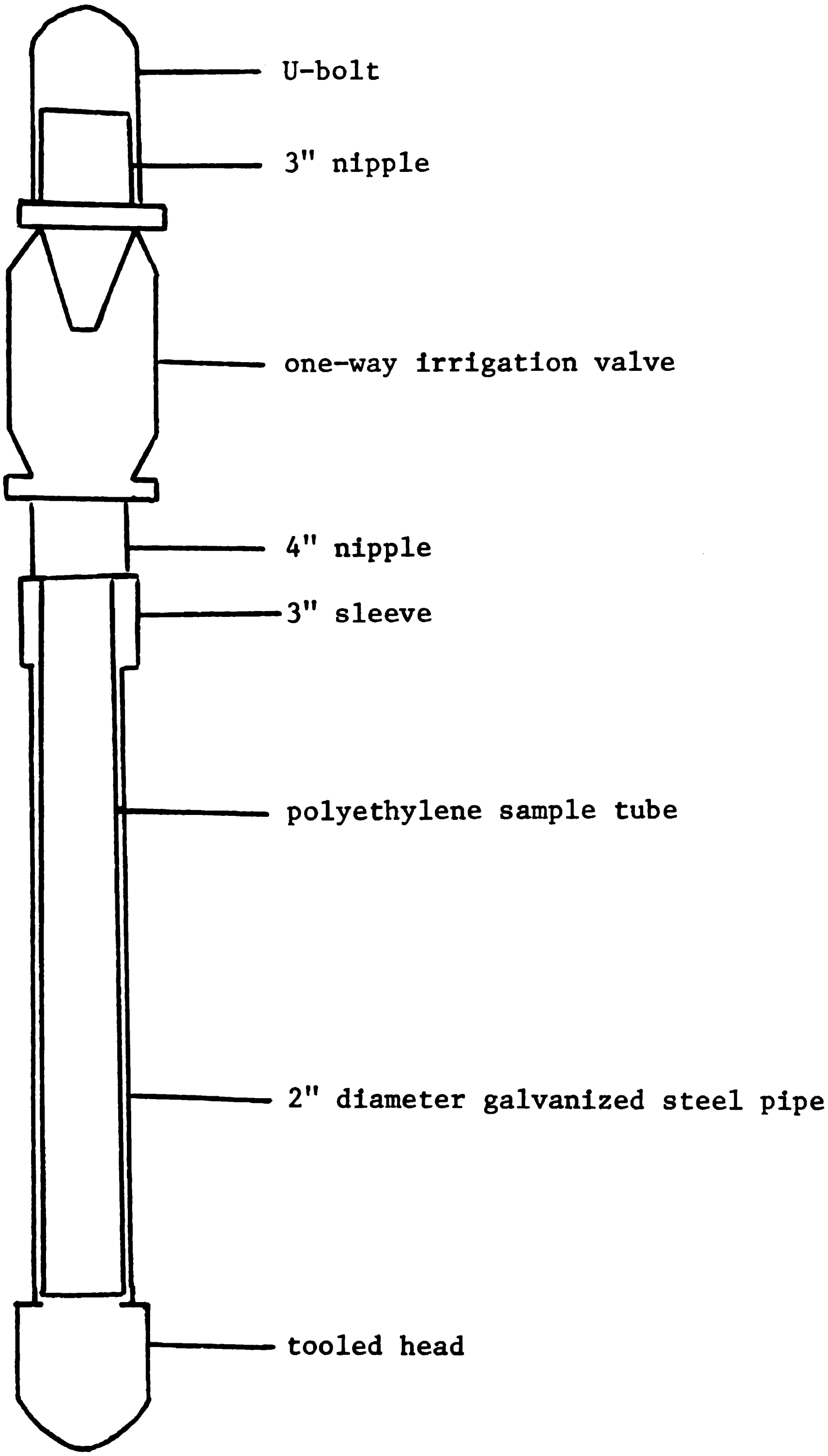

Figure 1. Schematic drawing of sampler used to obtain an undisturbed sample of the sediment-water interface (developed by Dr. George H. Lauff, Gull Lake Research Center).

removed from the stopper and the sample transfered to a glass container. In this study, pint canning jars that had a rubber serum stopper tightly placed in the cap were used. The jars were filled with sediment and water in about equal volume and tightly capped. Within a few hours after sampling, the samples were returned to the laboratory for analysis. A 50 ml volume of solution was extracted by inserting a hyperdermic needle into the jar. Another needle connected to a nitrogen tank was inserted and nitrogen gas bubbled into the jar to fill volume left by extracted water. The redox potential, pH, phosphorous, and iron were then rapidly analyzed on the sample.

Six lakes of diverse water quality characteristics were sampled in central-lower Michigan. It was suspected that conditions would get more reducing with depth, so each lake was sampled at 5 or 6 depths. Each lake was sampled in the spring or early summer and again in the fall to determine if seasonal variations were important.

The fact that this sampler could meet the criteria of taking an undisturbed mud core and the water just above it and still be used from a canoe and lowered and raised by hand using a 1/4 inch nylon rope made it the ideal apparatus for this research.

Redox Analysis

The redox potential was measured using a Sargent model DR pH meter. A 1 cm^2 bright platinum electrode was used along with a saturated calomel electrode to obtain the measurement. The polarity was determined by the use of a standard Weston cell with a 1,083 millivolt emf. Each reading was taken after a one minute equilibration period. In the final sampling, June 1970, the redox potential and pH were measured in the field using a Beckman model G portable pH meter.

Phosphorus Analysis

A chlorostannous-reduced molybdophosphoric blue color method in a sulfuric acid system was utilized in this study, Jackson (1958). It is believed that P serves as a central coordinating atom in the formation of heteropoly complexes with molybdate ions. These complexes are slightly yellow but appear colorless in lower concentrations. The addition of a reducing agent will bring about a reduction in the phosphomolybdic complexes yielding a blue color that can be measured colorimetrically at 660 mμ. The concentration of P, molybdate ion, pH, and reductant must be carefully controlled to take advantage of a narrow region where only the heteropoly complex is reduced and not the excess molybdate or an appreciable amount of interfering ions such as arsenic (As). This optimum plateau is found to occur in this method when the phosphorous concentration is less than .4 ppm and the pH is about 0.5.

This chlorostannous-reductant molybdophosphoric blue color method in a sulfuric acid system is the most sensitive analytical procedure for P and as such is well suited for analysis of infertile soils and low P waters. In systems where excessive Cl, As, Fe, and other complex forming ions are found, alternate analytical procedures should be employed.

An aliquot of 1 - 25 ml of sample was taken and 2 ml of 2.5% sulfomolybdic acid added, and the sample was diluted to 48 ml. Then .2 ml of .1N $SnCl_2$ was added to develop the color. The sample was diluted to 50 ml and the absorbence determined on an Evelyn photoelectric colorimeter at 660 mμ.

Iron Analysis

The orthophenanthroline analysis for iron was used in this work. This procedure is based on the principle that Fe^{+2} will form a stable, red complex with orthophenanthroline. The tri-(1,10) phenanthroline ferrous ion $Fe(C_{12}H_{10}N_2)_3^{2+}$ forms almost immediately and is stable for over two weeks. $NH_2OH \cdot HCl$ is added first to reduce Fe^{+3} to Fe^{+2} and then the orthophenanthroline is added to develop the color. The reaction follows Beer's Law up to 6 ppm and the absorption peak is at 508 $m\mu$. The color is stable within a pH range of 2 to 9, but for most soils the lower range is desired. This method is practically free from interference. Many constituents can be present in 200 - 500 times the concentration of Fe and not interfere with the color stability.

An aliquot of 10 - 25 ml was taken, 2 ml 5N NH_4OAC and 1 ml 10% $NH_2OH \cdot HCl$ added, and the sample was shaken. Then 1 ml orthophenanthroline reagent was added along with 0.5 ml of 6N HCl. The sample was mixed, diluted to 50 ml and the adsorbence determined at a wavelength of 520 $m\mu$.

Phosphorus Fractionation

Following the completion of the analysis of the water, each sample was drained and air dried for a week, finely ground in a mortar, mixed, and placed back in the sample jar. A one gram sample of the air dried sediment was placed in a 90 ml plastic centrifuge tube where the P forms were separately extracted and analyzed according to the method of Chang and Jackson (1957) and Chang (1962)

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The sample was shaken with 50 ml 1N NH_4Cl for one hour to remove exchangeable Ca and water soluble P. Then 50 ml of .5N NH_4F, pH 8.2 was added and the samples placed on a wrist action shaker for one hour to remove the Al-P fraction. The sample was centrifuged and 10 ml of the effluent was placed in a 50 ml volumetric flask; 15 ml of 0.8M boric acid, 10 ml of chloromolybdic acid solution, and 5 ml of chlorostannous reductant were then added, the sample being well mixed after each addition. The solution was brought up to volume and analyzed on the colorimeter at 660 mμ.

The soil sample in the tube was then washed twice with 25 ml portions of saturated NaCl. Then 50 ml of 0.1N NaOH was added, and it was placed on the shaker for twelve hours to remove the Fe-P fraction. The sample was centrifuged and the supernatant removed. Again the soil sample was washed twice with 25 ml portions of saturated NaCl which were discarded. The effluent was usually darkly colored by organic matter. This was removed by adding 2 ml of 2M H_2SO_4, two drops of concentrated H_2SO_4 and centrifuging. Then a 25 ml portion of the effluent was analyzed by the chlorostannous-reduced molybdophosphoric blue color method in sulfuric acid system as previously discussed.

Next, the soil sample in the tube was extracted with 1 gram of solid $Na_2S_2O_4$ and 40 ml of 0.3M $Na_3C_6H_5O_7 \cdot 2H_2O$ with constant stirring in a 90 C water bath for 15 minutes and centrifuged. The supernatant was placed in a 100 ml volumetric flask and the soil was again washed twice with 25 ml portions of saturated NaCl. The NaCl washings were then added to the effluent in the flask and the contents brought up to volume and mixed. A 5 ml aliquot of this solution was placed in a 250 ml conical flask. 10 ml of distilled water, a drop of 0.5M $FeCl_3$ and 10 ml of P-free 30% H_2O_2 were added. The flask was placed over a bunsen burner and the oxidation allowed to go to co

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to go to completion. The sample was then taken to dryness on a steam bath. 10 ml of 2N NaOH was added, the solution boiled for two minutes, and was placed back on the steam bath for five minutes. The sample was then placed in a 10 ml centrifuge tube and centrifuged to throw down the Fe precipitate. The supernatant liquid was placed in a 50 ml volumetric flask. The 250 ml flask was washed with 10 ml distilled water and the solution centrifuged and added to sample. This process was repeated twice and the contents were brought up to volume and mixed. This fraction, the reductant soluble Fe-P, was then analyzed by the chlorostannous-reduced molybdophosphoric blue method in sulfuric acid system procedure.

Finally, the Ca-P fraction was extracted by adding 50 ml of 0.5N H_2SO_4 to the soil sample in the tube, shaking for one hour and centrifuging. Analysis was by the chlorostannous-reduced molybdophosphoric blue method in sulfuric acid system.

This fractionation procedure is not without its drawbacks, and for some soils it will not yield valid results. For most soils, however, it yields results quite close to actual fact. The order of extraction, the proper extraction, solid to solvent ratio, and extraction time are all important considerations. The 50:1 solvent to solid ratio has proven the best. The NH_4Cl wash removes easily soluble phosphates such as di-calcium phosphate. NH_4F dissolves aluminum phosphates readily, calcium phosphates hardly at all, and iron phosphate slightly. By raising the pH of NH_4F to 8.2, the solubility of Fe-P is greatly reduced. The common ion influence of F^- hinders the solubility of the apatite form in this extract.

NaOH readily dissolves both Fe- and Al-P, but the high pH and common ion OH^- restricts apatite solubility. By removing Al-P first, this step is exclusive for Fe-P.

The reductant soluble P is thought to be protected by a coating of Fe oxide which resists NH_4F and NaOH solution. $Na_2S_2O_4$ and $Na_3C_6H_5O_7 \cdot 2H_2O$ reduce this coating of ferric oxide to a soluble ferrous oxide form and dissolve and extract the entrapped P forms.

Sulfuric acid will dissolve apatite, Fe-P and Al-P. If the latter two forms have already been preferentially removed, this treatment will serve as a good extractant of the Ca-P fraction in the soil sample.

Controlled Redox

A system was designed to control the redox potential in a flooded soil sample by taking a 17 inch long piece of clear plastic tubing, 2 inches in diameter, and stoppering the ends. The top stopper was fitted with a platinum electrode, saturated calomel electrode, a gas inlet tube, and a gas outlet tube. A sample containing 600 grams of soil and 600 ml of water was placed in the tube with the gas inlet tube extending to the bottom of the column to insure complete mixing. The electrodes were hooked to a Coleman titrion automatic titrator and companion pH meter. The instrument was modified to deliver nitrogen (N_2) or O_2 gas instead of liquid titrant. To obtain reducing conditions, the titrator was hooked to a N_2 tank. Bubbling N_2 through the sample de-aerated the system and brought the desired reducing conditions. Bubbling O_2 would bring oxidizing conditions. The desired redox potential was set on the instrument by the use of a variable resistor and a Weston cell. The titrator would then hold the potential in the sample at the set reading for any desired length of time by bubbling gas to raise or lower the potential whenever it deviated from the set end point. The sample was allowed to remain at each desired end point for at least two weeks to insure complete equilibration of the potential and the ions in solution. A 25 ml sample was withdrawn at sampling time for P and Fe analysis. The aliquot was replaced each time by an equal volume of deionized water.

RESULTS AND DISCUSSION

Phosphorus and Redox Potential

A simple regression analysis of the P content of water at sampling time and after 30 days of anaerobic incubation yielded the equation:

$$P_I = .88\ P_S + .34$$

where, P_I = P after incubation

P_S = P at sampling time.

The regression coefficient is 0.548 and the equation is significant to the 0.0005 level. Solving for this equation when $P_I = P_S$ yields a value of 2.87 ppm P. Any lake sample containing greater than 2.87 ppm P should undergo a decrease in P during anaerobic incubation according to this regression equation. In this study, 200 samples were taken and 198 of them fell below this upper limit and could be predicted to show an increase in P after incubation. This result indicates that anaerobically incubating a waterlogged sample does indeed result in an increase in P in solution. Examination of the redox data, however, indicated that almost half of the samples showed an increase in redox potential during incubation, indicating that air must have been trapped in the sediment during sampling causing the incubation period to be aerobic rather than anaerobic compared to the original redox condition of the sample. For this reason, the data was divided to compare the results for those anaerobically incubated with those aerobically incubated.

A regression analysis for the anaerobically incubated samples yielded the equation:

$$P_I = 3.51\ P_S + .09,$$

with a regression coefficient of 0.88, significant to the 0.0005 level. This equation indicates that a three and a half fold increase in P should be noted following incubation anaerobically. This result very definitely supports the view that P is more available under reducing conditions and explains why paddy soils show little response to P fertilization in many cases. Figure 2 from Fenton Lake shows an example of this increased P content with a lowering of potential.

Ninety-six samples showed a rise in redox potential during incubation, and regression analysis of the P data yields the following equation:

$$P_I = 0.587\ P_S + 0.184,$$

with a regression coefficient of .656 and significance to less than 0.0005. Solving for this regression equation yields an upper limit of 0.445 ppm P. This is an interesting result in that it indicates that in lakes with a P content below 0.445 ppm even incubation aerobically can result in an increase in phosphorous content. Figure 3 shows the results from Crooked Lake which demonstrate that large increases in P can also occur when the potential rises. For lakes high in P content, however, a rise in potential is accompanied by a loss of P from solution. Figure 4 from Ponemah Lake is an example of this result.

These results indicate that there must be something in addition to redox conditions that influence the amount of P in solution. The increase in P upon anaerobic incubation is dramatic and quite large, but the smaller increases during aerobic incubation indicate immediately that processes in addition to the redox equilibria must be occurring in the system. Biological

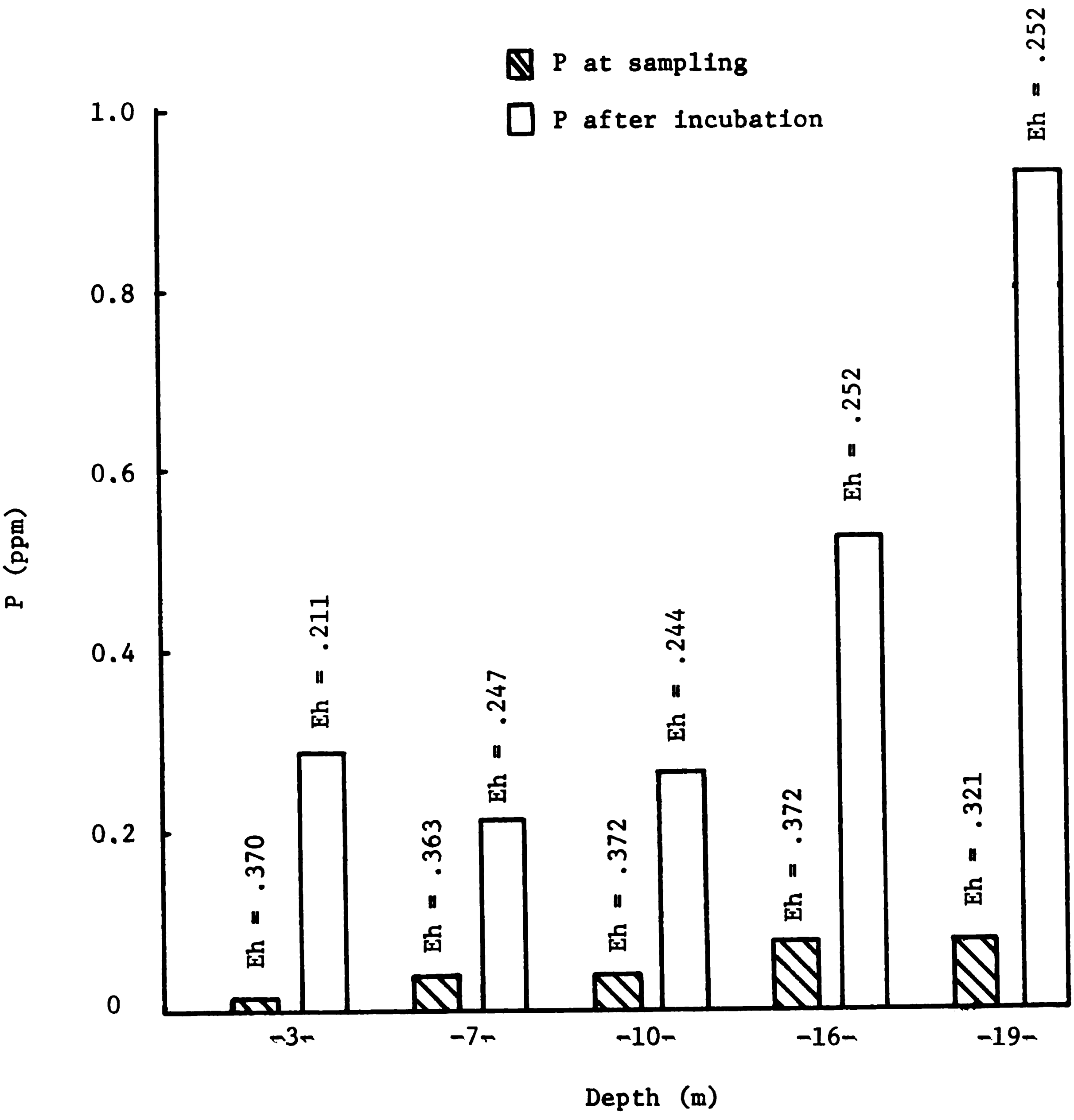

Figure 2. Increase in P during anaerobic incubation. Fenton Lake. Sampled July 1969.

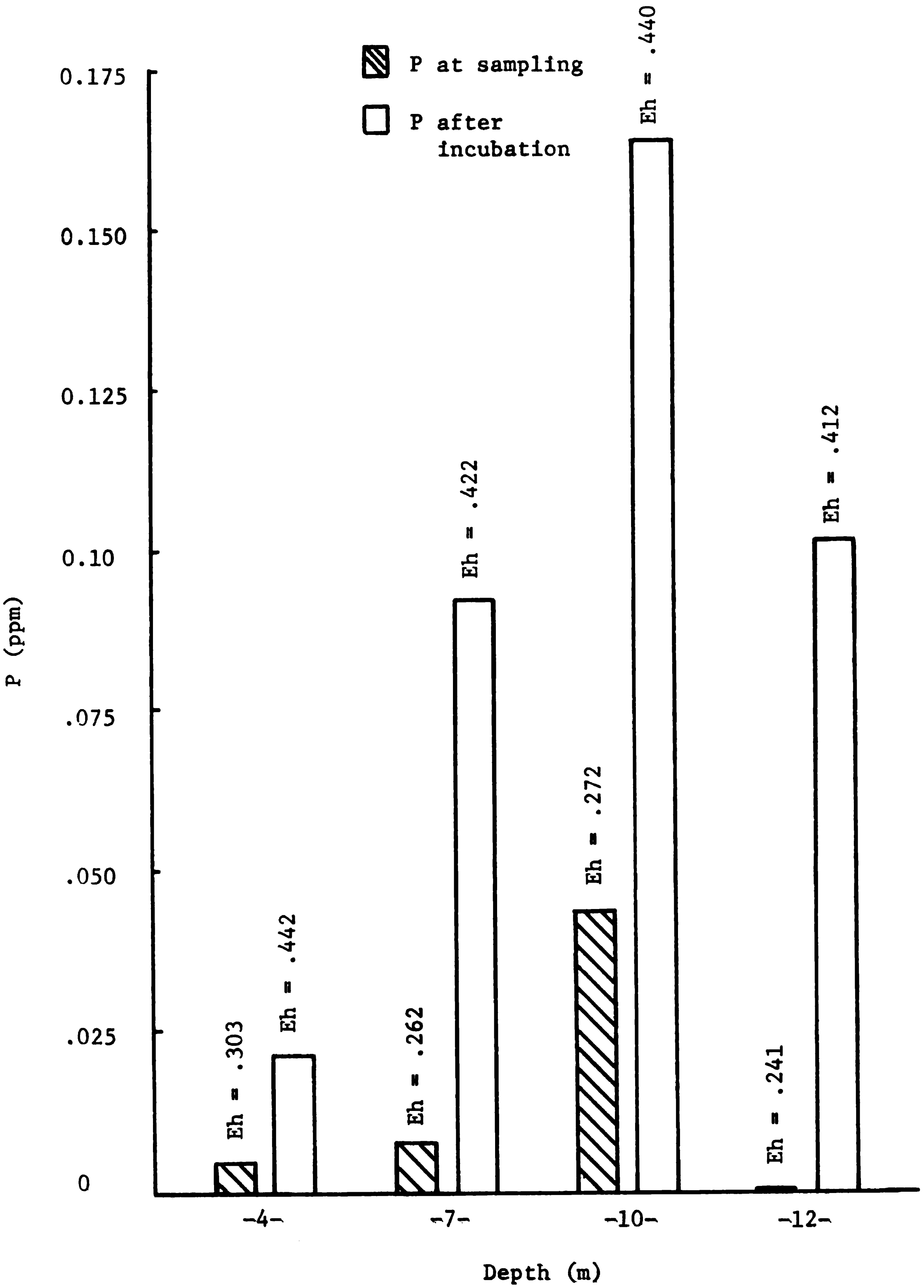

Figure 3. Increase in P during aerobic incubation. Crooked Lake. Sampled July 1969.

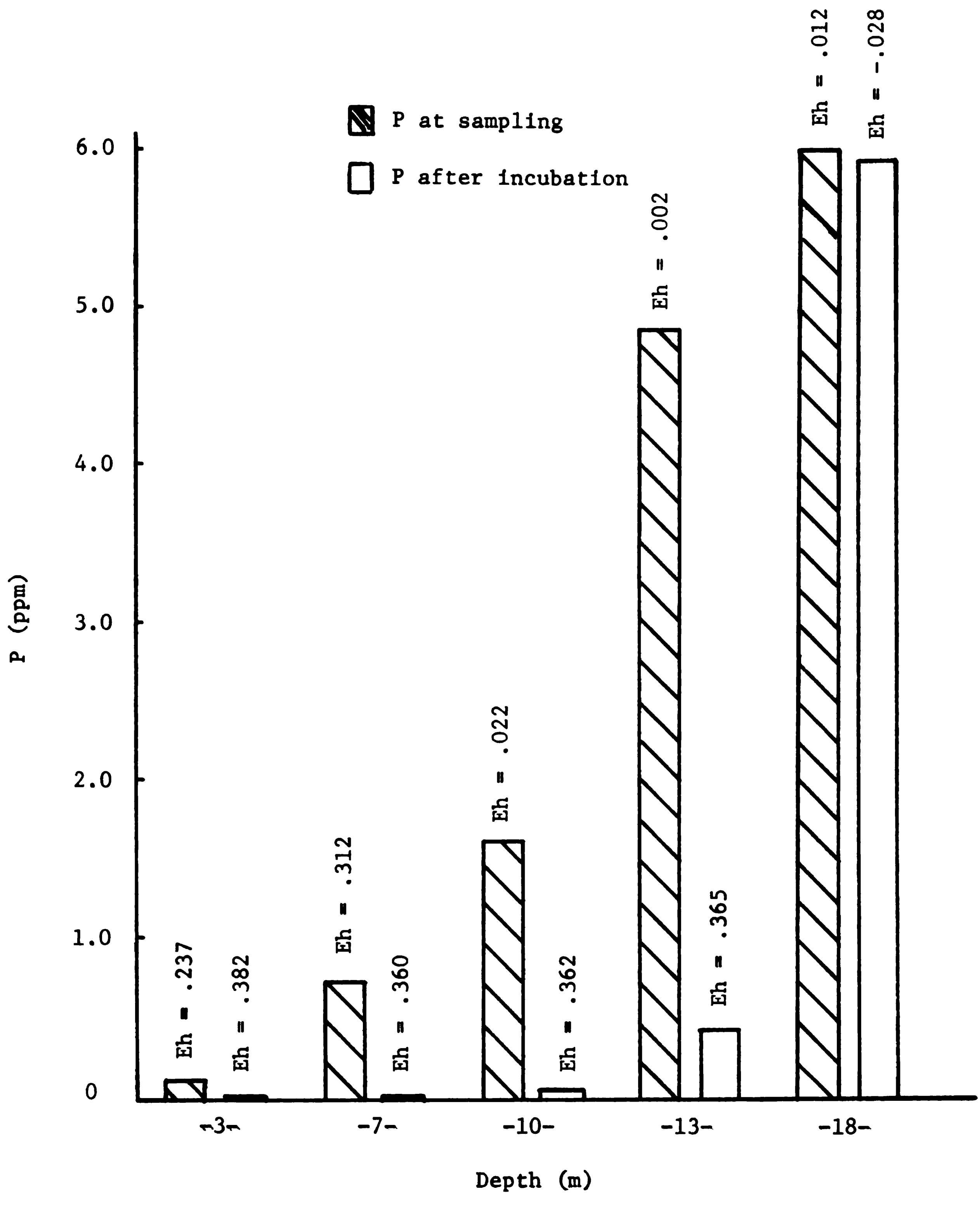

Figure 4. Decrease in P during aerobic incubation. Ponemah Lake. Sampled July 1970.

processes have been suggested by many to be more important than redox in controlling the level of P in solution, and perhaps many of the increases noted are attributable to biological activity.

From an examination of Tables 1 to 18, there appears to be a relationship between redox potential and P. In most cases, the sample with the highest P content is also the sample with the lowest redox reading. Figure 5 illustrates this finding. A definite inverse relationship is suggested by the results in this figure. These results support the view that P does become more soluble when placed under the reducing environment at lake bottoms. When sediment is deposited in lakes, the adsorbed P should become more available than under its natural oxidative environment. This being true, erosion from agricultural land could indeed contribute heavily to the eutrification of our lakes and streams by depositing sediments rich in fertilizer P which is more soluble under reducing conditions than under upland conditions. As noted by several workers, these sediments serve as a buffer for the P levels in solution and are capable of maintaining P contents at a high level for an extended period of time.

Phosphorus and Iron

Many researchers have attempted to account for the increase in P availability upon waterlogging by suggesting that reducing conditions cause a reduction of insoluble ferric phosphate to more soluble ferrous phosphate. If this process does indeed occur, then the increased P levels under reducing conditions should be associated with high Fe contents. An examination of the data shows that this is actually the case, as is illustrated in Figure 6. Quantitatively, however, the results do not support the ferric phosphate reduction proposal. If we assume that the ferrous phosphate is

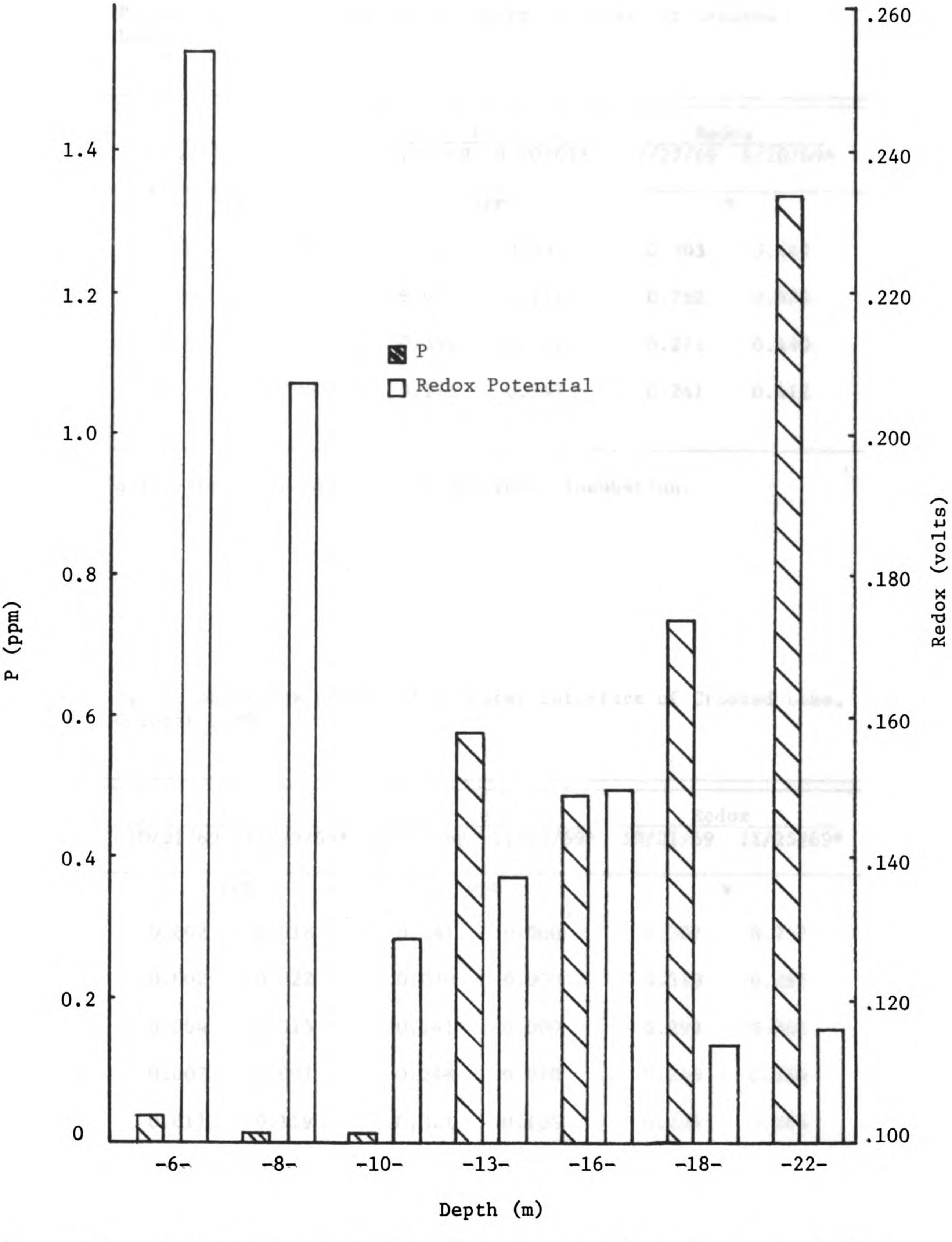

Figure 5. Relationship between P and Redox Potential. Ore Lake. Sampled October 1969.

Table 1. P, Fe, and redox potential of water interface of Crooked Lake, July 1969.

Depth	P		Fe		Redox	
	7/22/69	8/20/69*	7/22/69	8/20/69*	7/22/69	8/20/69*
m	ppm		ppm		v	
4	0.004	0.022	0.141	0.085	0.303	0.442
7	0.009	0.097	0.070	0.114	0.262	0.422
10	0.046	0.174	0.394	0.232	0.272	0.440
12	0.000	0.108	0.176	0.247	0.241	0.412

*Analyzed after approximately 30 days anaerobic incubation.

Table 2. P, Fe, and redox potential of water interface of Crooked Lake, October 1969.

Depth	P		Fe		Redox	
	10/21/69	11/25/69*	10/21/69	11/25/69*	10/21/69	11/25/69*
m	ppm		ppm		v	
4	0.002	0.018	0.141	0.000	0.307	0.267
7	0.002	0.022	0.070	0.000	0.310	0.267
9	0.004	0.015	0.141	0.000	0.299	0.264
11	0.007	0.097	0.248	0.070	0.240	0.256
12	0.011	0.119	0.321	0.105	0.205	0.248

*Analyzed after approximately 30 days anaerobic incubation.

Table 3. P, Fe, pH and redox potential of water interface of Crooked Lake, June 1970.

Depth	pH	P		Fe		Redox	
		7/2/70	8/18/70*	7/2/70	8/18/70*	7/2/70	8/18/70*
m		ppm		ppm		v	
4	7.10	0.018	0.041	0.000	0.056	0.417	0.352
7	6.85	0.046	0.058	0.404	0.325	0.417	-
9	6.90	0.076	0.244	0.143	0.114	0.412	-
11	6.70	0.022	0.032	0.028	0.056	0.417	0.352
12	6.55	0.051	0.056	0.993	0.325	0.422	0.342

*Analyzed after approximately 45 days anaerobic incubation.

Table 4. P, Fe, and redox potential of water interface of Chemung Lake, July 1969.

Depth	P		Fe		Redox	
	7/22/69	8/20/69*	7/22/69	8/20/69*	7/22/69	8/20/69*
m	ppm		ppm		v	
4	0.013	0.226	0.000	0.000	0.307	0.127
7	0.018	0.393	0.141	0.143	0.281	0.322
9	0.161	0.639	0.176	0.056	0.257	0.107
11	0.018	0.377	0.176	0.000	0.290	0.112
14	0.114	0.509	0.212	0.056	0.302	0.337
17	0.260	1.463	0.248	0.000	0.277	0.372

*Analyzed after approximately 30 days anaerobic incubation.

Table 5. P, Fe, and redox potential of water interface of Chemung Lake, October 1969.

Depth	P		Fe		Redox	
	10/21/69	11/25/69*	10/21/69	11/25/69*	10/21/69	11/25/69*
m	ppm		ppm		v	
4	0.007	0.215	0.070	0.000	0.291	0.141
7	0.007	0.013	0.070	0.000	0.284	0.142
10	0.013	0.013	0.000	0.000	0.287	0.157
13	0.056	0.111	0.035	0.000	0.292	0.192
15	0.131	0.753	0.105	0.000	0.207	0.122
19	0.248	0.856	0.141	0.035	0.203	-0.157

*Analyzed after approximately 30 days anaerobic incubation.

Table 6. P, Fe, pH and redox potential of water interface of Chemung Lake, June 1970.

Depth	pH	P		Fe		Redox	
		7/2/70	8/18/70*	7/2/70	8/18/70*	7/2/70	8/18/70*
m		ppm		ppm		v	
4	7.20	0.078	0.004	0.000	0.000	0.372	0.322
7	7.15	0.078	0.032	0.000	0.000	0.372	0.302
10	7.10	0.444	0.032	0.056	0.028	0.232	0.307
13	7.25	0.022	0.018	0.000	0.028	0.342	0.322
15	7.25	0.100	0.027	0.000	0.028	0.332	0.322
19	7.10	0.561	0.367	0.202	0.085	0.052	0.332

*Analyzed after approximately 45 days anaerobic incubation.

Table 7. P, Fe, and redox potential of water interface of Ore Lake, July 1969.

Depth	P		Fe		Redox	
	7/22/69	8/20/69*	7/22/69	8/20/69*	7/22/69	8/20/69*
m	ppm		ppm		v	
8	0.137	0.987	0.070	0.915	0.326	0.294
10	0.143	1.319	0.000	1.115	0.294	0.262
13	0.143	1.664	0.070	0.858	0.282	0.287
16	0.131	0.462	0.000	0.974	0.282	0.291
19	0.629	3.193	0.000	1.377	0.252	0.282
21	0.284	0.218	0.141	0.128	0.250	0.382

*Analyzed after approximately 30 days anaerobic incubation.

Table 8. P, Fe, and redox potential of water interface of Ore Lake, October 1969.

Depth	P		Fe		Redox	
	10/21/69	11/25/69*	10/21/69	11/25/69*	10/21/69	11/25/69*
m	ppm		ppm		v	
6	0.041	0.046	0.070	0.035	0.254	0.234
8	0.009	0.119	0.176	0.105	0.207	0.223
10	0.015	0.068	0.212	0.141	0.129	0.207
13	0.569	0.732	0.357	0.321	0.138	0.142
16	0.482	0.690	0.212	0.505	0.130	0.137
18	0.742	0.139	0.284	0.141	0.114	0.209
22	1.345	2.580	0.394	0.695	0.116	0.019

*Analyzed after approximately 30 days anaerobic incubation.

Table 9. P, Fe, pH and redox potential of water interface of Ore Lake, June 1970.

Depth	pH	P		Fe		Redox	
		7/2/70	8/18/70*	7/2/70	8/18/70*	7/2/70	8/18/70*
m		ppm		ppm		v	
6	6.85	0.056	0.033	0.172	0.056	0.092	0.362
8	6.79	0.046	0.189	1.287	0.143	0.092	0.342
10	6.98	0.036	0.133	0.293	0.085	0.112	0.347
13	6.78	0.076	0.033	0.453	0.071	0.132	0.347
16	6.60	0.066	0.102	0.587	0.293	0.142	0.317
18	6.93	0.268	0.145	0.519	0.202	0.252	0.322
22	6.72	0.114	0.151	0.293	0.420	0.142	0.322

*Analyzed after approximately 45 days anaerobic incubation.

Table 10. P, Fe, and redox potential of water interface of Lobdell Lake, July 1969.

Depth	P		Fe		Redox	
	7/22/69	8/20/69*	7/22/69	8/20/69*	7/22/69	8/20/69*
m	ppm		ppm		v	
3	0.108	0.387	0.141	0.000	0.362	0.202
7	0.092	0.347	0.105	0.056	0.352	0.212
9	0.174	0.468	0.212	0.247	0.292	0.190
12	0.229	0.942	0.321	0.143	0.290	0.372
16	0.306	1.383	0.394	0.128	0.284	0.162
20	0.208	0.146	0.468	0.000	0.284	0.434

*Analyzed after approximately 30 days anaerobic incubation.

Table 11. P, Fe, and redox potential of water interface of Lobdell Lake, October 1969.

Depth	P		Fe		Redox	
	10/21/69	11/25/69*	10/21/69	11/25/69*	10/21/69	11/25/69*
m	ppm		ppm		v	
3	0.051	0.208	0.035	0.000	0.264	0.217
7	0.022	0.029	0.070	0.000	0.260	0.222
9	0.051	0.063	0.105	0.000	0.257	0.202
12	0.100	0.462	0.035	0.000	0.245	0.145
16	0.222	0.092	0.070	0.000	0.259	0.187
22	0.066	0.602	0.431	1.132	0.140	-0.116

*Analyzed after approximately 30 days anaerobic incubation.

Table 12. P, Fe, pH and redox potential of water interface of Lobdell Lake, June 1970.

Depth	pH	P		Fe		Redox	
		7/2/70	8/18/70*	7/2/70	8/18/70*	7/2/70	8/18/70*
m		ppm		ppm		v	
3	6.25	0.092	0.043	0.056	0.143	0.262	0.362
7	6.90	0.058	0.022	0.000	0.071	0.312	0.357
9	6.72	0.215	0.041	0.000	0.085	0.342	0.372
12	6.59	0.161	0.620	0.000	0.325	0.332	-
16	6.65	0.328	0.131	0.014	0.056	0.112	0.362
21	6.70	0.377	1.056	0.293	0.622	0.102	-

*Analyzed after approximately 45 days anaerobic incubation.

Table 13. P, Fe, and redox potential of water interface of Fenton Lake, July 1969.

Depth	P		Fe		Redox	
	7/22/69	8/20/69*	7/22/69	8/20/69*	7/22/69	8/20/69*
m	ppm		ppm		v	
3	0.011	0.284	0.105	0.071	0.370	0.211
7	0.039	0.215	0.284	0.128	0.363	0.247
10	0.032	0.268	0.176	0.099	0.372	0.244
16	0.071	0.523	0.212	0.085	0.372	0.252
19	0.071	0.930	-	0.436	0.321	0.252

*Analyzed after approximately 30 days anaerobic incubation.

Table 14. P, Fe, and redox potential of water interface of Fenton Lake, October 1969.

Depth	P		Fe		Redox	
	10/21/69	11/25/69*	10/21/69	11/25/69*	10/21/69	11/25/69*
m	ppm		ppm		v	
3	0.004	0.027	0.212	0.000	0.202	0.164
8	0.013	0.022	0.284	0.000	0.218	0.177
10	0.007	0.032	0.105	0.000	0.226	0.141
12	0.015	0.032	0.105	0.000	0.232	0.162
16	0.256	-	0.394	-	0.220	-0.138
19	0.233	-	0.321	-	0.090	-0.103

*Analyzed after approximately 30 days anaerobic incubation.

Table 15. P, Fe, pH and redox potential of water interface of Fenton Lake, June 1970.

Depth	pH	P		Fe		Redox	
		7/2/70	8/18/70*	7/2/70	8/18/70*	7/2/70	8/18/70*
m		ppm		ppm		v	
3	7.85	0.000	0.091	0.114	0.000	0.022	0.332
8	7.50	0.067	0.011	0.085	0.028	0.212	0.342
10	7.40	0.079	0.039	0.071	0.028	0.247	0.342
12	7.25	0.229	0.056	0.202	0.056	0.152	0.352
16	7.15	0.357	0.139	0.143	0.232	0.052	0.347
19	7.05	0.127	0.121	0.128	0.056	0.212	0.347

*Analyzed after approximately 45 days anaerobic incubation.

Table 16. P, Fe, and redox potential of water interface of Ponemah Lake, July 1969.

Depth	P		Fe		Redox	
	7/22/69	8/20/69*	7/22/69	8/20/69*	7/22/69	8/20/69*
m	ppm		ppm		v	
3	0.119	2.409	0.105	0.325	0.353	0.202
7	0.585	3.012	0.248	0.143	0.324	0.372
10	0.187	1.747	0.357	0.783	0.315	0.332
13	0.690	4.351	0.357	1.095	0.260	0.312
16	1.421	6.795	0.394	0.820	0.231	0.252

*Analyzed after approximately 30 days anaerobic incubation.

Table 17. P, Fe, and redox potential of water interface of Ponemah Lake, October 1969.

Depth	P		Fe		Redox	
	10/21/69	11/25/69*	10/21/69	11/25/69*	10/21/69	11/25/69*
m	ppm		ppm		v	
3	0.111	0.048	0.141	0.000	0.246	0.157
7	0.260	0.256	0.105	0.000	0.244	0.192
10	0.268	0.053	0.141	0.000	0.201	0.204
13	0.904	0.418	0.212	0.000	0.152	0.162
19	1.991	7.423	0.284	0.071	0.158	-0.138

*Analyzed after approximately 30 days anaerobic incubation.

Table 18. P, Fe, pH and redox potential of water interface of Ponemah Lake, June 1970.

Depth	pH	P		Fe		Redox	
		7/2/70	8/18/70*	7/2/70	8/18/70*	7/2/70	8/18/70*
m		ppm		ppm		v	
3	7.20	0.114	0.011	0.202	0.000	0.237	0.382
7	7.10	0.753	0.011	0.071	0.143	0.312	0.360
10	6.90	1.597	0.079	0.692	0.085	0.022	0.362
13	6.85	4.843	0.453	1.354	0.263	0.002	0.365
18	6.71	6.012	5.918	0.954	0.519	0.012	-0.028

*Analyzed after approximately 45 days anaerobic incubation.

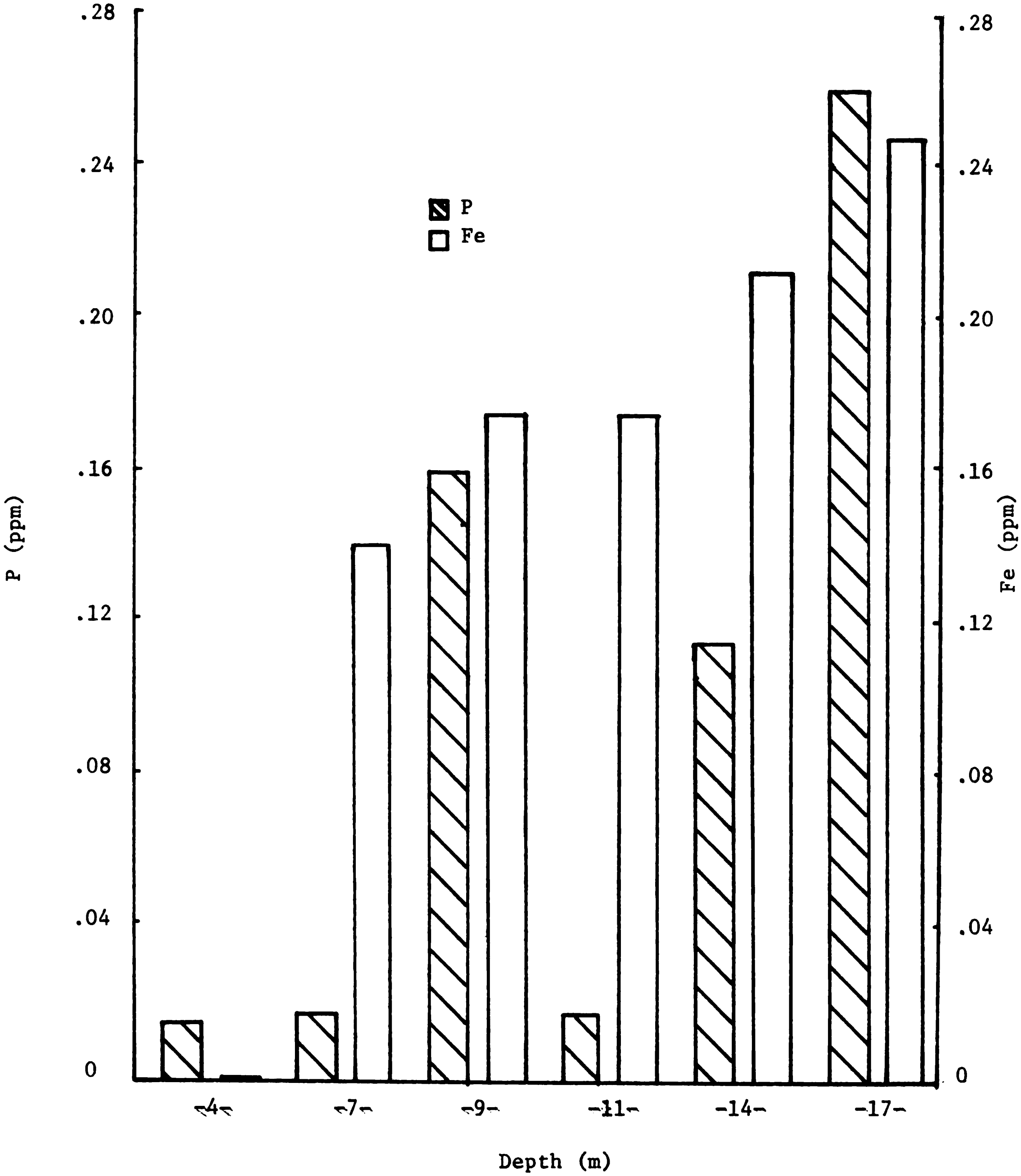

Table 6. Relationship between P and Fe. Chemung Lake. Sampled July 1969.

in the form $Fe_3\,(PO_4)_2$, then the analysis should yield an Fe content that is 2.7 times as large as the P content. Figures 6 and 7 both show that at shallow depths Fe is many times higher than P and that at deeper depths, both P and Fe greatly increase. At the deeper depths P is almost as high and in some cases higher than Fe. In addition to the higher molecular weight of Fe, another factor that causes one to expect higher Fe levels than P in lake waters is that the native Fe content in most soils is higher than the native P content. Also, it is legitimate to expect that while ferric phosphates are being reduced to ferrous phosphates, other relatively insoluble ferric precipitates are being reduced to the ferrous oxidation state, resulting in a higher Fe content in solution than P. Many industrial processes expel wastes high in heavy metals which also contributes to the higher Fe content, although no industrial plants were dumping wastes into the lakes in this study.

It would be reasonable to conclude from the data that Fe and P are related and that the level of P in solution could be partially controlled by the reduction of ferric phosphates to more soluble ferrous phosphates. However, the rate of P increase is greater than the rate of Fe increase with depth, and this suggests the presence of some other controlling factor in the release of P. The fact that the most dramatic effects of increased P release occur at the deeper depths lends strong evidence to the hypothesis that a reducible organic compound is this unknown controlling factor.

Phosphorous Fractionation

Tables 19 and 30 show the data obtained by the method of Chang and Jackson (1957) as revised by Chang (1962) to fractionate the various forms of P in the sediment.

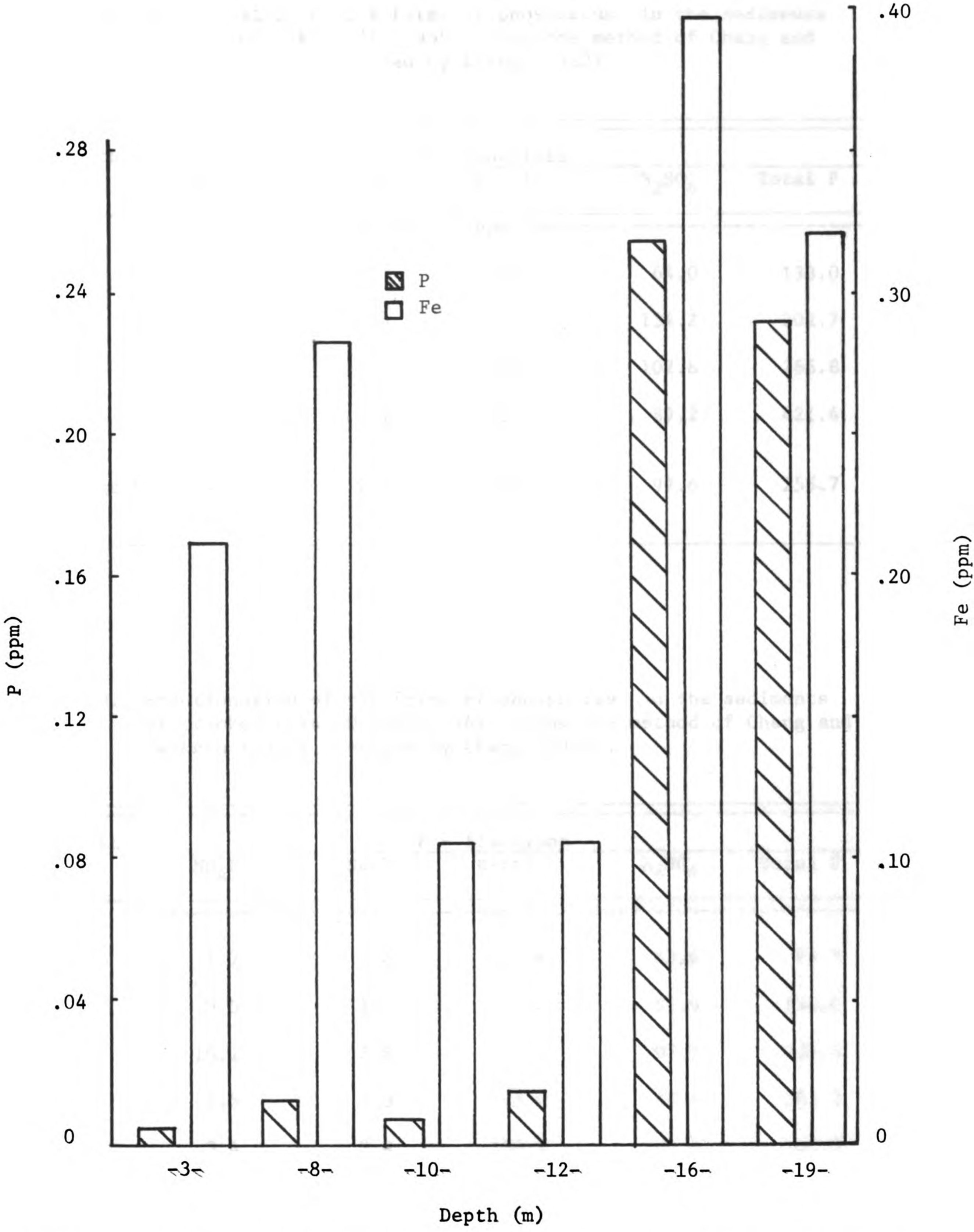

Figure 7. Relationship between P and Fe. Fenton Lake. Sampled October 1969.

Table 19. Fractionation of the forms of phosphorus in the sediments of Crooked Lake, July 1969, using the method of Chang and Jackson (1957), revised by Chang (1962).

Depth	P - fractions				
	NH_4F	NaOH	R-Sol.	H_2SO_4	Total P
m	ppm P				
4	1.1	1.7	66.2	64.0	133.0
7	10.1	3.4	55.0	134.2	202.7
10	2.2	3.1	157.7	102.8	265.8
12	3.4	1.1	327.7	89.2	421.4
Average P	4.2	2.3	151.6	97.6	255.7

Table 20. Fractionation of the forms of phosphorus in the sediments of Crooked Lake, October 1969, using the method of Chang and Jackson (1957), revised by Chang (1962).

Depth	P - fractions				
	NH_4F	NaOH	R-Sol.	H_2SO_4	Total P
m	ppm P				
4	1.7	5.6	21.8	60.6	89.7
7	0.5	1.6	100.0	51.9	154.0
9	10.1	2.8	122.9	103.7	239.5
11	2.5	3.3	193.0	84.4	283.2
12	3.4	3.9	253.2	99.5	360.0
Average P	3.6	3.4	138.2	80.0	225.3

Table 21. Fractionation of the forms of phosphorus in the sediments of Chemung Lake, July 1969, using the method of Chang and Jackson (1957), revised by Chang (1962).

Depth	P - fractions				
	NH_4F	NaOH	R-Sol.	H_2SO_4	Total P
m	ppm P				
4	2.2	1.1	228.9	104.7	336.9
7	18.6	3.9	378.8	172.4	573.7
9	12.5	3.9	253.2	162.4	432.0
11	10.8	3.4	404.9	152.7	571.8
14	8.8	7.2	43.9	138.7	198.6
17	9.1	8.8	88.7	162.4	269.0
Average P	10.3	4.7	233.1	148.9	397.0

Table 22. Fractionation of the forms of phosphorus in the sediments of Chemung Lake, October 1969, using the method of Chang and Jackson (1957), revised by Chang (1962).

Depth	P - fractions				
	NH_4F	NaOH	R-Sol.	H_2SO_4	Total P
m	ppm P				
4	3.4	1.1	512.2	114.9	631.6
7	7.9	1.6	775.0	152.7	937.2
10	16.4	2.8	744.2	157.5	920.9
13	16.0	6.3	284.0	146.3	452.6
15	10.4	7.6	411.0	127.2	556.2
19	10.1	14.2	242.4	120.4	387.1
Average P	10.7	5.6	494.8	136.5	647.6

Table 23. Fractionation of the forms of phosphorus in the sediments of Ore Lake, July 1969, using the method of Chang and Jackson (1957), revised by Chang (1962).

Depth	P - fractions				
	NH_4F	NaOH	R-Sol.	H_2SO_4	Total P
m	ppm P				
8	0.0	3.1	277.8	78.1	359.0
10	0.5	6.6	181.2	152.7	341.0
13	2.5	7.6	146.0	188.3	344.4
16	3.1	2.8	215.6	185.6	407.1
19	1.4	6.9	204.9	162.4	375.6
21	2.7	7.2	157.7	223.0	390.6
Average P	1.7	5.7	197.2	165.0	369.6

Table 24. Fractionation of the forms of phosphorus in the sediments of Ore Lake, October 1969, using the method of Chang and Jackson (1957), revised by Chang (1962).

Depth	P - fractions				
	NH_4F	NaOH	R-Sol.	H_2SO_4	Total P
m	ppm P				
6	1.6	3.3	0.0	76.3	81.2
8	1.6	6.7	100.0	104.7	213.0
10	1.6	6.7	21.8	175.0	205.1
13	4.5	6.7	553.8	159.9	724.9
16	4.2	6.7	134.4	172.4	317.7
18	2.2	5.6	122.9	167.3	299.0
22	3.4	5.6	181.2	199.3	389.5
Average P	2.9	5.9	159.1	150.7	318.6

Table 25. Fractionation of the forms of phosphorus in the sediments of Lobdell Lake, July 1969, using the method of Chang and Jackson (1957), revised by Chang (1962).

Depth	P - fractions				
	NH_4F	NaOH	R-Sol.	H_2SO_4	Total P
m	ppm P				
3	8.2	5.7	138.9	114.9	267.7
7	1.1	2.2	163.9	98.8	266.0
9	11.4	6.3	33.1	112.8	163.6
12	26.8	9.5	126.6	152.7	315.6
16	39.3	15.6	67.2	108.8	230.9
20	26.0	12.8	44.4	100.8	184.0
Average P	18.8	8.7	95.7	114.8	238.0

Table 26. Fractionation of the forms of phosphorus in the sediments of Lobdell Lake, October 1969, using the method of Chang and Jackson (1957), revised by Chang (1962).

Depth	P - fractions				
	NH_4F	NaOH	R-Sol.	H_2SO_4	Total P
m	ppm P				
3	3.4	5.0	88.7	63.0	160.1
7	0.8	1.1	77.4	146.3	225.6
9	5.7	10.2	157.7	105.1	278.7
12	6.3	9.1	111.4	93.0	219.8
16	1.4	10.8	100.0	93.0	205.2
20	9.5	13.3	134.4	100.9	258.1
Average P	4.5	8.2	111.6	100.2	224.6

Table 27. Fractionation of the forms of phosphorus in the sediments of Fenton Lake, July 1969, using the method of Chang and Jackson (1957), revised by Chang (1962).

Depth	P - fractions				
	NH_4F	NaOH	R-Sol.	H_2SO_4	Total P
m	ppm P				
3	1.4	1.4	90.6	64.0	157.4
7	1.6	3.4	90.6	89.2	184.8
10	54.0	38.8	176.6	108.8	378.2
16	49.8	14.2	189.4	121.2	374.6
19	18.6	8.8	189.4	150.3	367.1
Average P	25.1	13.3	147.3	106.7	292.4

Table 28. Fractionation of the forms of phosphorus in the sediments of Fenton Lake, October 1969, using the method of Chang and Jackson (1957), revised by Chang (1962).

Depth	P - fractions				
	NH_4F	NaOH	R-Sol.	H_2SO_4	Total P
m	ppm P				
3	1.6	1.6	21.8	141.0	166.0
8	5.7	1.6	683.8	93.0	784.1
10	13.5	67.0	759.5	114.9	954.9
12	8.2	1.1	596.3	114.9	720.5
16	26.0	7.9	806.3	150.3	990.5
19	23.4	12.7	683.8	138.7	858.6
Average P	13.1	15.3	591.9	125.5	745.8

Table 29. Fractionation of the forms of phosphorus in the sediments of Ponemah Lake, July 1969, using the method of Chang and Jackson (1957), revised by Chang (1962).

Depth	P - fractions				
	NH_4F	NaOH	R-Sol.	H_2SO_4	Total P
m	ppm P				
3	0.0	1.1	215.6	82.0	298.7
7	0.0	1.4	215.6	123.8	340.8
10	2.8	6.0	435.1	142.2	586.1
13	3.9	10.8	327.1	242.1	583.9
16	5.7	10.8	476.4	216.9	709.8
Average P	2.5	6.0	334.0	161.4	503.9

Table 30. Fractionation of the forms of phosphorus in the sediments of Ponemah Lake, October 1969, using the method of Chang and Jackson (1957), revised by Chang (1962).

Depth	P - fractions				
	NH_4F	NaOH	R-Sol.	H_2SO_4	Total P
m	ppm P				
3	0.0	2.1	146.0	71.0	219.1
7	0.0	2.8	146.0	106.6	255.4
10	3.9	9.1	253.2	196.5	462.7
13	5.4	12.0	277.8	242.2	537.9
19	9.1	15.1	277.8	245.5	547.5
Average P	3.7	8.3	220.2	172.4	404.5

It should be noted that the levels of NH_4F extractible P and NaOH extractible P are quite low, each representing less than 5% of the total P extracted. In mineral soils under natural conditions, these fractions are often as high or higher than H_2SO_4-extractible P or reductant soluble P. It is apparent that if the sediments sampled were actually deposited in the lake from the erosion of agricultural soils then the P in the NH_4F extraction (Al-P) and in the NaOH extraction (Fe-P) has undergone a transfer to other forms. With the exception of Ponemah Lake, the Al-P fraction has its peak in the intermediate depths of the lakes. The Fe-P fraction is a little more erratic, having little apparent correlation with the sampling depth.

The H_2SO_4-extractible (Ca-P) levels, ranging from 63 - 245 ppm P, are similar to those found in many mineral soils. It is surprising, with the marl bottoms of these lakes, that a larger percentage of the total extracted P was not in this form. Fenton Lake, with the highest pH's of the lakes sampled, had an average of 125.4 ppm P in the Ca-P form; but this was only 12% of the average total P extracted per depth in the October sample. Ore Lake, with pH values among the lowest of the lakes sampled, had an average of 150.7 ppm P in the Ca-P form, representing 47% of the average total extracted P per depth in the October sample. This is quite different from that found in mineral soils, where there is usually a high correlation between high pH and the predominance of Ca-P forms.

Obviously the factor that is causing the entire P system to react differently in the sediments than in mineral soils is the influence of the lake environment upon the reductant soluble P fraction. In mineral soils, the amount of reductant soluble P is usually quite small and is often neglected as negligible, although in some soils there may be a considerable amount of this form. In the 6 lakes sampled in this study, reductant soluble P predominates, reaching a maximum average level of 591.9 ppm P in the October sampling of Fenton Lake. In fractionation work on numerous Michigan soils, Thurlow (1965), Juo (1966), and Rinkenberger (1966) found that most soils fell in the range of 200 - 500 ppm P removed by all four extractants totally, and that the amount of reductant soluble P was negligible compared to the other fractions.

Several things are readily apparent here: (1) there may be wholesale shift of Al-P and Fe-P to the reductant soluble P form within a lake environment; (2) the levels of reductant soluble P alone is higher in many lakes than the total P in most soils, indicating that other sources of P besides erosion of agricultural soils are contributing heavily to the P load in sediments; (3) the large amount of P stored in the reductant soluble fraction indicates that under the reducing environment at many lake bottoms there is a large source of P that can be brought into solution by reduction to a more available form; (4) that P entering the lake water is precipitated and coated by an insoluble ferric oxide coating or some undetermined form that is soluble in reductant extract.

The first result is not too surprising since the P system in soils is known to undergo shifts and transformations in response to pH changes and other factors. The stresses of the anaerobic waterlogged environment could very likely cause these shifts from Al- and Fe-P to reductant soluble P.

The second finding is also expected since, as mentioned in a previous section, industrial and municipal discharges of P are much greater than the contribution from agricultural sources.

Factor 3 is very significant when the task of cleaning up our aquatic environments is considered. With this large storehouse of P that can be made available continuously under the natural conditions of many lakes, it is apparent that the levels of P in solution in the lakes are quite well buffered. To bring about any significant improvement in this level would require the stoppage of any new inputs of P and the exhaustion of this readily available storehouse. It is the immediate goal of environmental researchers today to greatly reduce or stop the input of new P into our waters. In light of these findings, however, this alone may not be enough to bring any significant change in the quality of our lakes and streams for several years.

Finding 4 is quite surprising. Most of the lakes in this study have marl bottoms, and calcium ion should predominate all cations in solution. According to the theory behind the Chang and Jackson Fractionation procedure, an insoluble ferric oxide coating around a particle containing P is reduced to a soluble ferrous oxide by a reductant solvent, enabling the P to be extracted. If this is the process occurring in these lakes, then there must be sufficient ferric iron present to coat most of the P entering the water. It is surprising that this much iron is available in the calcareous lake bottoms. This process also must occur against the reducing gradient of the anaerobic environment.

An alternative explanation that could bear more research is that as P is incorporated into the bodies of plant and animal organisms, and as these organisms die and settle to the bottom the P is stored in an organic form that happens to be soluble in the reductant solvent. The sediment samples taken were all very high in organic matter, and organic matter is capable of sorbing a large amount of P. This explanation is quite possible.

Controlled Redox

It was hoped that by bubbling oxygen or nitrogen through a waterlogged sample that we could manipulate and control the redox potential with sufficient accuracy to be able to obtain analysis of P and Fe levels at a series of varying potentials. This data would then be valuable in determining the influence of redox potential upon the solubility of P and Fe. This attempt produced erratic data for the following reasons:

(1) Chemical buffering in many soils resisted the lowering of the redox potential to reducing levels. One Iron River soil sample was waterlogged for over a year and the potential was still greater than +200 millivolts.

(2) To maintain redox potentials at highly oxidizing or reducing conditions usually meant that oxygen or nitrogen needed to be introduced continually for several hours at a time. This action kept the sample stirred up and the clay particles suspended. This condition differs greatly from those of waterlogged soils or lake bottoms.

(3) Poisoning of the platinum electrodes caused uncertainties about the accuracy of the measurements over the two week periods.

(4) The lack of immediate control over the volume of gas introduced often meant that in the more poorly poised soils, the potential would go over or under the desired level before the instrument could stop the flow of gas. The potential would then have to slowly drift back towards the equilibrium level.

(5) The uncertainty about the time required for the chemical equilibrium to catch up to the redox potential. At least two weeks was usually allowed.

(6) The necessity to replace the withdrawn aliquot at sampling time with distilled water may have caused dilution effects within sample.

The results of the controlled redox experiment upon two Michigan soils is shown in Tables 31 and 32. The results are erratic and cannot be considered quantitatively meaningful in relating P, Fe and redox potential.

Table 31. P and Fe analysis of solution after controlled redox incubation of a waterlogged Wisner soil.

Date	P	Fe	Redox
	ppm	ppm	v
10/16/29	0.114	0.212	-0.058
11/22/29	0.066	0.176	0.142
12/6/69	0.068	0.141	0.342
12/22/69	0.143	0.141	0.472

Table 32. P and Fe analysis of solution after controlled redox incubation of a waterlogged Locke soil.

Date	P	Fe	Redox
	ppm	ppm	v
7/4/70	.379	15.440	- .208
7/20/70	.392	3.460	+ .092
8/18/70	.540	26.855	+ .392
9/15/70	.485	518.381	+ .142

SUMMARY AND CONCLUSIONS

Six lakes were sampled at 5 or 6 depths at 3 m intervals in June 1969, October 1969 and June 1970. The sediment-water interface was analyzed for Eh, P and Fe immediately after sampling and after 30 days of anaerobic incubation. After the incubation period, each sample was air dried and a P fractionation analysis was performed on the sediments according to the revised method of Chang and Jackson (1957, 1962).

The first objective was to study the effects of a reducing environment upon the solubility of P. The second objective was to determine the forms that most P is stored in when sorbed by the sediment and the degree to which it might be soluble under reducing conditions. The final objective was to study the influence of a laboratory controlled redox potential upon the solubility of P.

The data may be summarized as follows:

(1) Anaerobic incubation of waterlogged sediments resulted in an increase in P in solution. A predicted regression equation indicates a 3.5 fold increase in P occurred.

(2) Aerobic incubation of waterlogged sediments resulted in an increase in P in solution in lakes low in P originally, but a decrease in P with lakes high in P at sampling.

(3) Redox potentials had no quantitative control over the levels of P or Fe in solution although a qualitative influence was strongly evident. The sample with the lowest Eh within a lake usually had

the highest levels of P and Fe.

(4) The Al-P and Fe-P fractions were very small in the sediments sampled, usually representing less than 5% of the total P.

(5) The Ca-P fraction was similar in magnitude to the amount found in many common Michigan soils.

(6) The reductant soluble-P fraction predominated all but one of the lakes sampled. This varies quite radically from most Michigan soils.

(7) The levels of P extracted from the sediments are much too high to have been contributed only by the sediments themselves as they were deposited. P must have been introduced by other sources such as sewage effluent and industrial discharges, and adsorbed by the sediment in the reductant soluble form.

(8) Even in these calcareous lakes there must be enough Fe to precipitate large amounts of P into the reductant soluble form or there must be other P precipitating substances present.

(9) Efforts to control the redox potential of a waterlogged soil sample for two weeks before analysis yielded erratic and unsatisfactory results that could not be treated as quantitatively significant.

BIBLIOGRAPHY

1. Bartholomew, R. P. 1931. Changes in the Availability of Phosphorus in Irrigated Soils. Soil Science 31:209-218.

2. Bohn, H. L. 1968. Electromotive Force of Inert Electrodes in Soil Suspension. Soil Sci. Soc. Am. Proc. 32:211-215.

3. _______________. 1970. Redox Potentials. Paper in printing.

4. Broeshart, H., Haunold, E. and M. Fried. 1965. The Effect of Water Conditions and Oxidation-Reduction Status of Rice Soils on the Availability of Soil and Fertilizer Phosphate. Plant and Soil 23:305-313.

5. Chakravarti, S. and T. K. Ghoshal. 1968. Anaerobic Reduction and Phosphate Solubility. J. Indian Soc. Soil Sci. 16:409-413.

6. Chang, S. C. and M. L. Jackson. 1957. Fractionation of Soil Phosphorus. Soil Science 91:133-144.

7. Chang, S. C. 1962. Modified Procedure of Fractionation of Soil Phosphorus. Agric. Chem. Bull. National Taiwan University. pp. 28-31.

8. Chiang, Ching-Tsun. 1968. Availability and Forms of Phosphorus in Paddy Soils: V. Factors Affecting the Solubility of Soil Phosphorus. Tiawan Fertilizer Company, Ltd., Res. Bull. No. 30. pp. 11-37.

9. Frink, C. R. 1969. Chemical and Mineralogical Characteristics of Eutropic Lake Sediments. Soil Sci. Soc. Am. Proc. 33:369-372.

10. Furukawa, H. and K. Kawaguchi. 1969. Contribution of Organic Phosphorus to the Increase of Easily Soluble Phosphorus in Waterlogged Soils, Especially Related to Phytic Phosphorus (Inositol Hexaphosphate). Nippon Dojo-Hiryogaku Zasshi 40:141-148.

11. Gasser, J. K. R. 1956. The Effects of Anaerobically Fermenting Rice Straw on the Mobilization of Aluminum, Calcium and Iron Phosphate. 6th International Congress of Soil Science, Volume C, pp. 479-491.

12. Harter, R. D. 1968. Adsorption of Phosphorus By Lake Sediment. Soil Sci. Soc. of Am. Proc. 32:514-518.

13. Hayes, F. R. and J. E. Phillips. 1958. Lake Water and Sediment: IV. Radiophosphorus Equilibrium With Mud, Plants, and Bacteria Under Oxidized and Reduced Conditions. Limnology and Oceanography 3:459-475.

14. Jackson, M. L. 1958. Soil Chemical Analysis. Prentice-Hall, Inc., Englewood Cliffs, N. J.

15. Jeffery, J. W. O. 1961. Measuring the State of Reduction of a Paddy Soil. J. of Soil Science 12:317-325.

16. Jeffery, J. W. O. 1961. Defining the State of Reduction of a Paddy Soil. J. of Soil Science 12:172-179.

17. Juo, A. S. R. 1966. Chemical and Physical Factors Affecting the Relative Availability of Inorganic Phosphorus in Soils. Ph.D. thesis, Michigan State University.

18. Mahapatra, I. C. and W. H. Patrick, Jr. 1969. Inorganic Phosphate Transformation in Waterlogged Soils. Soil Science 107:281-288.

19. Mandal, L. N. 1964. Effect of Time, Starch and Lime on the Transformation of Inorganic Phosphorus in a Waterlogged Rice Soil. Soil Science 97:127-132.

20. Olson, R. V. 1965. Colorimetric Determination of Total Iron in Methods of Soil Analysis. C. A. Black, Editor. American Society of Agronomy, Madison, Wisconsin. pp. 966-967.

21. Patrick, W. H., Jr. and I. C. Mahapatra. 1968. Transformation and Availability to Rice of Nitrogen and Phosphorus in Waterlogged Soils. Advances in Agronomy 20:323-359.

22. Patrick, W. H., Jr. 1964. Extractable Iron and Phosphorus in a Submerged Soil at Controlled Redox Potentials. 8th International Congress of Soil Science. Bucharest, Romania. pp. 605-609.

23. Pomeroy, L. R., Smith, E. E. and C. M. Grant. 1965. The Exchange of Phosphate Between Estaurine Water and Sediments. Limnology and Oceanography 10:167-172.

24. Ponnamperuma, F. N., Tianco, E. M. and T. Loy. 1967. Redox Equilibria in Flooded Soils: 1. The Iron Hydroxide Systems. Soil Science: 103:374-382.

25. Rinkenberger, G. D. 1966. Transformation of Added Phosphorus in Three Michigan Soils. M.S. thesis, Michigan State University.

26. Shapiro, R. E. 1958. Effect of Flooding on Availability of Phosphorus and Nitrogen. Soil Science 85:190-198.

27. Shapiro, R. E. 1958. Effect of Organic Matter and Flooding on Availability of Soil and Synthetic Phosphates. Soil Science 85:267-272.

28. Taylor, A. W. 1967. Phosphorus and Water Pollution. J. of Soil and Water Conservation 22:228-231.

29. Terman, G. L., Allen, S. E., and O. P. Engelstad. 1970. Response by Paddy Rice to Rates and Sources of Applied Phosphorus. Agronomy Journal 62:390-394.

30. Thurlow, D. L. 1965. Interaction of Rate and Method of Fertilizer Application and Soil Phosphorus with Yield and Chemical Composition of Sugar Beets. Ph.D. thesis, Michigan State University.

31. Yamane, I. and K. Sato. 1968. Measurement of Redox Potentials of Submerged Soils. Nippon Dojo-Hiryogaku Zasshi 39: 535-542.

32. Williams, C. H. and J. R. Simpson. 1965. Cultivation and Waterlogging on Soil Phosphorus Availability. Aust. J. of Agric. Res. 16:413-427.