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# ADSORPTION OF PHOSPHORUS BY FIVE MICHIGAN SOILS UNDER ANAEROBIC CONDITIONS

By

Mancowetaya Srisen

# A DISSERTATION

Submitted to Michigan State University in partial fulfillment of the requirements for the degree of

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### ABSTRACT

# ADSORPTION OF PHOSPHORUS BY FIVE MICHIGAN SOILS UNDER ANAEROBIC CONDITIONS

By

### Nanoowetaya Srisen

Chemistry of P in flooded paddy soils, in lakes and in streams is important for rice cultivation in Thailand and for the control of P level in natural waters in the United States as well as other parts of the world.

Flooded soils as well as air dried soils can adsorb applied P from dilute solutions. It is known that P availability will increase upon flooding.

This study was designed to investigate the behavior of P adsorption by Michigan soils under anaerobic conditions and to examine the Langmuir adsorption isotherm as a method of evaluating P adsorption by flooded soils.

Five Michigan soils varying in chemical and physical properties were used for the laboratory study. The anaerobic chamber with  $10\% H_2$  and  $90\% N_2$  atmosphere was used to keep the flooded soils under anaerobic conditions.

Preliminary studies showed that air dried soils adsorbed more P from 0.01 M CaCl<sub>2</sub> than from a water solution. At high P concentration soils adsorbed more P from the 0.01 M CaCl<sub>2</sub> solution where it was adjusted to pH 6 than when pH was not. The P adsorption reaction in 0.01 M CaCl<sub>2</sub>, for both adjusted and unadjusted pH treatment, reached equilibrium faster than in water solution treatment. Phosphorus adsorption isotherm showed that for air dried soils, subsoils adsorbed more P and with greater bonding energy than surface soils. Fine textured soils adsorbed more P than coarse textured ones. For coarse textured soils, subsoils adsorbed more P than surface soils, but for fine textured soils the difference between the amount of P adsorbed by A and B horizons was not significant.

Langmuir adsorption isotherms showed that soils have at least two different components with respect to P adsorption, one involving tightly bound and the other involving loosely bound P.

In flooded surface soils, the P adsorption behavior changes with the chemical changes upon flooding. The adsorption changes occurred mostly in the loosely P bound portion in the soils. The amount of P adsorbed increased with lower bonding energy of P adsorption upon submergence. Extractable Fe apparently played an important role in the change in P adsorption after flooding. The P adsorption in the loosely bound portion apparently is responsible for the increase in the extractable P for flooded soils and may be considered to be of benefit for rice cultivation.

For flooded subsoils, the change in P adsorption also occurred in the loosely bound portion, with increases in the amount of P adsorbed and with lower bonding strength. But the change was not as great as that which occurred in surface soils due to the lesser degree of reduction upon flooding. To my parents and Thai farmers.

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### INTRODUCTION

Phosphorus has long been recognized as an important element in plant nutrition. All plants require P for growth and development because P is a constituent of metabolism, and plays a key role in energy conservation and biosynthetic reactions in plants.

Nutrient enrichment in natural water, a natural process which may be accelerated by man, is one of the main problems in water ecology. However, P is most often considered the limiting nutrient for plant growth in lakes and streams (Ellis and Erickson 1969; Syers et al., 1973 a). Because of the low natural levels of P and the nature of the source of P to the natural waters, prevention or reversal of eutrophication through control is generally more feasible with P than with other nutrients. Therefore the behavior of P in paddy soils and in lakes and streams are important for rice cultivation and the control of P level in natural waters.

Soil has ability to adsorb P from dilute solution. The applications of adsorption isotherm equations to describe the behavior of P adsorption by soil have been intensively studied (Olsen and Watanabe, 1957; Shapiro and Fried, 1959; Udo and Uzu, 1972; and Syers et al., 1973 b). A P adsorption equation appears to be useful in describing P availability to plants (Fried and Broeshart, 1967) and the correlation between P adsorption isotherms and plant growth also have been studied (Woodruff

and Kamprath, 1965). The use of P adsorption isotherms to describe and predict the reduction of P level in sewage effluent by soils has been reported (Ellis and Erickson, 1969). However, the P adsorption study and its application was limited to upland and dried soils.

The solubility and availability of soil and applied P increases upon flooding (Shapiro, 1958a and b; Patrick and Mahapatra, 1968; and Ponnaperuma, 1972). But applied P can also be adsorbed by paddy soils, muds, and lake sediments (Mandal and Das, 1970; Hesse, 1962; Harter, 1968; Shukla et al., 1971). However, few of these studies used the P adsorption isotherm to describe the behavior of P adsorption by anaerobic soils. The adsorption of P by submerged soils in Michigan has not been studied.

The first objective of this study was to investigate the behavior of P adsorption by Michigan soils under anaerobic conditions. The second objective was to determine if the Langmuir adsorption isotherm could be used to predict P adsorption by anaerobic soils.

### LITERATURE REVIEW

### 2,1 Soil Chemical Changes After Submergance,

Submerging or waterlogging a soil creates conditions markedly different from those of a well-drained soil. The most important chemical and electro-chemical changes that take place when a soil is flooded are 1) decrease in oxidation-reduction potential (Eh) and change in pH value; 2) reduction of Fe and Mn with the accompanying increase in their solubilities; 3) change in availability of P and Si; 4) denitrification; 5) accumulation of ammonia; 6) generation of toxic organic compounds such as fatty acids, mercaptans, sulfides, amines and other unidentified substances; and 7) release of cations such as  $NH_{l_{1}}^{+}$ ,  $Na^{+}$ ,  $K^{+}$ ,  $Ca^{+2}$  and  $Mg^{+2}$  from the colloidal complex into soil solution (IRRI, 1963; Ponnamperuma, 1965).

Some of these chemical changes were reviewed and will be discussed in the following paragraphs.

# 2.1.1 Oxidation-Reduction Potential and Soil Acidity.

Reduction of the soil is one of the most important changes caused by flooding. In the absence of  $O_2$ , facultative and obligate anaerobes use  $NO_3^-$ , Mn(IV), Fe(III),  $SO_4^{-2}$ , dissimilation products of organic matter,  $CO_2$ ,  $N_2$  and even  $H^+$  as electron acceptors in their respiration, reducing  $NO_3^-$  to  $N_2$ , Mn(IV) to Mn(II), Fe(III) to Fe(II),  $SO_4^{-2}$  to  $H_2S$ ,  $CO_2$  to  $CH_4$ ,  $N_2$  to  $NH_3$  and  $H^+$  to  $H_2$ . Anaerobic respiration also produces substances that reduce soil components chemically (Ponnamperuma, 1972).

The intensity of soil reduction can be measured quantitatively as the oxidation-reduction potential (Eh) of the soil. Because of its diagnostic and interpretative value in the study of anaerobic condition

of environments, such as waterlogged soils, marsh soils, lake muds, and marine sediments, redox-potential (Eh) has been intensively measured and its ecological significance indicated (Gillespie, 1920; Mortimer, 1924, Pearsall and Mortimer, 1939; Zobell, 1946; Pierce, 1953; Jefferry, 1960; and Aomine, 1962). However, the high promise this property has for diagnostic and interpretative purposes in rice production cannot be fully exploited without a clear understanding of redox-potential in waterlogged soils (Ponnamperuma and Castro, 1964).

Because the redox-potential is a mixed potential in most natural systems, it is very difficult to understand. The theory of redoxpotential, both in pure and mixed systems, equilibrium potentials and nonequilibrium potentials was well explained by Bohn (1971). The redox-potential or electron availability affects the oxidation states of H, C, N, O, S, Mn, Fe, Co and Cu in the systems. Any chemical reaction which involves exchange of electrons will be influenced by Eh.

Ponnamperuma (1972) comprehensively explained the measurement of the state of reduction -- both intensity (redox-potential) and capacity (total concentration of reduction products). He reviewed and discussed the problems, advantages and disadvantages of Eh measurements, and also reviewed the reducing capacity measurement in natural systems, including soils.

Because the hydrogen ion concentration affects Eh by direct participation in exidation-reduction or by influencing the dissociation of exidant or reductant, Ponnamperuma and Castro (1964) proposed the idea of dE/dpH expression to evaluate the reduction of soils. They noted some similarities between the potentials and dE/dpH values of the reduced

soils and those of bacterial suspension. Ponnamperuma (1972) noted that dE/dpH varies with the system. Although most workers use - 59 m.v./pH unit (at 25 C) as the correction factor, Patrick (1960) found that the experimental values ranged from about -60 for aerobic soils to as steep a slope as -232 for some reduced soils. This uncertainty makes many potentials corrected to pH 7 unreliable. But Ponnamperuma et al. (1967) have shown theoretically and experimentally that the dE/dpH slope for the solutions of reduced ferruginous soils after the peak of water-soluble  $Fe^{+2}$  is -59 m.v./pH. This corrected value is also reported as a good conversion factor if the redoxpotential is an equilibrium potential (Aomine, 1962; Bohn, 1968, 1971; and Patrick and Mahapatra, 1968):

> $Eh_7 = Eh_x - 60(7-x)$  ... (1) where x is the pH of the soil suspension, and Eh is in  $m_v V_v$ .

Practically speaking, Eh is the single electrochemical property that serves to differentiate waterlogged soils from well-drained soils. Ponnamperuma (1972) stated that the low potentials (+200 to -400 m.v.) of submerged soils and sediment reflect this reduced state; whereas, high potentials (+300 to +800 m.v.) of aerobic media reflect their oxidized conditions. However, Patrick and Mahapatra (1968) concluded that aerated soils have characteristic redox-potential in the range +400 to +700 m.v.; waterlogged soils exhibit potentials from +700 m.v. to as low as -250 to -300 m.v. In well-drained soils the Eh is difficult to reproduce because of a lack of poising (easy to change in Eh) and the range in Eh values is narrow. Expected Eh values corrected to

pH 7.0 are shown below:



Fatrick and Mahapatra (1968), noted that in waterlogged soils Eh is the best available measurement of oxidation-reduction status of soils because; 1) the range of Eh values in submerged soils is much wider, approximately 1,000 m.v. as compared to a range of approximately 300 m.v. in well-drained soils; 2) in waterlogged soils the higher concentration of reduced components contributing to the potential results in better reproducibility of the potential reading although reproducibility is still one of the main limitations of Eh measurements in waterlogged soils; 3) because of the ease of which it is reduced,  $0_2$  is usually absent from submerged soils and methods used for measurement of  $0_2$  content and  $0_2$  diffusion rates employed in well-drained soil cannot be used in waterlogged soils.

Reduction of a submerged soil proceeds roughly in sequential reductions, and can be predicted by thermodynamics, (Ponnamperuma and

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Castro, 1964; Turner and Patrick, 1968). Many researchers studied and/or summarized these phenomena. Aomine (1962), reviewed the studies on Eh of paddy soils in Japan and noted that there are 7 steps of microbic metabolism in waterlogged soils; 1)  $O_2$  disappearance; 2) NO<sub>3</sub> reduction; 3) Mn<sup>+2</sup> formation (all of these steps occurred at the initial Eh of +600 to +500 m.v.); 4) Fe<sup>+2</sup> formation (Eh +500 to +300 m.v.); 5) sulfide formation and sulfate reduction (Eh 0 to -190 m.v.); 6) H<sub>2</sub> formation (-150 to -220 m.v.); and 7) CH<sub>4</sub> formation (-150 to -190 m.v.). This is reflected in the microbial succession -- aerobic, facultative anaerobic and strict anaerobic -after submerging of the soils.

As long as  $0_2$  is present in the soil, other oxidized components of soil are relatively safe from biological and chemical reductions. After  $0_2$  has disappeared from a waterlogged soil, the need for electron acceptors by facultative anaerobic and true anaerobic micro-organisms results in the reduction of several oxidized components. If an energy source is available to micro-organisms  $N0_3^-$ , higher oxides of Mn, hydrated ferric oxides and  $S0_4^{-2}$  will be reduced (Patrick and Mahapatra, 1968).

 $0_2$  is the first oxidant to be reduced, and it becomes unstable within one day after submergence. The next component to be attacked is  $NO_3^-$  but its reduction begins only after  $0_2$  concentration has been reduced to a very low value (Bremner and Shaw, 1958; Greenwood, 1962; and Turner and Patrick, 1968). Nitrate also retards the reduction of other redox components. It will stabilize the potential at +200 m.v. to +400 m.v. and retard the production of Mn<sup>+2</sup>, Fe<sup>+2</sup>, S<sup>-2</sup>, and CH<sub>4</sub> in submerged soils (Ponnamperuma and Castro, 1964; Turner and Patrick, 1968).

Patrick (1960), showed that under controlled redox-potential conditions, NO<sub>3</sub><sup>-</sup> in a waterlogged soil was unstable at Eh of +340 m.v. at pH 5.1. Turner and Patrick (1968), found that the Eh at which O<sub>2</sub> disappeared was in the range +320 to +340 m.v. (assuming the Eh/pH slope of -60 m.v. per pH unit with Eh<sub>7</sub> = +225 m.v.).

Mn follows  $NO_3^-$  in the reduction sequence. But its influence is weaker than that of  $NO_3^-$  because it is insoluble in water and is used as an electron acceptor in respiration by only a limited number of microorganisms. However, added and/or native  $MnO_2$  retards the decrease in Eh of flooded soils and prevents the accumulation of Fe<sup>+2</sup> and other products (Ponnamperuma and Castro, 1964; Ponnamperuma et al., 1965).

The next mineral system in reduction sequence is the  $Fe(OH)_3$ -Fe<sup>+2</sup> system. But its influence on soil reduction is not as obvious as that of  $NO_3^-$  or  $MnO_2$  due to its low standard potential. However, soils rich in Fe(III) showed a slower reduction in Eh in the zone -50 to -200 m.v. (Ponnamperuma, 1965), and the addition of  $Fe_2O_3$  to paddy soil depressed  $CH_4$  production (Asami and Tarki, 1970). The reduction sequence that may be expected is shown in the following table: Table 1. Reduction sequence as related to Eh.<sup>1/</sup>

Component	Detectability	Eh <sub>7</sub>
0 <sub>2</sub>	undetectable	<b>*</b> 330
ло <mark>-</mark>	ta 61	220
Mn	detectable	200
Fe	B1 BT	120
so <sub>4</sub> -2	undetectable	-150

1/ Ponnamperuma (1972)

Studies of redox systems in waterlogged soils have been conducted in two ways: 1) the soil is waterlogged and changes in Eh and concentration of reducible substances are determined; or 2) the Eh of the waterlogged soil is controlled at a constant potential and the concentration of reducible substances are determined. According to Patrick (1966) one of the biggest limitations of the use of Eh for studying reactions in waterlogged soils has been the difficulty of maintaining the Eh of the soil at a particular value throughout an experiment. He designed an apparatus used for controlling the redox-potential. This system allows waterlogged soils to become highly reduced (as low as -200 to -280 m.v.). This controlled Eh method has been used to study many redox systems in waterlogged soils. (Patrick, 1960; Patrick, 1964; Turner and Patrick, 1968; Cornell and Patrick, 1968; Gotoh and Patrick, 1972, 1974). The details of their studies on the influence of Eh and/or pH upon Fe, Mn, and P transformation will be discussed in the Fe. Mn and P sections.

Ponnamperuma and his colleages studied the redox system by measuring Eh and reducible materials with time of submergence (IRRI, 1963, 1964, 1965, 1966; Ponnamperuma, 1965). The quantitative treatment of redoxequilibria has been formulated. The iron hydroxide redox system has been intensively studied and described by Ponnamperuma et al. (1967). The manganese oxide redox system also has been studied and explained by Ponnamperuma et al. (1969).

The pH value of waterlogged soils tends to become neutral. When acid soils are submerged the pH increases; whereas that of calcareous and alkaline soils decrease, (IRRI, 1963; IRRI, 1964; Mahapatra, 1968; and Ponnamperuma, 1972).

The tendency and the magnitude of pH change depends upon soil characteristics, such as the initial soil pH, active Fe and Mn contents, organic matter content and cation exchange capacity (C.E.C.) of the soils. IRRI (1963) reported that in acid soils (pH 4.4-5.8) high in active Fe contents, pH values decreased shortly for a few days after flooding and then increased sharply to a maxima between 6.5 to 7.0 within 20 days of submergence. The slightly acid soils, which were low in active Fe but high in active Mn content, with initial pH values of 6.2-6.6, increased somewhat more slowly in pH to a steady maxima of 7.0-7.2. A soil with an active Mn content of more than 2,000 ppm gave a maximum pH of 7.5. The neutral and slightly alkaline soils showed slight decreases in pH a day after submergence, then resumed and maintained almost their initial values. Another acid soil, low in both active Fe and Mn but high in organic matter, showed more fluctuations in pH than the others and the pH increased with the mean maximum pH value less than 6.5.

Puttaswamygowda and Pratt (1973), demonstrated that pH of sodic soils was decreased by the addition of straw and  $\operatorname{CaCl}_2$  with accompanying increases in  $\operatorname{Ca}^{+2}$ , Na<sup>+</sup>, Mg<sup>+2</sup> concentrations. Submerged anaerobic conditions have the largest effect on promoting these reactions. However, Olomu et al. (1973), found that pH of soil solution extracted from calcareous soils (pH 7.4 - 7.9) changed little upon flooding. These soils were high in C.E.C. and high in organic matter contents. But coarse-textured soils exhibited relatively large changes in their pH values. It appears that the buffering capacity of the soils influenced the relative changes of soil pH upon flooding. Liming the soil has no effect on pH change due to submergence. Mukhopadhyay et al. (1967), found that with an acid soil with pH 4.4, the pH decreased within the first 17 days and then increased and reached stability near pH 7.0 about 62 days after flooding. Heavily limed soil (pH changed to be 7.7 initially), showed a decrease in its pH value and stabilized at pH 7.0 within the same period of submergence.

Ponnamperuma (1972) concluded that when an aerobic soil is submerged, its pH decreases during the first few days, reaches a minimum, and then increases to a very stable value of 6.7 - 7.2 a few weeks later. The overall effect of flooding is to increase the pH of acid soils and to depress the pH of sodic and calcareous soils.

Draining and exposure to air reverses the pH changes in paddy soils, mangrove swamps, lake muds and bogs, and anaerobic soils, (Ponnamperuma, 1972).

The mechanism of pH change including quantitative interpretation of pH change has been intensively studied (IRRI, 1964). It was concluded that the increase in pH of an acid soil upon flooding is caused by reduction of Fe and Mn; pH throughout submergence in calcareous soils is regulated by the partial pressure of  $CO_2$  and the pH value of the soil solution of reduced soil lies between 6.5 and 7.0 regardless of initial pH and other properties of the soil. Ponnamperume et al. (1966 a) concluded that the pH of alkali and calcareous soils decreased, while those of acid soils increased to a fairly stable value of 6.7 to 7.2 twelve weeks after flooding. At this time the solution pH values

were 6.5 to 7.0. The pH of the soil solutions were lower than those of the soil suspensions for the alkali and calcareous soils from the start of submergence, and for the acid soils after soil reduction.

The increase in soil solution pH of acid soils was quantitatively related to the potential of the  $Fe(OH)_3$ -  $Fe^{+2}$  system, while the decrease in pH of the alkali and calcareous soils was defined by the partial pressure of  $CO_2$  through the  $Na_2CO_3$ -H $_2O-CO_2$  and  $CaCO_3$ -H $_2O-CO_2$  systems, respectively. The pH of reduced-acid soils high in Fe appears to be determined by the  $Fe_3(OH)_8$ -H $_2O-CO_2$  system (Ponnamperuma et al., 1966 a,b; Ponnamperuma et al., 1967; and Ponnamperuma, 1972).

Ponnamperuma (1972) noted that the decrease in pH shortly after submergence is probably due to the accumulation of  $CO_2$  produced by respiration of aerobic bacteria, because  $CO_2$  depressed the pH even of acid soils. The subsequent increase in pH of acid soils is due to the reduction. The pH of submerged calcareous and sodic soils are lower than those of aerobic soils because of the accumulation of  $CO_2$ . The pH of alkaline soils is also sensitive to  $CO_2$  changes as shown by Ponnamperuma et al. (1966 a).

The important reduction reactions that occur in nature involve the consumption of  $H^+$  ions. This means a decrease in acidity or net gain in  $OH^-$  concentration (Ponnamperuma, 1972). Since most soils contain more Fe(III) oxide hydrates than any other oxidants, the increase in pH of acid soils is largely due to the reduction of Fe, (Ponnamperuma et al., 1967).

The pH change influences  $OH^-$ ,  $CO_3^{-2}$ ,  $S^{-2}$ , P and Si equilibria in submerged soils. These equilibria regulate the precipitation and

dissolution of solids, the sorption and desorption of ions, and concentrations of such ions or substances as  $Al^{+3}$ ,  $Fe^{+2}$ ,  $H_2S$ ,  $H_2CO_3$ , and undissociated organic acids. The details of these phenomena were discussed by Ponnamperuma (1972).

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2.1.2 Manganese and Iron Related to Reducing Condition.

When areated soils are submerged, Mn reduction from insoluble oxidzed forms to slightly reduced forms occurs. Together with disappearance of  $0_2$  and  $N0_3$ , an increase in Mn<sup>+2</sup> in the soil solution and on the cation exchange complex is one of the first measurable effects of reducing conditions caused by waterlogging (Patrick and Turner, 1968).

Submerged soil solutions were different from aerated soil solutions in that they contained high concentrations of Fe and Mn present as protobicarbonates. Submerged soil solutions were also high in Ca and Mg and contained  $H_2S$  and other sulfides (Robinson, 1930). It was noted that the high concentration of Fe, Mn, Ca and Mg was caused directly by microbiological action on the organic matter which produced  $CO_2$ and other gases. This  $CO_2$  was mainly responsible for holding Fe, Mn, Ca and Mg in the solution. In the absence of organic matter the solubility of Fe, Mn, Ca and Mg was not increased under submerged soil conditions. It also found that toxic concentrations of Fe<sup>+2</sup> and sulfides developed in a few days after submergence. Toxic concentrations of Mn developed somewhat more slowly.

The main transformations of Mn in submerged soils are the reduction of Mn(IV) oxides to Mn(II), (resulting in increased solution  $Mn^{+2}$ ), precipitation of MnCO<sub>3</sub> and oxidation of Mn<sup>+2</sup> diffusing or moving by mass flow to oxygenated interfaces in the soil (Ponnamperuma, 1972).

There were marked differences among the soils in the pattern of Mn reduction. Soils with a high content of active Mn, regardless of pH and organic matter content showed a rapid increase in  $Mn^{+2}$ 

concentration during the first 30 days of waterlogging and then decline slowly thereafter. Soils low in active Mn increases slowly in  $Mn^{+2}$ concentration and reached maximum values which were very much lower than in soils with higher Mn content. The overriding factor that determined the kinetics of Mn reduction was the active Mn content of the soil (IRRI, 1963).

IRRI (1964), reported that within 1 to 3 weeks of flooding almost all of the EDTA-dithionate extractable Mn present in the soils, except those low in organic matter, is reduced. They concluded that the reduction is both chemical and biological and precedes the reduction of Fe. The kinetics of water-soluble  $Mn^{+2}$  reflects the influence of soil properties on the transformation of Mn.

Patrick and Turner (1968), noted that Mn exists in at least four forms in waterlogged soils: 1) water soluble: 2) exchangeable: 3) easily reducible; and 4) residual Mn or that remaining after extraction of the other three forms. The first two forms are largely Mn<sup>+2</sup> while the easily reducible fraction is composed of higher oxides of Mn. In addition to these forms. chelated Nn may also be an important form in some soils. Studying anaerobic silty clay soil with low organic matter, they found that with 25 days of submergence as the content of reducible Mn decreased the content of exchangable Mn increased. These two fractions accounted for most of the total Mn present in the soil, Water-soluble Mn did not increase until after several weeks of waterlogging in that soil and accounted for only a very small fraction of the total soil Mn, Residual Mn was little affected by flooding. They also found that with controlled Eh of waterlogged soil samples, the abrupt changes occurred in

distribution of Mn between the easily reducible and Beginning at this fraction at a potential of about +400 m.v.  $(Eh_7)$ . Beginning at this potential there was a pronounced conversion of easily reducible Mn to exchangeable forms as the soil became more reduced. The transition of Mn from easily reducible to the exchangeable form was greatest over the range +400 to +300 m.v. and was essentially completed at +200 m.v. Solution Mn also increased in concentration at a potential below +400 m.v., but not to the extent of the exchangeable fraction. Residual Mn was not affected by changes in Eh.

For paddy soils, Gotoh and Yamashita (1966), reported that there was a rapid increase in  $Mn^{+2}$  content in the early stage of flooding; after that successive rises and falls in  $Mn^{+2}$  content were observed. The rapid increase in  $Mn^{+2}$  content was promoted by the addition of organic matter. They concluded that the oxides of Mn comprising  $MnO_2$ ,  $Mn_2O_3$ , and  $Mn_3O_4$  are easily reducible under strong reducing conditions upon waterlogging soils.

The effects of organic matter level, time of incubation and moisture content on extractable Fe and active Mn in acidic, neutral, calcareous and saline-alkaline soils were also reported, (Takkar, 1969). They found that Fe and Mn availabilities were influenced by soil temperature. On incubation at 60 percent water holding capacity, Fe increased greatly after 35 days and Mn decreased after 7 days. These changes were accompanied with increasing organic matter and with time in most soils except in acidic soils in which Mn was found to increase after 69 days. Under waterlogged conditions, marked increases of Fe and decreases of Mn were noticed after 7 days. The lower amount of Fe and the time lag in its release in calcareous soils were due to the presence of iron oxide in highly crystalline forms in these soils. High content of free Fe and low pH resulted in higher amounts of extractable Fe in acid soils. Under waterlogged and high organic matter conditions a decrease in Eh and a high concentration of  $Fe^{+2}$  were observed. As reported before, soil pH tended to become neutral.

Most flooded soils contain sufficient water-soluble Mn for growth of rice and Mn toxicity has not been shown to occur in flooded soils. But native or added  $MnO_2$  retards  $Fe^{+3}$  reduction and counteracts the adverse effect of excess  $Fe^{+2}$  and other reduction products. Yuan and Ponnamperuma (1966) found that  $MnO_2$  retarded the decrease in Eh of the soils. In spite of the slight pH increase, it generally depressed the concentration of water-soluble  $Fe^{+2}$  and oxidizable organic matter and increased the concentration of water-soluble  $Mn^{+2}$  in soils. Nhung and Ponnamperuma (1966) found that  $MnO_2$  at 1.0 percent markedly retarded the fall in Eh and reduction of  $SO_{44}^{-2}$ , slightly increased pH, depressed the concentration of  $Al^{+3}$  and  $Fe^{+2}$  and oxidizable materials, and markedly increased the concentration of  $Mn^{+2}$  in the soil solution.

Temperature also affects the kinetics of  $Fe^{+2}$  and  $Mn^{+2}$  in low-land rice soils. Cho and Ponnamperuma (1971), found that  $Fe^{+2}$  and  $Mn^{+2}$ increased after flooding, reached peak values, and then declined. In the 38  $\Rightarrow$  20 C and 30 C regimes the peaks were early, short and sharp, while in the 20 C and 15  $\Rightarrow$  31  $\Rightarrow$  18 C regimes they were late, high, and broad.

The transformation of Mn and Fe upon flooding were studied by Mandal (1961). He reported that Mn transformation was somewhat different

from that of Fe. It enters into exchangeable complexes and also appeared in soluble form much earlier than Fe. The reducible Mn, comprising higher oxides such as  $MnO_2$ ,  $Mn_2O_3$ , and  $Mn_3O_4$  showed a decrease for some time after the soil had been waterlogged and then began to increase to a level that was more than at the start. Iron and Mn in the organic complex fraction was not affected to any appreciable extent by the flooding condition with or without the addition of organic matter.

Ponnamperuma, et al. (1969), noted that the chemistry of manganese oxides is very complex since; 1) Mn can exist in several oxidation states; 2) it forms non-stoichiometric oxides with the metal in mixed valences states; 3) higher oxides exist in several crystalline or pseudo crystalline states; and 4) the oxides form co-precipitates, soild solution and perhaps superstructures with iron oxides. Therefore the application of thermodynamics to the study of Mn systems in flooded soil is very difficult. They formulated the redox-equilibria in terms of pE, (Where  $pE = -\log (e^-) = Eh/0.059$  at 25 C), of the MnO<sub>2</sub>, Mn<sub>2</sub>O<sub>3</sub>, and Mn<sub>3</sub>O<sub>4</sub> systems. In studies to test these formulas, they found that the observed data supported the hypothesis that the manganese oxides involved in redox-equilibria in soil that undergo seasonal oxidation-reduction are complex nonstoichiometric oxides of variable composition whose apparent standards free energy of formation are considerably less than those of their ideal compounds.

In addition to reduction processes soil pH also has a marked effect on the activity of soil Mn, with a low pH readily bringing Mn into soil solution under aerobic conditions. A combination of low pH and restricted soil aeration, such as occurs in poorly-drained acid

soils, may sometimes result in the release of a large amount of Mn (Gotoh and Patrick, 1972). The distribution of different forms of Mn in a water-logged soil over a wide range of controlled Eh-pH conditions was studied. The results show that at pH 5 almost all of the soil Mn was converted from easily reducible to water-soluble plus exchangeable fraction even at an Eh as high as +500 m.v. In sharp contrast, at pH levels between 6 and 8 most of the conversion took place at a relatively lower Eh of +200 to +300 m.v. When the water-soluble plus exchangeable fractions were further divided into two components, low pH and low Eh were found to increase water-soluble Mn at the expense of exchangeable Cation-exchange reactions were apparently important in regulating forms. the equilibria between water-soluble and exchangeable Mn. The observed pMn/pH slope and E were much lower at pH 6 to 8 than they calculated for pure equilibrium systems. They concluded that Eh and pH of flooded soils provide general control of Mn transformation which probably include both chemical and biological processes, the complexity of which makes it difficult to explain the reaction in terms of a simple chemical system.

The reduction of Fe has important chemical consequences: 1) the concentration of water-soluble Fe increases; 2) pH increases; 3) cations are displaced from exchange sites; 4) the solubility of P and Si increases; and 5) new minerals are formed (Ponnamperuma, 1972). He also summarized that reduction of Fe is a consequence of the anaerobic metabolism of bacteria and appears to be chiefly a chemical reduction by bacterial metabolites, although direct reduction coupled with respiration may be involved. The kinetics of Fe(II) follow roughly an asymptotic course. Five to 50 percent of the free iron oxides present in a soil may be

reduced within a few weeks of submergence depending on temperature, organic matter content, and the crystallinity of oxides. The lower the degree of crystallinity, the higher is the reduction percentage.

Soil characteristics influence the kinetics of  $Fe^{+2}$  in the soils. IRRI (1963), reported that, after flooding, Fe solubility increased, but only a small amount of the reduced Fe was in the soil solution. The bulk of it was in the solid phase as hydroxides, carbonates and sulfides or exchange  $Fe^{+2}$ .

Clayey, latosolic, rice soils with high active Fe and organic matter contents (and also low pH) showed steep increases in reduced Fe concentration within 30 days of flooding. The concentration reached maximum values of about 10,000 to 15,000 ppm and remained more or less constant. Soils with lower organic matter or active Fe contents, regardless of pH and texture, attained lower maxima, (6,000 to 9,000 ppm) and the rate of reduction is slower than the first group. Soils low in Fe irrespective of pH and organic matter content reach still lower maxima (500 to 4,000 ppm) at an even slower rate (Ponnamperuma, 1965). He suggested that the reduction of Fe in flooded soils is favored by: 1) the absence of substances at a higher level of oxidation, such as  $NO_3^{-}$  and  $MNO_2$ ; 2) the presence of readily decomposable organic matter; and 3) a good supply of active Fe. The pH of soil is relatively less important.

The distribution of  $Fe^{+2}$  between the solid and solution phases is controlled by pH, organic matter content, C.E.C. of the soils, and duration of submergence (Ponnamperuma, 1965).

The amount of Fe<sup>+2</sup> in the flooded soil solution also depended on

soil properties (IRRI, 1965; Ponnamperuma, 1965). Soil characteristics influenced the kinetics of water-soluble  $Fe^{+2}$  more drastically than that of total  $Fe^{+2}$ . Acid soils high in organic matter and Fe build up water-soluble  $Fe^{+2}$  concentrations as high as 600 ppm within 1 to 3 weeks of submergence and showed a steep roughly exponential decrease to lavels of 50 to 100 ppm which persist for several months. Soils high in organic matter but low in Fe gave high concentrations that persist for several months. In neutral and calcareous soils  $Fe^{+2}$ rarely exceeds 20 ppm (Ponnamperuma, 1972).

Gotoh and Yamashita (1966), found that the increases in the amount of  $Mn^{+2}$ , Fe<sup>+2</sup> and S<sup>-2</sup> with consequent decrease in Eh was enhanced by the level of organic matter. Drainage caused a sharp decrease in the amount of reduced compounds, especially Fe<sup>+2</sup>. This decrease is favored by the addition of organic matter which leads to an increase in soil pores. They also suggested that Eh in paddy soils which lies between +200 and -200 m.v. would be controlled largely by the Fe system.

Patrick (1964) found that  $Fe^{+3}$  predominated in the soil when Eh was above +200 m.v. The maximum concentration of  $Fe^{+3}$  extracted from soil was approximately 200 ppm and was fairly constant at Eh between +200 to +500 m.v.  $Fe^{+3}$  was detected only in trace amounts at an Eh of 0 m.v. or lower. The Fe<sup>+2</sup> predominated at Eh of +200 m.v. and lower. The amount of extractable  $Fe^{+2}$  increased with a decrease in Eh and ranged from a trace amount at +200 m.v. to 4,300 ppm at -200 m.v.

One of the soil properties which has a marked effect on Fe behavior

is Eh. Even though Eh of many natural systems is a mixed potential, (Bohn, 1971); however, Hem (1960) found that the behavior of Fe in natural systems is to a large extent predicted by fluctuation in Eh and pH in the environment. While the physico-chemical relation to flooded soils are rather complex, chemists in the past two decades have correlated the formation of Fe compounds with Eh and pH (Eriksson, 1952; Jeffery, 1960; Ponnamperuma et al., 1967; Collins and Buol, 1970; and Bohn, 1971). Most of these studies of Fe behavior have been restricted to a narrow range of Eh and pH.

Gotoh and Patrick (1974), conducted the studies over a wide range of closely controlled redox-potential and pH conditions and found that the increase in water-soluble and exchangeable Fe was favored by a decrease in both redox-potential and pH. The critical Eh values for Fe reduction and consequent dissolution was about +300 m.v. at pH 6, +100 m.v. at pH 7 and -100 m.v. at pH 8. While at pH 5 apprecialbe reduction occurred at +300 m.v. The distribution of water-soluble and exchangeable Fe fractions was highly pH dependent, with a decrease in pH at a given Eh increasing the relative amount of Fe<sup>+2</sup> in the soil solution at the expense of that on the exchange complex. A thermodynamic approach to the equilibria between solid phase ferric oxyhydroxide and a water-soluble species of Fe,  $(Fe^{+2})$ , indicated that it was largely governed by the Fe<sup>+2</sup>-Fe(OH)<sub>3</sub> system in which the ferric oxyhydroxides was a mixture of geothite and amorphous material.

Because flooded soil is a very complex system, the quantitative treatment of redox-equilibria in waterlogged soil is very difficult. Ponnamperuma et al. (1967), discussed this difficulty. They formulated the Fe(III) - Fe(II) hydroxides equilibira, and found that the

test data were closely related to hypothetic equations. The increase in concentration of water-soluble Fe can, in most soils, be related to the Eh and pH of the Fe<sup>+2</sup>-Fe(OH)<sub>3</sub> system. The details of these subjects were well explained by Ponnamperuma (1972), Ponnamperuma et al. (1967), and Gotoh and Patrick (1974).

The dynamics of the concentration of Fe<sup>+2</sup> (and Mn<sup>+2</sup>) affects the concentrations of other cations. This is clear from the similarity of the kinetics of  $(Ca^{+2} + Mg^{+2} + Na^{+2} + K^+ + NH_4^+)$  to that of  $(Fe^{+2} + Mn^{+2})$ . These dynamics were well discussed by Ponnamperuma (1972).

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## 2.1.3 Phosphorus and Anaerobic Condition.

P like N, can exist in valence states from +5 to -3. Phosphate in anaerobic media can be reduced to form phosphite, hypophosphite and phosphine. But the main transformation of P in anaerobic soils is the mobilization of orthophosphate ions (Ponnamperuma, 1972). Many studies have shown the increase in solubility and availability of P caused by flooding soils (Gasser, 1956; Shapiro, 1958 a, b; Mitsui, 1960; Chiang, 1963 a; and Mahapatra, 1968).

The amount and the pattern of solubility of native P increase upon flooding depends on soil characteristics, including amount and kind of P compounds, organic matter content, texture and acidity of soil. It was reported (IRRI, 1964) that the increase in available P on flooding was highest and the subsequent decline least in coarse textured calcareous soils low in active Fe and medium in organic matter. Soils high in organic matter and low in active Fe showed moderate increases in water-soluble P: strongly acid soils, high in active Fe showed moderate increases followed by a quick decline to levels even below the initial. Ponnamperuma (1965) reported that the largest increase in Morgan's extractable P was observed in neutral soils with a moderate content of organic matter. On the other hand for soils low in organic matter, P concentration in the soil solution hardly increased. It was shown (IRRI, 1966) that the increase in P availability was highest and most stable in sandy soils high in organic matter and less in acid soils low in organic matter. Recently Ponnamperuma (1972) concluded that the P concentration in solution increased on flooding and the peak values were highest in sandy soils low in Fe, moderate in acid sandy soils

low in Fe, still smaller in nearly neutral clays and smallest in acid clays high in Fe.

When soils are submerged, not only native P but also P added prior to flooding increase in solubility and availability. This increase is enhanced by organic matter and/or lime application. Gasser (1956) noted that waterlogging acid soils caused an increase in the dilute acidsoluble  $PO_{i\mu}$ . Addition of glucose, potassium-citrate, or green manure increased both  $Fe^{+2}$  and dilute acid-soluble  $PO_{i\mu}$ . He concluded that the increase in P solubility is due to the reduction of ferric phosphate to ferrous phosphate. He proposed that in an acid soil with high Fe content, ferric phosphate should be considered as a source of P to rice. Mitsui (1960) stated that the increase in P availability by submergence is mainly due to the combination of  $PO_{i\mu}$  with  $Fe^{+2}$  instead of  $Fe^{+3}$  as in upland soils. In anaerobic conditions, solubility of P on acid soils proceeds by ordinary solution, while an alkaline soils hydrolysis of Fe-phosphate, a kind of exchange between  $PO_{i\mu}$  and  $OH^-$ , occurs first.

Flooding soils caused an increase in the availability of native P, applied P and N to rice. Yield of rice, P and N uptake on both lowland and upland soils were increased by flooding (Shapiro, 1958 a). It was noted that submergence increased the availability of native P, but had no apparent effect on that of native N. Applied P and N were both utilized more effectively under flooding conditions. The increase in availability of P could be due to reduction conditions or hydrolysis or both. Broeshart, et al. (1965) found that in rice soils with absence of free-CaCO<sub>3</sub>, the available P increased upon submergence. The availability of fertilizer P was similar under lowland and upland conditions but that the efficiency of use is greater under flooded conditions.

Terman et al. (1970) conducted a series of green-house pot experiments with flooded rice on a soil which was low in available P for upland crops. They found that a marked yield response of rice was obtained, but the maximum yields were obtained at much lower rates of applied P than was true for most upland crops. Applied P decreased with liming of the soils and with increasing levels of acid-soluble soil P. Granular, water-soluble P sources were most effective. The P in Fe-P form was more available than that in Al-P form in flooded soils. Both forms were more available in fine particles than as granules and in colloidal form than as fine crystals. Chakravarti and Ghoshal (1968) mixed two acid soils with 50% dried grass and added Fe-P, Al-P, and Fe-P plus Al-P. After the samples were flooded and incubated for 53 days, the amount of P released was found to be greatest in the Fe-P treatment, followed by Fe-P plus Al-P, Al-P and control in decreasing order.

Shapiro (1958 b) found that availability of natural P and applied synthetic Fe-P and Al-P increased in acid soils upon flooding. Application of P-free cellulose increased the availability of native and applied P. He noted that the increase in P availability came from both Fe and Al-phosphate but that Fe-phosphate was affected to a much greater degree. The increase in available Fe-phosphate was due to the reduction brought about by the addition of organic matter and flooding. The increase in Al-phosphate availability was due to the chelation reaction. His data showed that the availability of applied amorphous Fe and Al-phosphate were greater than that of the crystallized ones in both flooded and unflooded soil conditions.

Transformations of P after flooding soils have been studied by

many workers. Furukawa and Kawaguchi (1969) found that organic P decreased up to 21 percent upon submerging paddy soils samples for 2 weeks at 40 C. This decrease correlated well with an increase in Bray-2 extractable P and was attributed to mineralization of organic P. This increased mineralization was thought to be due to the enhanced solubility of Fe and/or Al salts of inositol hexaphosphoric acid, the prominent organic P constituent in the soil.

Mandal (1964) tested the effects of starch and lime on the transformation of P in waterlogged soils and found that submerging a soil, only slightly increased acetic-acid soluble P and slightly decreased Fe-P with no change in Ca-P and Al-P fractions. But when starch was added, a considerable increase in acetic-acid soluble P and a decrease in the Ca-P fraction occurred. He stated that the release of large quantities of CO<sub>2</sub> formed during starch decomposition may have caused tricalcium phosphate to convert to more soluble di-and mono-calcium phosphates. Although a large amount of Fe<sup>+2</sup> was formed, the Fe<sup>+3</sup> phosphate fraction showed no decrease and Al-P also showed no change. With the addition of lime, Fe-P decreased considerably and Al-P decreased slightly. This decrease might be due to the hydrolysis of Fe and Al-P due to liming. Ca-P was increased appreciably, the effect seemed to be a conversion from Fe-P to Ca-P upon flooding. He suggested that in acid soils having most of their inorganic P in the Fe<sup>+3</sup> form. liming followed by the addition of organic matter will result in a few days in an increase in P under waterlogged conditions.

Mahapatra and Patrick (1969) showed that in air dried soils, the more acid soil had a greater fraction of Al- and Fe-P while Ca-P was

highest in the less acid soils. After flooding these soils for 2 months transformation of P occurred. The Al-P fraction increased except in finer textured soils. Fe-P also increased in most of the soils except one, and generally increased more than the Al-P fraction. Ca-P did not change much as a result of flooding, while the reductant soluble Fe-P was greatly decreased. They suggested that the Fe-P increase was due to the conversion from reductant soluble Fe-P and other inorganic fractions.

They also studied the transformation of P added as  $AlPO_{4.}2H_2O_{2.}$ FePO<sub>4.2H2O and Ca(H<sub>2</sub>PO<sub>4</sub>)<sub>2.H2O</sub> under optimium moisture and waterlogged conditions, and found that after 2 months of incubation regardless of the source of added P, P in the soil was present as Al and Fe-P. Little of the added P was present as Ca-P. They concluded that waterlogged soils definitely accelerated the conversion of soluble P to the Fe-fraction.</sub>

They also found that after flooding the soils for 55 days, the amount of Bray-2 extractable P increases an average of 53 percent. Multiple regression analysis show that water soluble and loosely bound P, Al- and Ca-P were highly correlated with the amount of phosphate extracted in air dry samples, while Fe-, Ca- and Al- phosphate apparently account for most of the phosphate extracted under waterlogging condition.

The relationship between Eh of flooded soils and P availability and solubility also have been studied. Savant and Ellis (1964) found that Eh decreased rapidly within 15 days of submergence in acid soils and within 30 days in calcareous soils. Organic matter enhanced the Eh drop during this period in both soils. But at field capacity (F.C) the Eh of the soils was not affected by the addition of organic matter. However, Eh drop was affected by organic matter at two times F.C. on acid soils.

At F.C., changes in availability of native P varied less than changes in availability of applied P. The over all availability of both native and applied P as a function of time are: P available at F.C. < at 2F.C.<submerged condition in acid soils. But in calcareous soils, the availability of applied P fluctuated widely and soil moisture inconsistently affected P availability. Increases in availability of native P were more closely correlated with a decrease in Eh than was the increase in availability of applied P. A negative linear relationship between available P and Eh was distinct in acid soils. But the relationship was not evident in the calcareous soils.

Hayes and Phillips (1958) reported that the Eh has little or no effect upon the level of P in the soil solution. They feel that the biological 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 10 the difference was less than 5%. They concluded that their results indicated the minor influence of inorganic reducing system upon P levels in solution.

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

Under controlled Eh level of submerged soil, Patrick (1964) found that extractable  $Fe^{+3}$  and  $Fe^{+2}$  were very sensitive to changes in Eh of the soil.  $Fe^{+3}$  predominated at Eh above +200 m.v. and extractable Fe was mostly  $Fe^{+2}$  below +200 m.v. At the same time he found that the extractable P increased more than three fold between Eh +200 and -200 m.v. The sharp break in the P release curve at +200 m.v. is the same point at which  $Fe^{+3}$  begins to be reduced, indicated that the conversion of P to an extractable P form is dependent upon the reduction of  $Fe^{+3}$ compounds in the soil.

The effect of Eh and pH on the reduction of strengite (FePO<sub>4</sub>.2 $H_2$ 0) in a pure system to more soluble compounds has been studied by Williams and Patrick (1971). Under controlled Eh and pH conditions they found that at pH 4.0, Eh values of less than +100 m.v. have a marked effect on the solubility of strengite and reaches rapid dissolution at Eh about -240 m.v. at higher pH values (>5.0), however, even with considerably lower Eh value (i.e. -240 m.v.), rapid dissolution of strengite did not take place. This suggests that a critical H<sup>+</sup> concentration is required before added electrons chemically reduce Fe-P to more soluble reduced forms. They concluded that the results are in contrast with those described for a flooded soil system (Patrick, 1964) where the amount of reductant-soluble P increase rapidly at Eh of less than -200 m.v. and within the range of pH 6 to 7. This difference may indicate the presence in soils of P compounds other than FePO4.2H20 which are susceptible to reducing condition or may simply reflect the well known ability of various soil micro-organisms to overcome the energy barrier necessary to change the chemical state of sparingly soluble Fe compounds.

Patrick et al. (1973) investigated the effects of Eh and pH on the reduction of  $\text{FePO}_{4}$ .2H<sub>2</sub>O in flooded soils. They controlled Eh of the soil suspension (25 g of soil and 80 g of H<sub>2</sub>O) at +300, +100, -100 and -250 m.v. in combination with pH values of 5, 6, 7 and 8, respectively. The samples were incubated for 3 days. Then fine  $^{59}\text{FePO}_{4}$ .2H<sub>2</sub>O was added and additional incubation continued for 7 to 10 days. They found that both Eh and pH had a great effect on the dissolution of FePO<sub>4</sub>.2H<sub>2</sub>O in flooded soils. At the highest combination of Eh and pH (pH 8, Eh + 300 m.v.) there is no dissolution of FePO<sub>4</sub>.2H<sub>2</sub>O. At all pH levels, a decrease in Eh caused an increase in the amount of extractable Fe and PO<sub>4</sub>. The amount of both were greatest at the lowest pH values (pH 5). Eh showed similar trend; at lowest Eh (-250 m.v.), a decrease in pH caused a large increase in Fe and PO<sub>4</sub> dissolved, but at +300 m.v. pH has much less effect on the amount of Fe and P

They concluded that  $\text{FePO}_{4} \cdot 2\text{H}_20$  partially dissolves under reducing conditions such as exist in flooded soils deprived of  $0_2$ . A closed relationship existed between the amount of  $\text{FePO}_4 \cdot 2\text{H}_20$  dissolved and both Eh and pH of the soil suspension. There is a marked interaction between acidity and Eh, with  $\text{FePO}_4 \cdot 2\text{H}_20$  reduction and solubilization being more pronounced under conditions of low pH combined with low Eh.

The dissolution of complex ferric phosphates  $(CaFe_2H_4(PO_4)_4.8H_2O_4)$ and  $KFe_3H_{14}(PO_4)_8.4H_2O)$  under controlled Eh and pH was also studied by Williams and Patrick (1973). In a pure chemical system study they found that calcium ferric phosphate (CFP) dissolved incongruently to release Ca and P in a molar ratio of 1:2 and solid FePO<sub>4</sub> was formed. At pH 4, Ca, Fe, and P in solution increased with each successive lowering of Eh. Between pH 5 and 6, the amount dissolved remained constant until an Eh less than -200 m.v. was reached. Below an Eh of -200 m.v. further P was released due to FePO<sub>4</sub> dissolution. Potassium ferric phosphate (KFP) crystals dissolved rapidly with complete release of K. At pH 4 an increase in P was accompanied by an increase in soluble Fe at all Eh values. At pH 5 to 7 the amount of P in solution remained constant except for a slight increase at pH 5 and Eh -300 m.v. The P concentration corresponded closely to total dissolution of the KFP crystals, leaving an insoluble FePO<sub>4</sub> residue. They concluded that the dissolution of CFP was retarded probably due to the precipitation of FePO<sub>4</sub>. The solubility of precipitated FePO<sub>4</sub> differed slightly from that observed with crystalline FePO<sub>4</sub>.2H<sub>2</sub>O and at pH 6 and 7, Fe<sup>+3</sup> hydroxides apparently entered into the reaction.

The mechanism of the increase in P solubility upon flooding in acid soils was summarized as: 1) hydrolysis of Fe(III) and Al-phosphate; 2) release of P held by anion exchange on clay and hydrous oxides of Fe(III) and Al; and 3) reduction of Fe(III) to Fe(II) with liberation of sorbed and chemically bound P. The first two reactions are due to increases in alkalinity upon soil reduction. In alkaline soils an increase in solubility of P is caused by the increase in acidity of these soils upon flooding (for the solubility of hydroxyl apatite increases as pH decreases), (Ponnamperuma, 1972).

Patrick and Mahapatra (1968) and Patrick et al. (1973) explained the mechanism of P liberation on flood soils as: 1) the reduction of highly insoluble  $Fe^{+3}$  to the more soluble noncrystalline form; 2) the displacement of PO<sub>l</sub> from Fe<sup>+3</sup> and Al-P by organic anions produced

in anaerobic flooded soils; and 3) the hydrolysis of  $Fe^{+3}$  as a result of the almost inevitable increase in the soil pH which results when an acid soil is flooded. In addition to these major mechanisms, the release of occluded P by reduction of hydrated ferric oxide coating, hydrolysis of Al-phosphate and anion (phosphate) exchange between clay and organic anions may also occur.

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# 2.2 Phosphorus Adsorption Isotherms of Soil.

Applied P in soils is retained and immobilized by P fixation processes. Two mechanisms, adsorption and precipitation, are considered to be responsible for this fixation.

Precipitation of P occurs when phosphate ions in the solution react with components of the soil such as Al, Fe and Ca to form slightly soluble crystallized components. The reaction occurs when P concentration is sufficiently high and the solubility products are higher than the solubility product constant of the respective P compounds. But P can also be adsorbed by reactive sites existing on the surface of soil particles. Adsorption differs from precipitation in that one component of the reaction is already a solid. (Ellis, 1973).

The extent of P adsorption from dilute solution by soil depends on the nature of soil, P solution and temperature. At a given concentration of P the amount of P adsorbed increases with an increase in temperature. Therefore a P adsorption isotherm should be used for P adsorption study. The effect of temperature on P adsorption (by Kaolinite) was demonstrated by Low and Black (1950).

Phosphorous adsorption by soils and clay minerals has been investigated, and adsorption isotherms have been used to describe the experimental data, (Kurtz et al., 1946; Low and Black, 1950; Olsen and Watanabe, 1957; Shapiro and Fried, 1959; Weir and Soper, 1962; Woodruff and Kamprath, 1965; Udo and Uzu, 1972; and Syers et al., 1973 b).

2.2.1 Theory of Adsorption Isotherm .

The atoms or molecules are said to be <u>adsorbed</u> on the solid surface and it is distinguished from penetration of a component throughout the body of a second, called <u>absorption</u>. The distinction between the two processes is not always clear-cut and the word <u>sorption</u> is sometimes used, but when the process is essentially surface effects, the word adsorption is preferred, (Barrow, 1966).

Adsorption occurs on the solid surface because of the attraction forces of atoms or molecules in the surface of the solid. The potential energy of a surface plus molecules decreases as the molecules approach the surface. When a molecule approaches the surface it is attracted and this leads to an increase in kinetic energy, but the molecule will bounce away from the surface unless some of its momentum in the component normal to the surface is lost so that the molecule is trapped into a potential well. The adsorption process continues until the free surface energy of the system due to imbalance of surface forces, has been reduced to a minimum value.

It is convenient to classify adsorption behaviors into physical adsorption and chemisorption. Physical adsorption is due to the operation of forces between the solid surface and the adsorbate molecules. (similar to Van de Waals forces between the molecules). This adsorption is reversible. The energies of adsorption evolved are of the order of  $300 \text{ to } 3000 \text{ J mol}^{-1}$  (this corresponds to a heat of adsorption less than about 10 K cal/mole), and the amount of material adsorbed may correspond to several monolayers. Chemisorption is the result of much stronger binding forces comparable with those leading to the formation of chemical compounds.

Such adsorption may be regarded as formation of a surface compound. The energies range from 40 to 400 k j mol<sup>-1</sup> (The heat of adsorption is greater than about 20 k cal/mole). At lower temperatures, chemisorption is seldom reversible and no more than a monolayer may be adsorbed (Earrow, 1966; Moore, 1972).

Two commonly used adsorption isotherms to quantitatively describe adsorption of phosphate ions from solution onto soil particles are Freundlich Isotherm and Langmuir Isotherm.

A) Freundlich Isotherm.

$$x/m = kC^n$$
 (2)

where: x/m = the quantity of ions adsorbed per unit weight of adsorber,

- C = the equilibrium concentration of the adsorbate after adsorption occurred.
- k = a constant,

and n = a constant

This equation can be determined by using a log - log plot, since the following equation is linear.

 $\log x/m = \log k + n \log C$  (3)

Thus, n is the slope of the line and k is the antilogarithm of the intercept. According to the Freundlich equation, the amount of adsorption increases indefinitely with increasing concentration. This empirical equation does not predict a maximum quantity of adsorption, which has been considered a limitation.

B) Langmuir Adsorption Isotherm.

This theory was developed by Langmuir (1918) to explain gas adsorption onto solid surfaces. There are many assumptions in this theory. However, Olsen and Watanabe (1957) have suggested a method for application of Langmuir Adsorption Isotherm to the study of P adsorption from solution by soils. A rigorous, theoretical development for application of this equation to adsorption of ions from solution has not been presented; thus a simplified derivation for P adsorption by soils is given below.

The following assumptions and notation are made,<sup>1</sup>

- 1. It is assumed that each adsorption site had an equal probability of adsorption of P from solution, i.e. this requires a constant free energy of adsorption.
- 2. (P) = activity of P in solution (mole/liter).
- 3. x/m = mg P adsorbed per 100 grams of soil.
- 4. b = the maximum amount of P that will be adsorbed by a given soil (mg/100 g soil).

However, these assumptions are somewhat different from that of the original Langmuir theory for gas adsorption on the surface of soild.

The rate of P adsorption will be proportional to (P) and to the sites yet unoccupied by P (b - x/m). Thus:

Rate of adsorption =  $k_1(P)(b-x/m)$  (4)

The rate of dissociation (desorption) will be proportional to the occupied sites. Thus:

Rate of dissociation =  $k_2(x/m)$  (5)

At equilibrium, both rates must be equal. Thus, equating (4) and (5):

$$k_{2}(x/m) = k_{1}(P)(b-x/m)$$
(6)  
$$x/m = \frac{k_{1}(P)b}{k_{2}+k_{1}(P)} = \frac{(k_{1}/k_{2})(P)b}{1+(k_{1}/k_{2})(P)}$$
(7)

1 Taken From Ellis and Erickson (1969); and Ellis and Knezek (1972).

or 
$$x/m = \frac{K(P)b}{1+K(P)}$$
 (8)

where:  $k_1$  and  $k_2 =$  the proportional constants

 $K = k_1/k_2$ , is sometimes called the adsorption coefficient. It is related to bonding energy of P adsorption on soil, (Olsen and Watanabe, 1957).

This is the common form of the Langmuir equation. The typical curve is obtained by plotting x/m versus (P). The limit of x/m as (P) approaches infinity is b, the adsorption maximum. However, this is not a particularly useful form of the equation from which to obtain b and K. The linear form can be obtained by rearranging equation (8). Thus:

$$\frac{(\mathbf{P})}{\mathbf{x}/\mathbf{m}} = \frac{1}{\mathbf{K}} + \frac{(\mathbf{P})}{\mathbf{b}}$$
(9)

This form of the equation lends itself well to evaluation by computer methods in that the best fit of the linear relationship may be obtained by standard least squares method. The adsorption maximum, b, is the reciprocal of the slope of the regression line, and K may be obtained as the slope divided by the intercept.

Using the equation  $-F^{0} = RT$  in K, the standard free energy of P adsorption may be calculated, which constitutes a measure of the strength of adsorption bond.

Another useful form of the Langmuir equation may be obtained as follows:

- 1. Let  $\theta$  be the fraction of possible sites occupied by P.
- 2. Other symbols and assumptions are as stated above. Then:

$$\frac{x/m}{b} = \Theta \tag{10}$$

and equation (6) divided by b, gives.

$$k_1(P) (1 - \frac{x/m}{b}) = k_2(\frac{x/m}{b})$$
 (11)

or

$$k_{1}(P)(1-\theta) = k_{2}\theta \qquad (12)$$

$$K = \frac{k_1}{k_2} = \frac{\Phi}{(P)(1 - \Phi)}$$
 (13)

Since K is known from fitting experimental data into equation (9), equation (13) can be used to predict the concentration of P in solution at any level of P adsorption up to the adsorption maximum.

Langmuir theory does not describe the mechanism of adsorption, but the model is based on many assumptions including the chemical adsorption type. However, Low and Black (1950) demonstrated, by using ln K =  $-\Delta H^{0}$  + constant, that the nature of P adsorption reaction (by Kaolinite) did not change and the standard heat of reaction ( $\Delta H^{0}$ ) was positive, therefore P is chemisorption. The reactions that are responsible for adsorption from solution have been discussed by Giles (1959). They may be classified as; 1) non-polar Van de Waals attraction; 2) formation of H bond; 3) ion-exchange; and 4) covalent bond formations.

# 2.2.2 Application of Adsorption Isotherm to P Adsorption.

Experimental data of P adsorption by soil has been reported to conform to Freundlich equation (Kurtz et al., 1946) and by kaolinite (Low and Black, 1950; Russell and Low, 1954), at high concentration of P solution (up to 50 ppm). Kurtz et al. (1946) indicated that at the low concentration of P (less than 1 ppm) their data dit not conform to the Freundlich equation.

Langmuir equation has been widely used to describe P adsorption by soil and clay minerals. Ellis and Knezek (1972), pointed out that this

equation was derived by assuming constant free energy of adsorption (no interaction between adsorbed ions and a surface is uniform), but this situation would not be expected to occur in mature. They noted that the heat of adsorption, the mest important factor in the constant K, should be expected to decrease with increasing surface coverage. But the interaction of ions already adsorbed with the ions being adsorbed would increase the heat of adsorption with increasing coverage. The two changes would in part compensate, tending to give a constant heat of adsorption. They indicated that even though the Langmuir equation is still theoretically sound, one should avoid extrapolation of the regression beyond experimental data. Deviations from Langmuir isotherm also are expected if precipitation of the ion being adsorbed occurs. Precipitation is indicated by a rapid increase in x/m with a small change in equilibrium in solution.

Many workers found their experimental data on P adsorption by soils conformed to the Langmuir Isotherm at low equilibrium P concentration (Olsen and Watanabe, 1957; Weir and Soper, 1962; Rennie and McKercher, 1959, etc.). They also found that the deviations from a single linear Langmuir relationship at higher equilibrium P concentration (above approximately 15 mg/ml, or ppm P which is equivalent to about 48.45 x  $10^{-5}$  mole/ liter.) Udo and Uzu, (1972) reported that a straight line was obtained from Langmuir equation at (P) up to 2.5 to 5.5 ppm, for tropical Nigerian soils. Gunary, (1970) reported that deviations were found with P concentrations above 5 to 5.5 ppm. Recently Syers et al. (1973 b) found that there are two straight lines for the Langmuir plot for P concentration up to 14 ppm. The first straight line was for low P (up to 1.5 to 3.15 ppm).

Deviations were found for P concentrations higher than these, but these deviations also yielded a straight line which conformed to Langmuir Isotherm. They postulated that two populations of sites exist which have different affinities for P. They concluded that the sites in part I, at low (P) had a very much higher binding energy constant (K) than in part II, at high (P). They rewrote the Langmuir equation for two population of sites as:

$$\mathbf{x/x} = \frac{\mathbf{K}^{\mathrm{I}}\mathbf{b}^{\mathrm{I}}(\mathbf{P})}{\mathbf{1} + \mathbf{K}^{\mathrm{I}}(\mathbf{P})} + \frac{\mathbf{K}^{\mathrm{II}}\mathbf{b}^{\mathrm{II}}(\mathbf{P})}{\mathbf{1} + \mathbf{K}^{\mathrm{II}}(\mathbf{P})}$$
(14)

where: superscript I and II refer to part I and II of the population sites.

For clay minerals Cole et al. (1953) found that P adsorption on the surface of CaCO<sub>3</sub> yielded a straight line for a Langmuir equation up to 9.6 ppm P. Higher P concentrations caused precipitation. Muljadi et al. (1966) found that there are two or more straight lines for P adsorption by Kaolinite, gibbsite and pseudoboehmite. Hau and Rennie (1962) found that P adsorption gave a straight line up to 12 ppm P for amorphous Al hydroxide. The deviation also yielded a straight line which conformed to the Langmuir relationship.

Even though the Langmuir Isotherm does not always accurately describe P adsorption by soil, as pointed out by Olsen and Watanabe (1957), a major advantage of the Langmuir equation is that it is possible to calculate an adsorption maximum and a relative bonding energy term for P sorption. Agreement of P adsorption data with Langmuir Isotherm does not necessarily imply any specific adsorption or reaction mechanism. However, if the data obeys the Langmuir Isotherm the adsorption maximum (b) and a constant related to binding energy of the soil for P are very useful to describe the behavior of adsorbed P.

Ellis and Erickson (1969), used Langmuir Isotherm successfully to describe and predict the reduction of P level in sewage effluent by soils in Michigan. Their study was very useful in evaluating a sewage treatment system for eliminating P from municipal waste by spreading it on soils.

## 2.2.3 Factors Affecting P Adsorption.

Phosphorus adsorption from dilute solution by soil depends not only on temperature but also on soil characteristics such as soil acidity, amount of Al, Fe and their oxides, amount and kind of clay minerals, specific surface area or texture, organic matter content, and Ca in the soil and P solution.

For P solution, factors including salt effect, anion competition and pH of the solution may affect P adsorption. Kurtz et al. (1946) reported the amount of P adsorbed in the presence of KCl in the solution is greater than that of water solution. Barrow (1972) found that at a given concentration of phosphate, sulfate or molybdate, the adsorption of each respective anion increased as Ca concentration in the initial solution increased. Therefore salt concentration in P solution should be kept the same as the ionic strength of the natural soil solution.

Phosphorus adsorption is not affected by soil solution ratio (Kurtz et al., 1946; Shapiro and Fried, 1959). Shapiro and Fried (1959) found that the characteristics of P adsorption by equilibrium method is not dependent on soil:P solution ratio of 1:5 to 1:2000.

Phosphorus adsorption is also affected by other anions contained in

the P solution and pH of the solution. Adsorbed P on the surface of soil can be replaced by other anions. The replacing ability at a neutral pH are in the order fluoride> oxalate> citrate> bicarbonate> borate> acetate > thiocyanate> sulfate> chloride. The ability of soil to adsorb acid is: oxalate> citrate> phosphate> sulfate (Kurtz et al., 1946). Barrow (1970) reported that as the pH of the soil decreased from 6 to 4 (in 0.01 M CaCl<sub>2</sub> solution), the ratio of sulfate:phosphate adsorbed increased. Adsorption was measured at concentrations of 20 and 0.2 ppm for sulfate and phosphate, respectively.

The P adsorption by amorphous Al hydroxide from buffer P solution (buffer with acetate) increased as pH of the solution increased (Hsu and Rennie, 1962). Black (1942) also found that pH of the P solution affected the amount of P adsorbed by kaolinite, bentonite, illite and soil.

Soil characteristics have greatly affected P adsorption. Kurtz et al. (1946) discussed that P adsorption might take place at a point where OH<sup>-</sup>, silicate or organic anions could be exchanged, or at a point where Al or Fe are exposed on the surface. If OH<sup>-</sup> was present where Al and Fe occurred at lattice edges, adsorption at these points would be an exchange of OH<sup>-</sup> and phosphate ions. Black (1942) explained that fixing power of the clay fraction was attributed to reaction of phosphate with Fe and Al present as exchangeable cations, as hydrous oxides or in solution, and to reaction with Ca. Russell and Low (1954) found that kaolinite saturated with exchangeable Al<sup>+3</sup> adsorbed about ten times more P than that of control. Kaolinite treated with oxalate or flouride and then washed to remove Al markedly reduced the amount of P adsorbed. However, oxalate treated and washed kaolinite adsorbed P from solution greater than that from P plus

oxalate solution. They concluded that exchangeable  $Al^{+3}$  or hydrous oxides were responsible for P adsorption.

(1957) In the application of Langmuir equation, Olsen and Watanabe found that the adsorption maximum, (b), was closely related to the specific surface area of soils. Acid soils adsorbed more P per unit surface area and held P with a greater bonding energy (indicated by the constant K) than alkaline soils. They indicated that acid soils are weathered more than alkaline soils, and have more weathering products such as the hydrous Fe and Al oxides, which may be responsible for P adsorption. Udo and Uzu (1972) reported that tropical acid soils adsorbed a large amount of P added to them. The capacity of P adsorption generally depends on degree of weathering. The P adsorption was positively correlated with sesquioxides and exchangeable forms of Al and Fe as well as clay content and was negatively correlated with pH of soils. The citrate-dithionite and the oxalate extractable oxides were of equal importance in P adsorption, but the role of Al was more important than that of Fe. They suggested that sesquioxides (probably amorphous form) were reactive in adsorbing P. Clay also provides adsorption sites for P. It is likely that clay forms a part of complex gel which consists of hydrate Fe203 along with small amounts of organic matter,  $Al_20_3$  and associated  $Si(OH)_4$  and P, which is considered as a major site for P adsorption. The P adsorption increases as pH of soil decreases which may be due to the effect of pH on the exchangeable Al which is strongly correlated with P adsorption. Ellis and Truog (1955) also found that montmorillonite would not fix P after all of Al and Fe were removed.

Hau (1964) stated that the adsorption of P by a slight acid soil from dilute P solution at pH 7 is due to a morphous Al and Fe oxides in soil.

They discussed that activity of  $Al^{+3}$  and  $Fe^{+3}$  in solution is limited by pH, and becomes negligible at pH 5 or above. But the surface reactivity of amorphous Al and Fe oxides have no such limitation.

Harter (1969) stated that organic matter provides the major site for P adsorption. Rennie and McKercher (1959) also noted that organic matter is considered to be equally as important as inorganic colloids in P adsorbing capacity of four Canada soils. They also found that Ca is not closely related to the P adsorption maximum. Whereas, Udo and Uzu (1972) found no correlation between organic matter and Nigerian soils. However, they suggested that organic matter could be part of the complex gel responsbile for P adsorption.

Ellis (1973) stated that the adsorption maximum, (b), depended on soil texture and horizon. Sandy soils have lower P adsorption maximum than heavy texture soils. The A horizon adsorbed less P than the B horizon in soils. This is due to the accumulation of Fe in subsoil.

Syers et al. (1971) found that P adsorption from dilute solution by tropical soils was correlated with exchangeable Al, with oxalate and citrate-dithionite, bicarbonate, Fe and Al and with clay content. Sorption of added P was always better correlated with Al parameters than with Fe parameters. It is difficult to identify the soil parameters most responsible for P sorption because they are themselves correlated to a considerable degree. Fried and Dean (1955) reported that the retention of P by soil probably involves exchange of phosphate from solution with anions on the surface of the particle. Hydrous oxides of Fe and Al are involved in this adsorption. The presence of cations such as Ca, Na, and H, affect the extent of this retention. Shapiro and Fried (1959) stated that P can be adsorbed on the surface of clay, surface of Fe and

Al oxides or hydroxides and  $CaCO_3$ , and indirectly adsorbed by means of cation bridge to the clay. Adsorbed P is either hydrolytically displaced or displaced by another anion.

# 2,2.4 Correlation Between P Adsorption and P Availability.

The availability of P is related with the reactive surfaces of soil material. Olsen (1953) pointed out that the amount of surface P as measured by  $P^{32}$  exchange is closely related to plant available P. Fried and Shapiro (1956) and Olsen and Watanabe (1957), showed a close agreement between the adsorbed P based on Langmuir Isotherm and surface P measured by  $P^{32}$  equilibrium.

Olsen and Watanabe (1957) also pointed out that the range in value covered by P adsorption maximum will lie within the range of P fertilizer addition to soils.

Phosphorus adsorption maximum as measured by Langmuir isotherm and its relationship to plant availability was studied by Woodruff and Kamprath (1965). They found that conversion of exchangeable Al to  $Al(OH)_3$  remarkedly reduced P adsorption maximum. The growth of plants was related to the degree of saturation of the P adsorption maximum. The soils with a large P adsorption maximum did not require as high a P saturation as those with a low P adsorption maximum. The soils with a higher P adsorption maximum apparently are able to supply sufficient P for growth at a lower saturation than the soils with a low P adsorption maximum. The maximum yields on the limed soils were obtained when P was greater than 1 x 10<sup>-5</sup> moles/liter. Much higher P was needed on the soils with a high saturation of exchangeable Al to give maximum yields; however, the yields were lower than on the limed soils. Fried and Broesshart (1967) noted that there are three methods of describing soil P system in relation to solution concentration; 1) phosphate potential, 2) solubility diagram, 3) adsorption equation. The adsorption equation appears to be the most useful description for plant nutrition.

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## 2.3 Phosphorus Adsorption by Flooded Soils.

Even though the availability of native P and added P before flooding increases upon submergence, when water-soluble P was applied to waterlogged soils, rapid removal of P from the solution occurred (De Datta et al., 1966; Mandel and Das, 1970).

Acid, lowland rice soils generally contained large amounts of hydrated ferric oxides, which are highly reactive in removing P from solution. Besides, such soils, under waterlogging conditions, also contain higher quantities of soluble Fe (IRRI, 1963; Mandal, 1964), which can rapidly precipitate the added water-soluble P from the soil solution (IRRI, 1964).

Fixation of added P occurs in both acid and calcareous paddy soils. Chiang (1963 b) reported that the fixation of P compounds added to acid paddy soils was generally very rapid and completed within 5 - 9 days; then there was a slight increase of soluble P which in the later stages declined to nearly the same extent as in the untreated soil samples. In alkaline soils, fixation was generally completed in about 13 days after P application; and the soluble P present was in greater amounts than that of acid soils.

Williams and Simpson (1965), studied the effect of waterlogging in clover cultivation on pasture soils and found that short periods of flooding (1-2 days) produced anaerobic conditions that caused a decrease in P availability and an increase in sorption capacity, particularly in disturbed (mixed) soil. This reduced P availability applied to both native and added P.

De Datta et al. (1966), showed that the disappearance of added P in solution in equilibration with acid and neutral lowland rice soils is

very rapid. For two acid soils with pH of 5.1 and 6.0, none of the added P remained in the solution after 4 days of equilibration.

The mechanism of P fixation also was observed. Chiang (1963 b) noted that the chief forms of P fixed upon the addition of soluble P are Al-P and Fe-P in acid soils and Ca-P in alkaline soils. De Datta et al. (1966) reported that the amount of P remaining in the solution within a period of 4 days from application was lowest for those acid latosolic soils containing kaolin type minerals and slightly higher in soil containing predominantly montmorillonite. In calcareous soil (pH 7.6), the added P remaining in solution was unaltered during 4 days of equilibrium.

Williams and Simpson (1965), stated 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 occuluded by reprecipitation of Fe upon restoration of aerobic conditions. They felt that the increase in soil P availability upon waterlogging must be due to the presence of easily reducible ferric phosphate. Soils low in ferric phoshpate would not be expected to increase in P availability upon submergence.

Mandal and Das (1970), studied the transformation of applied watersoluble P in three acidic lowland rice soils by incubating the soil samples with distilled water for 7 days and then adding P solution (as  $KH_2PO_4$ , 20 mg  $P_2O_5$  per 100 gm of soil). Each week after P application, they analyzed for P in both soil and solution and found that the amount of added P remaining in the solution in equilibrium with the soil declined sharply in all three soils. But the rate at which it declined was found

to be influenced more by the  $Fe_20_3$  and active Fe content than by the pH of the soils.

They also reported that the solid-bound P fraction in the treated soils showed practically no increase over the control. The Al-phosphate fraction in the treated soil, showed a marked increase over the untreated sample in all three soils. The magnitude of increase appeared to be influenced by  $Al_20_3$  content rather than the pH of the soils. The maximum fixation as Al-phosphate occurred within the first week of P application. The transformation of added P into Fe-phosphate fraction indicated that the magnitude of P fixation was affected by  $Fe_20_3$  and active Fe content, not by the initial pH of the soils. The rate of fixation of applied P as Fe-phosphate was progressive with time of incubation in the soil which was rich in the amount of  $Fe_20_3$  and active Fe.

Mud and Lake sediment have the ability to adsorb P from introduced solution, (Hesse, 1962; Harter, 1968; and Shukla et al., 1971).

Hesse (1962) found that the fixation of P by fresh and dried mud is extremely rapid. Equilibrium was almost attained within 30 minutes and considerable fixation had occurred within 5 minutes. The difference in amount of P fixed in 30 minutes and 30 days of contact time was very small. However, Harter (1968) found that with low concentrations of P, the dried sediment was nearly identical to mud in its adsorption characteristics. He suggested that sediment can be dried at 110 C without much change in P adsorption ability. But when more P was added the dried sediment adsorbed less P than did the fresh mud. The dried sediment did not wet easily and its adsorption capacity was likely decreased due to inaccessibility of a portion of reactive sites. The P-free sediment wetted more easily, and its adsorption isotherm followed by that of fresh sediment throughout the range of P concentration used.

Like air dried soil, there are many factors affecting P adsorption by lake sediment. Shukla et al. (1971) found that in general, noncalcareous sediments adsorbed more added P than calcareous sediments. They stated that  $CaCO_3$  was not the major component responsible for sorption of P by the calcareous sediments. The proportion of added P sorbed was closely related to the amount of oxalate soluble Fe and to the levels of native total inorganic P in the sediments. They suggested that the best single criterion indicating P adsorption in both non- and calcareous sediments was the amount of oxalate-extractable Fe presumed to be derived from amorphous Fe oxides, and proposed that a gel complex of hydrated Fe oxide which contains small amounts of  $Al_2O_3$ , Si(OH)<sub>4</sub> and organic matter, is the main P sorbing components of sediments.

Form of adsorbed P by mud and lake sediments also have been investigated. Hesse (1962) found that when Ca-P was added to mud at 20 ppm P, the Al-P after an initial increase, decreased within 30 days to its original value. He explained that the Al bounded P decreased due to a transfer to Fe-P.

According to Harter (1968), when 0.1 mg P or less was added to lake sediments,  $NH_{ij}F$  extracted a tightly bound form of P, probably occurring as Al-P. However, when more than 0.1 mg P was added, additional P in a more loosely bounded form was adsorbed into  $NH_{ij}F$  extractable fraction. The loosely bounded P appeared to be independent of Al content and could be removed by successive water extractions.

Phosphorus isotherms of lake sediments studied by Harter (1968) showed that total adsorption as measured by loss from solution and by

extraction with 0.5 NH<sub>4</sub>F followed Langmuir Isotherm at low concentrations of P but at high P concentration the isotherm curve deviated from the conventional Langmuir Isotherm. However, adsorbed P recovered by extraction with 0.1 N NaOH followed Langmuir Isotherm throughout the P concentration used.

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3.1 Materials.

## 3.1.1 Soil Samples .

Five Michigan soils were selected to give a variation in chemical properties such as pH, organic matter content, amount of Fe and Mn, and physical characteristics including texture ranging from sandy loam to clay loam.

Both surface soil (A horizon) and subsoil (B horizon) were collected from each soil series. Soil samples were air-dried, ground and passed through a 1 m.m. sieve. The soil characteristics are shown in Table 1.a. of the Appendix.

## 3.1.2 Phosphorus Analysis.

#### 3.1.2.1 Murphy and Riley or Ascorbic Method.

Murphy and Riley (1962) proposed use of a single reagent for determining P in natural water. The reagent and procedure of this method are as follows:

# Reagents:

(1) <u>Reagent A</u>. Dissolve 12 g of ammonium molybdate in 250 ml of distilled water. Antimony potassium tartrate 0.2908 g is dissolved in 100 ml of distilled water. In 1,000 ml of  $5 \text{ N} \text{ H}_2\text{SO}_4$  (148 ml of concentrated,  $36 \text{ N} \text{ H}_2\text{SO}_4$  is carefully added in to about 700 ml of distilled water, cooled to room temperature and then made to volume with distilled water), both dissolved reagents are added, mixed thoroughly and made to 2,000 ml with distilled water. Reagent A is stored in pyrex glass bottle in a dark and cool compartment at 4 C.

(2) <u>Reagent B.</u> Dissolve 1.056 g of ascorbic acid in 200 ml of

reagent A and mix. This working reagent is light yellow in color and should be prepared as required since it does not keep for more than 24 hours.

#### Procedure:

Pipette aliquots containing 1 to 40 µg of orthophosphate into 50-ml volumetric flasks. Add distilled water to make the volume to 40 ml, and then add 8 ml of reagent B. Make to volume with distilled water and mix thoroughly. After 10 minutes and within 24 hours, the color is read on an Evelyn photoelectric colorimeter at 660 mu. A standard P curve is prepared in the same manner as the samples, with P concentration ranging from 0 to 1 ppm.

In this method, the reagent contains  $H_2SO_4$ , ammonium molybdate, ascorbic acid and antimony potassium tartrate in a single solution reacts with orthophosphate to produce a blue-purple complex compound within 10 minutes. Antimony accelerates color development and the color remains stable for at least 24 hours. The complex obeys Beer's law up to a P concentration of 2 ppm. The sensitivity of this procedure is comparable with that of the SnCl<sub>2</sub>-H<sub>2</sub>SO<sub>4</sub> method for P determination in sea water (Murphy and Riley, 1962), and water extract (Watanabe and Olsen, 1965).

# 3.1.2.2 SnCl\_-H\_SOn Method.

Chlorostannous-reduced molybdophosphoric blue color method, in a sulfuric acid system was widely used for determining P in the solution samples (Jackson, 1965). The reagents and procedure of this method are as follows:

# Reagents:

(1) <u>Solution I</u>. Dissolve 25 g ammonium molybdate in 200 ml of distilled water, and warm at 60 C. The reagent is filtered if necessary. (2) <u>Solution II</u>. Add 275 ml of concentrated  $H_2SO_4$  carefully to 425 ml of  $H_2O$ . The solution is cooled to room temperature and Solution I added slowly. Then dilute the solution to one liter and protect it from light.

(3) <u>Chlorostannous acid reagent</u>. 25 g of  $SnCl_2.2H_20$  is dissolved in 50 ml of concentrated HCl. The solution is added to 500 ml of distilled water and then make volume to 1 liter with distilled water. The final solution is 1M  $Sn^{+2}$ .

## Procedure:

25 ml of the test solution (the final concentration of P ranges from 0 to .8 ppm), is placed in a 50 ml of volumetric flask, and 2 drops of 2, 4-dinitrophenol indicator is added, and pH is adjusted with 2 <u>N</u>  $H_2SO_4$  or 4 <u>N</u>  $Na_2CO_3$  until one drop of 4 <u>N</u>  $Na_2CO_3$  produces a faint yellow color (pH about 3). Two ml of solution II is added and the samples are diluted nearly to volume with distilled water and thoroughly mixed. Then 0.2 ml of chlorostannous solution is added to develop the color and the sample is diluted to 50 ml with distilled water. After 5 minutes, but not later than 10 minutes the color is read photometrically on an Evelyn photoelectric colorimeter at 660 mu. Calibrate the method using a standard P in the same manner as the sample with P concentration ranges from 0 to 1 ppm P.

This method has a very high sensitivity per unit of P content, providing a working range from 0.02 to 0.6 of P. It provides for noninterference of Si in solution up to 200 ppm, Fe<sup>+2</sup> up to 100 ppm, Fe<sup>+3</sup> up to 2 ppm, Ti up to 20 ppm, Ca and Mg up to 500 ppm or more, NO<sub>3</sub> up to 100 ppm, F up to 5 ppm, Cl up to 250 ppm, SO<sub>4</sub><sup>-2</sup> up to 1000 ppm --- but it includes arsenate in chemical equivalence to P (Jackson, 1965).

#### 3.2 Methods.

3.2.1 <u>A Study of the Methods Used in the Determination of P.</u>

The  $\operatorname{SnCl}_2$ -H<sub>2</sub>SO<sub>4</sub> method was widely used for P determination in water sample and soil extract because of its sensitivity. However, this method is not convenient when working with several samples at the same time. The pH of the samples must be adjusted to pH 3 before color development and the color must be read between 5 and 10 minutes after mixing with all of the reagents.

The Ascorbic method, on the other hand is easier to handle, with no pH adjustment and allows for working with several samples at the same time due to the very stable color complex. This method also uses only a single reagent solution.

Both methods are sentitive in the lower range of P concentration of 0.02 ppm to 0.6 ppm. The  $SnCl_{\overline{2}}$  H<sub>2</sub>SO<sub>4</sub> method is the standard method for determining P in the solution in this low range of concentration. This preliminary study was designed to test P determination in P adsorption isotherm experiments, comparing Ascorbic and  $SnCl_2-H_2SO_4$  methods.

50 ml of 0.01 M CaCl<sub>2</sub> solution, containing  $\text{KH}_2\text{PO}_4$  at a concentration ranges from 0 to 30 ppm, was added to 5 g of prepared soil samples in 125 ml Erylenmeyer flasks. The samples were shaken on a rotary shaker machine at 200 rpm for 5 hours at room temperature. The samples were then filtered. The concentration of P in the filtrates were determined by both methods. The amount of P adsorbed (x/m) were calculated by substracting the P remaining in the filtrate from P in the initial solution. The data of this study is shown in Table 2.

The results of this study are shown in Figure 1. The amount of P

Soils	Initial P	Equilibrium 1/		P adsorbed 1/		
		P		<u>(x/m)</u>		
		Ascorbic	$\text{SnCl}_2-\text{H}_2\text{SO}_4$	Ascorbic	SnCl <sub>2</sub> -H <sub>2</sub> S04	
	~ppm			ng/100 g soil		
Hillsdale A	0,0	0.06	0.12	# <b>7</b>		
	3.0	0.65	0.70	2,35	2,30	
	6.0	1.82	1.78	4,18	4.22	
	9.0	3.20	3,18	5,80	5,82	
	12.0	5.30	5.35	6.70	6,65	
	15.0	7,55	7,68	7.40	7.32	
	20.0	11.2	11.2	8,80	8.75	
	30.0	18.4	19.9	11.6	10.0	
Hoytville A	0,0	0.06	0,12			
	3.0	0,15	0,25	2.85	2.75	
	6.0	0,29	0.55	5.72	5.50	
	9.0	0.70	0.95	8,30	8.05	
	12.0	1.35	1.45	10,6	10.5	
	15.0	2,12	2,45	12,9	12.7	
	20,0	3.62	4.88	16.4	15.1	
	30.0	8.62	8.92	21.4	21.1	

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Table 2.	Comparison	of two anal;	ytical methods	for P	analysis	in	P
	adsorption	studies.					

1/ average of 2 replications.



Figure 1. P adsorbed calculated form Ascorbic and SnCl<sub>2</sub>-H<sub>2</sub>SO<sub>4</sub> methods for P determination.

adsorbed which was obtained by both methods of P determination is closely agreement, especially at low concentration of P. At higher P concentration, the amount of P adsorbed obtained from the Ascorbic method deviated somewhat from that obtained by the  $SnCl_2-H_2SO_4$  method. For Hoytivlle A a deviation occurred at 20 ppm P of initial solution but the higher concentration of 30 ppm of initial solution, gave little deviation. For Hillsdale A, the deviation occurs at 30 ppm of the initial solution.

It could be concluded that at low concentration of P in the initial solution the Ascorbic method gives comparable results to that of  $SnCl_2-H_2SO_4$  method.

Since the Ascorbic method is more convenient to work with, the P determination by this method is selected to use in the study of P adsorption in this thesis.
#### 3.2.2 Phosphorous Adsorption by Flooded Soils.

#### 3.2.2.1 Anaerobic Condition.

An anaerobic glove chamber (Coy manufacturing Co., Ann Arbor, Mich.) was used to keep soil samples under anaerobic conditions. This anaerobic system was described by Aranki et al. (1969). The atmosphere is composed of 10 percent  $H_2$  and 90 percent  $N_2$ . Oxygen gas, if present, is reduced by means of Palladium catalyst diffusion box system by the reaction:

$$2H_2 + 0_2 - Pd_2 + 2H_2 0$$
 (14)

Silica gel was used to remove  $H_2^0$  generated by the Pd catalyst and Hydrogen sulfide absorbent, (dissolve .5 g  $Ag_2SO_4$  in 100 ml hot distilled water, and add 1 ml <u>N</u>  $H_2SO_4$  plus 100 ml glycerol) was used to remove  $H_2S$ gas which may be produced by bacteria since  $H_2S$  gas will poison the Pd catalyst. This anaerobic chamber reduced  $O_2$  to less than 5 ppm.

3.2.2.2 Phosphorus Solution.

The P solutions used in this study were prepared as follows:

(1) <u>CaCl</u><sub>2</sub> solution.

11.099 g of anhydrous  $CaCl_2$  (analytical grade) was dissolved in distilled water to obtain a stock solution of 0.1 M CaCl\_2. Working solutions of 0.01 M CaCl\_2 were obtained by dilution of this stock solution with distilled water.

(2) <u>Phosphorus in 0.01 M CaCl<sub>2</sub> (pH 6)</u>.

2,6362 g of analytical grade  $KH_2PO_4$  was dissolved in 0.01 M CaCl<sub>2</sub> to obtain a 600 ppm P stock solution.

The working P solutions were prepared by diluting the stock solution with 0.01 M CaCl<sub>2</sub>. These solutions contained P concentrations ranging from 0 to 300 ppm P. The P solutions were adjusted to pH 6, using a Beckman pH meter, by addition of .02 M  $Ga(OH)_2$ . The adjusted P solutions were stored overnight and the pH values measured and readjusted to pH 6 if necessary. Because the P solutions were adjusted to pH 6, P in the solutions was measured by the Murphy and Riley method to obtain the P concentration in each solution. Solutions containing 34.5, 62.0, 88.6, 107.2, 147.0, 167.5, 214.5, 294.0 ppm P and 35.0, 63.0, 89.2, 96.25, 117.13, 170.0, 242.1 ppm P were used for surface (horizon A) and subsoils (horizon B) respectively.

# 3.2.2.3 Phosphorus Adsorption Isotherm.

## (1) Air dried soils.

Five g soil samples were placed in 100 ml plastic centrifuges tubes and 45 ml 0.01  $\operatorname{CaCl}_2$  (adjusted to pH 6) and 5 ml of adjusted pH P solutions were added to five initial P concentration varying from 3 to 30 ppm. The samples were shaken on a wrist-action shaker for 24 hours, centrifuged at 2,200 rpm for 15 minutes, filtered and the filtrates analyzed for P concentration by Murphy and Riley method. The amounts of adsorbed P, (x/m), were calculated.

### (2) Anaerobic soils.

40 ml of 0.01 CaCl<sub>2</sub> (adjusted to pH 6) were added to each set of soil samples in 100 ml plastic centrifuge tubes. A set of P solutions was prepared as follows: 5 ml of 0.01 CaCl<sub>2</sub> (adjusted to pH 6) in 25 ml Erylenmeyer flask were mixed with adjusted pH P solution (see above). Both soil samples and the set of P solutions were placed in the entry lock portion of the anaerobic glove chamber (see Figure 2). After closing the outside door of the entry lock, the entry lock was evacuated and then

flushed with  $N_2$  two times, then evacuated and flushed with a gas mixture, (10 percent  $H_2$  and 90 percent  $N_2$ ). The samples and the set of P solutions were transferred from the entry lock into the glove chamber, and closed with parafilm papers. The samples were incubated in the glove chamber for 1, 3, 7, days. After incubation, the prepared P solutions were added to the soil samples in the glove chamber, and the tubes were closed with parafilm papers. The tubes were transferred via entry lock and were shaken, centrifuged, filtered, and the filtrates were analyzed for P concentration in the same manner as air dried soils.



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Figure 2. Diagram of anaerobic glove chamber.

#### RESULTS AND DISCUSSION

The first portion of this study was designed to determine the optimum time of contact, salt concentration and pH of P solution for the best data for the Langmuir Adsorption Isotherm. Many conflicting reports in the literature have made these preliminary experiments essential.

#### 4.1 Preliminary Studies.

## 4.1.1 Study of Contact Time and Effect of Salt Solution.

The typical time P adsorption curve indicates a fast reaction initially, followed by a reaction which proceeds at a slow and almost constant rate. Researchers have attempted to adjust the contact time to where the rate of P adsorption and desorption are at equilibrium. Practically they attempt to get the time period to where the rate of P change in solution is small.

The contact period required to reach equilibrium depends on many factors including soil properties, P solution and rate of shaking. The contact period ranged from a few hours to 3 days or more. Syers et al. (1973 b) used 72 hours, Olsen and Watanabe (1957) used 24 hours, Shapiro and Fried (1959) used 18 hours for shaking, while Hau (1964) and Rennie and McKercher (1959) allowed a contact period of 6 hours.

The P solution used in adsorption studies varied from researcher to researcher. Some workers used P in salt solutions such as 0.01 M CaCl<sub>2</sub> (Ellis and Erickson, 1969; Gunary, 1970; and Udo and Uzu, 1972) or 0.1 M NaCL (Syers et al., 1973 b). However, P in water solution also has been used, (Olsen and Watanabe, 1957; Hsu, 1964). The purpose of having salt in the solution is to keep the ionic strength of the suspension the

same as that of the natural soil solution. The following study was designed to determine the appropriate contact period and the effect of 0.01 M  $CaCl_2$  on P adsorption. The study was conducted in 0.01 M  $CaCl_2$  and  $H_2O$ solution containing 6 and 12 ppm P. The shaking times were 3, 5, 12, 24, and 48 and 72 hours. The data of this study are shown in Table 1.b. of the Appendix.

The results of this study are shown in Figures 3 and 4. The amount of P adsorbed by both Hoytville A and Locke A soils in 0.01 M CaCl<sub>2</sub> P solution is greater than that of P in water solution at each time interval. The reaction rate is fast initially and is followed by a slow rate and apparently approaches equilibrium with time of shaking for all treatments. However, rate of P adsorption in salt treatments was initially faster than that of water treatments at all P concentrations, and eventually approached equilibrium at about 24 hours of contact time. But in  $H_20$ treatment, the contact period of 24 hours was insufficient to reach equilibrium. For the Hoytville A the contact period for equilibrium P adsorption from  $H_20$  solution was about 48 hours, while Locke A soil can adsorb more P and the contact period of this soil is apparently longer than 72 hours.

When solution was added to soil, the ionic strength in the soil solution was dilute and the ions in liquid and solid \_hase were not in equilibrium. It takes time to allow the ions in the soil which is a heterogeneous system to reach an equilibrium state. When we introduce P into this system, the P adsorption reaction is also dependent on the strength of other ions species. For the system in which the native ionic state is in equilibrium or near equilibrium, the P adsorption reaction would reach equilibrium faster than in the other system. Therefore the P adsorption in salt solution reached equilibrium faster than that in



Figure 3. Effect of contact time, CaCl, and H<sub>2</sub>O solution on P adsorption by Locke A soll.



Figure 4. Effect of contact time, CaCl<sub>2</sub> and H<sub>2</sub>O solution on P adsorption by Hoytville A soil.

H<sub>2</sub>0 solution. In addition to the P directly adsorbed on the surface of clay material, P can be adsorbed indirectly by means of cation bridge to clay or other soil materials (Shapiro and Fried, 1959). This mechanism of P adsorption could explain the greater and faster P adsorption in 0.01 M CaCl., solution than in water treatment.

From this study, it could be concluded that 24 hours is the appropriate contact period for P adsorption isotherms using P in 0.01 M CaCl<sub>2</sub> with shaking the soil suspension on a wrist-action shaker. The advantage of 0.01 M CaCl<sub>2</sub> for the P adsorption study in the Michigan Soils is not only the faster equilibrium adsorption, but also a clear solution is obtained for P analysis after centrifugation at 2,200 rpm (1500 RCF). With P in water solution treatments, the suspension need further contrifugation at the faster speed of 6100 rpm (4500 RCF) to set the appropriate clear solution for P determination. 4.1.2 Effect of the pH of the Initial P Solution.

Most studies of P adsorption isotherms have been carried out either at uncontrolled pH values (Syers et al., 1973 b; Weir and Soper, 1962; and Kurtz et al., 1946) at a buffered pH (Hsu and Rennie, 1962; Bache, 1964); or adjusted to a certain pH initially without buffering (Olsen and Watanabe, 1957; Rennie and McKercher, 1959; Woodruff and Kamprath, 1965).

Phosphorus adsorption is not a single mechanism or type of reaction -- it is partially anion exchange because P can be replaced by other anions such as flouride, oxalate, citrate, bicarbonate, borate, acetate, thiocyanate, sulfate and chloride (Kurtz et al., 1946). Therefore the P solution with pH controlled by a buffer appears not to be satisfactory because anions used in the buffer are likely to compete with phosphate ions for reactive sites, complicating the interpretation of the results.

However, the pH of P solution in 0.01 M  $\operatorname{CaCl}_2$  is not constant initially. As the P concentration increases the pH of 0.01 M  $\operatorname{CaCl}_2$  solution decreases (Table 3). Thus, the effect of pH of P solution on P adsorption must be studied.

The studies were conducted in 0.01 M CaCl<sub>2</sub> solution with pH adjusted to 6 (with 0.02 M Ca(OH)<sub>2</sub>) or the same solution with pH unadjusted. The amount of adsorbed P, (x/m), was calculated. The data from this experiment is shown in Table 1.c. of the Appendix.

The amounts of P adsorbed as a function of P equilibrium, at low concentrations of P of both treatments are equal in all three soils (See Figures 5, 6 and 7). For higher P concentrations, the amount of P adsorbed at pH 6 became somewhat greater at each P increment. The pattern of adsorption curves in both treatments are the same -- starting with a fast adsorption rate, followed by a slow rate and approaching the maximum adsorption

P concentration	pH	
	0.01 M CaCl2	H <sub>2</sub> 0 1/
ppm		
0.0	5.45	6.30
30.0	5.10	5.85
60.0	4.85	5.30
90.0	4.65	
120.0	4.55	5,20
150.0	4.62	
200.0	4.62	5.10

Table 3. The pH of increasing  $KH_2PO_4$  concentrations in solutions of 0.01 M CaCl<sub>2</sub> and  $H_2^{0}$ .

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1/ deionized distilled water.





Figure 7. Effect of pH of P solution on P adsorption by Hoytville A soil.

as P increased.

The amount of P adsorbed from the P solution adjusted to pH at 6 at higher P concentration was somewhat greater than that of the uncontrolled treatment. This may be due to pH effects or the amount of Ca in solution. According to Black (1942) the pH of solution affected the amount of P adsorption by clay minerals such as kaolinite, hydrated halloysite, illite and bentonite and by soil, each of which had a range of pH of final solution for its maximum adsorption. He found that finely ground kaolinite showed a maximum adsorption at a final pH of 3 to 4. For another kaolinite clay the maximum adsorption occurred at pH about 6 to 7 with 1 and 10 ppm P solutions. At 1 ppm P, the maximum adsorption by Cecil clay in which free Fe oxide was removed occurred at a final pH of 6 to 7 with smaller quantities being adsorbed at lower or higher pH values. The adsorption from a solution concentration of 10 ppm P showed two distinct maxima, one in the range of pH 6 to 7 and the other at pH 3.2. However, for untreated Cecil clay, at 1 ppm P concentration the maximum adsorption occur at about pH 4.5. These studies show that the P maximum adsorption as a function of pH of the solution depends on the soil properties including kind and quantities of free oxides and type and size of clay mineral and P concentration.

However, in adjusted pH treatment the amount of  $Ca^{+2}$  in the P solution was somewhat greater than that of uncontrolled treatment. This may more or less account for the increase in the amount of P adsorption in pH adjusted treatment. Barrow (1972) found that the amount of P adsorbed increased as Ca concentration in P solution increased.

4.1.3 Effect of Contact Time on P Adsorption from 0.01 M CaCl, at pH 6.

Because 24 hours was selected as the appropriate contact period for P adsorption from 0.01 M CaCl<sub>2</sub> solution, this study was designed to determine the contact time for P adsorption from P solution in 0.01 M CaCl<sub>2</sub> which was adjusted to pH 6 with 0.02 M Ca(OH)<sub>2</sub>.

The experiment was conducted in 0.01 M  $CaCl_2$  (pH 6) containing 6.2 and 14.7 ppm P. The shaking times were 3, 5, 10, 16, 24, 48 and 72 hours. The data is shown in Table 1.d. of the Appendix.

The results are summarized in Figure 8. As expected the P adsorption curve is a function of time as was the case in the previous study with P solution in which pH was not adjusted. The rate of P adsorption was first fast, followed by a slower rate and proceeded to reach the equilibrium eventually. At the lower concentration of P (6.2 ppm) the equilibrium was reached in 24 hours of contact time in both Sims A and Locke A soils. But at the higher P concentration (14.7 ppm P) the shaking time of 24 hours approached equilibrium, but equilibrium was not reached until about 48 hours in both soils.

It could be concluded that the appropriate contact period for P adsorption by the soils under study, from P solution in 0.01 M  $CaCl_2$  which was adjusted pH at 6, is about 24 hours. This contact period of 24 hours will be used in the P adsorption isotherm study for anaerobic soils in the next section.



Figure 8. Effect of shaking time on P adsorption from 0.01 M CaCl<sub>2</sub> adjusted to pH 6.

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## 4.2 Phosphorus Adsorption Isotherm.

## 4.2.1 Phosphorus Adsorption by Air Dried Soils.

The amount of P adsorption by soils (x/m) as a function of P equilibrium concentration, (P), is shown in Figures 9 to 13.

The amount of adsorbed P increased as (P) increased. The increment of P adsorbed,  $\left(\Delta (x/m) \atop (P)\right)$ , decreased as (P) increased, and x/mapparently approached the P adsorption maximum, (b). For example, when (P) increased from 2.5 x 10<sup>-5</sup> to 5 x 10<sup>-5</sup> mole/1, the increase in adcorbed P,  $(\Delta (x/m))$  was about 2.2 and 1.8 mg P/100 g for Hillsdale B and A horizons. When (P) increased from 5 x 10<sup>-5</sup> to 7.5 x 10<sup>-5</sup> mole/1, (x/m) became about 1.0 and 1.4 mg P/100 g for the same soil samples. This indicated the typical curve of P adsorption isotherm.

The amount of P adsorbed, (x/m), at any given (P) by subsoils is greater than that of surface soils. For example, at  $5 \times 10^{-5}$  mole (P)/ 1, the amount of P adsorbed by soils in B horizon of Hillsdale, Locke, Hiami, Sims and Hoytville, are 15.2, 14.2, 13, 10, and 17.5 mg/100 g soil, compared with 6, 6.7, 5.8, 8.5, and 13.0 mg/100 g soils in the respective A horizons. However, with coarse textured soils, (Hillsdale, Locke, and Miami) the amount of P adsorbed by the B horizon is much greater than that adsorbed in the surface, i.e. at  $5 \times 10^{-5}$  mole(P)/ 1, x/m of subsoils were approximately 2.5, 2.1, 2.2 times of the surface ones. The differences are 9.2, 7.6, and 6.2 mg/100 g soil respectively. But with the fine textured soils, Sims and Hoytville, the difference in the amount of adsorbed P between the two horizons is not so pronounced, i.e. at  $5 \times 10^{-5}$  mole (P)/1 the differences are about 1.5 and 4.5 mg/100 gm soil. Sims B and Hoytville B adsorbed 1.2 and 1.4 times more P than the A horizons at the same (P) values. Figure 9. Amount of P adsorbed by Hillsdale soils as a function of (P),

Figure 10. Amount of P adsorbed by Locke soils as a function of (P).

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Figure 11. Amount of P adsorbed by Niami soils as a function of (P).

Figure 12. Amount of P adsorbed by Sims soils as a function of (P).

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Figure 13. Amount of P adsorbed by Hoytville soils as a function of (P).

The amount of P adsorbed in the subsoils is greater than that adsorbed by surface soils because of the accumulation of Fe and clay minerals in the B horizon, Ellis and Erickson (1969) also reported that B horizons have the ability to adsorb more P than A horizons.

The results also showed that fine textured soils adsorbed more P than coarse textured ones. Sims A and Hoytville A soils with clay loam texture, adsorbed more P than Hillsdale A, Locke A and Miami A, (sandy loam and loam texture). At  $5 \times 10^{-5}$  mole(P)/1, Sims A and Hoytville A adsorbed about 8.5 and 13.0 mg P/100 g soil, whereas Hillsdale A, Locke A and Miami adsorbed about 6, 6.7 and 5.8 mg P/100 g soil respectively.

For subsoils at the same values of (P), Hoytville adsorbed 17.5 mg P/100 g soil (Hoytville B), while Hillsdale B, Locke B, and Miami B adsorbed only about 15.2, 14.3 and 13 mg P/100 g soil, However, the Sims B adsorbed only about 10 mg P/100 g soil. This may be due to a lower accumulation of Fe and clay in this soil than in Hillsdale B, Locke B, and Miami B or it may be due to some other factors.

Olsen and Watanabe (1957) found a close relationship between adsoprtive capacity and the specific surface area of soils. Black (1942) reported that ground kaolinite adsorbed more P than the unground mineral. Syers et al. (1971) and Udo and Uzu (1972) found that soil adsorption capacity and the amount of clay content were correlated.

Because for a given amount of soil, fine textured soil has a greater number of reactive sites than coarse textured soil, clay soils will adsorb more P than sandy soils.

Figures 9-13 show that almost all of the P in the low initial P solution was adsorbed by subsoil, indicated by the steep increase in x/m as P increased. But for surface soils the amount of x/m increased as a

function of (P) was lower. This would indicate that there are more sites for P adsorption in B horizons than in A horizons.

Langmuir adsorption isotherm for air dried soils are shown in Figures 14 to 18.

A plot of (P)/(x/m) versus (P) gave a straight line at low P concentrations -- up to about  $5 \times 10^{-5}$  mole (P)/1 for surface soils except Hoytville A (at about 2.5  $\times 10^{-5}$  mole (P)/1) and up to 1  $\times 10^{-5}$  to 5  $\times 10^{-5}$  mole (P)/1 for subsoils. At higher (P) the deviation also yield another straight line for levels up to 10  $\times 10^{-5}$  to 30  $\times 10^{-5}$  mole (P)/1. That Langmuir P adsorption data yielded two straight lines for P levels of about 14 ppm or about 45  $\times 10^{-5}$  mole (P)/1 was also found by Syers et al. (1973 b). They noted that there are two components of soils which are very different with respect to P adsorption.

The constant K, related to bonding energy, and b, the adsorption maximum of the two parts were calculated from the slopes and the intercepts of both straight lines. The value of K and b were shown on Table 4.

The  $K_1$  (K value for the first straight line) values vary from about 0.2 to 0.7 x 10<sup>5</sup> 1/mole for surface soils, and range from 0.86 to 8.8 x  $10^5$  1/mole for subsoils. While  $K_2$  (corresponds to the second straight line) vary from about 0.07 to 0.22 x  $10^5$  1/mole for surface soils and about 0.15 to 0.77 x  $10^5$  1/mole for subsoils.

For all soils,  $K_1$ , is greater than  $K_2$  (See Table 4) which indicated that P was adsorbed in part I more tightly than by part II, since the greater the K value the greater the energy of P adsorption on the surface of soil particles. However, the difference between this bonding energy constants ( $K_1$  and  $K_2$ ) is greater in subsoils with  $K_1/K_2$  ratios varying from about 5.8 to 15.5, (See Table 4). The  $K_1/K_2$  ratios of surface soils

	Part I		Part II		K. /K.	ъ_/ъ,	ED
Soil	ĸ	<sup>b</sup> 1	к2	<sup>b</sup> 2	1. 2	<i>c</i> 1	
	× 10 <sup>-5</sup>	mg/100 g soil	x 10 <sup>-5</sup>	mg/100 g soil	<u> </u>	,	ng/100 g soil
Hillsdale							
A	.205	12.9	.087	17.9	2.35	1.4	30.8
В	8.33	12.0	.769	20.0	10.8	1.6	32.0
Locke							
A	•354	10.5	.126	15.2	2.80	1.5	25.7
В	5.92	11.2	.694	18.0	8.53	1.6	29.2
Miami							
A	.259	10,7	.073	17.9	3.53	1.7	28.5
в	4,28	11.7	.431	19.3	9.94	1.7	31.0
Sims							
A	.389	12.9	.135	20.0	2.88	1.6	32.9
В	.857	11.7	.149	21.0	5.76	1.8	32.7
Hoytville							
A	.706	15.0	,227	26.7	3.36	1.8	41.7
В	8.88	11,2	.578	29.0	15.5	2.6	40.2

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Table 4. Langmuir adsorption parameters for air dried surface and subsoils.



Figure 14. Langmuir P adsorption isotherms for Hillsdale soils.



Figure 15. Langmuir P adsorption isotherms for Locke soils

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Figure 17. Langmuir P adsorption isotherms for Sims soils.



Figure 18. Langmuir P adsorption isotherm for Hoytville soils.

range from about 2 to 3.5. However, Syers et al. (1973 b) found that  $K_1/K_2$  values range from 33 to 91 for their soils.

Bond strength indicated by K values of both regions showed that subsoils adsorbed P more strongly than do surface soils. In coarse textured soils (Hillsdale, Locke and Miami), the difference between K values of A and B horizons in both regions is greater, which is indicated by  $K_B/K_A$  value (Table 5). These values ( $K_B$  and  $K_A$ ) range from about 16 to 40 in part I and about 5.5 to 8.8 for part II. For fine textured soils, Sims and Hoytville, the  $K_B/K_A$  values are about 2 and 12 for region I and about 1 and 2.6 for region II respectively.

The  $b_1$  (adsorption maximum in region I) values vary from 11 to 15 mg P/100 g soil for A horizon and range from 11 to 13 mg P/100 g soil for B horizon. While  $b_2$  values (adsorption maximum in region II) vary from about 15 to 26.7 mg P/100 g soil and about 18 to 29 mg P/100 g soil for horizon A and B respectively.

In region I, the adsorption maximum indicated by  $b_1$  values, was similar for sub and surface soils, except for Hoytville. For example,  $b_1$ values are about 10.5 and 11.25 mg P/100 g soil for Locke A and B, and about 10.7 and 11.7 mg P/100 g soil for Miami A and B respectively. But Hoytville A and B have  $b_1$  values about 15 and 11 mg P/100 g soil.

The adsorption maximum of region II,  $b_2$ , of subsoils is greater than that of surface soils, except Sims. For example, for Locke soil the adsorption maximum of region II are about 15.2 and 18.0 mg P/100 g soil for horizon A and B respectively. While Sims A and B, the  $b_2$ values are about 20 and 21 mg P/100 g soil.

Figures 14 to 18 showed that at any given (P) the amount of P adsorbed by subsoils is greater than that of surface soils, indicated

Soil	Part	I	Part II		
	ĸ <sub>₿</sub> ∕ĸ	<sup>b</sup> <sub>B</sub> / <sup>b</sup>	к <sub>в</sub> /к	<sup>b</sup> B∕p♥	
Hillsdale	40.7	.93	8.8	1,12	
Locke	16.8	1,17	5.5	1,18	
Miami.	16.5	1.09	5.9	1.07	
Sims	2,2	.91	1.1	1.05	
Hoytville	12.0	•75	2,6	1.09	

•

Table 5. Ratio of bonding energy constant and adsorption maximum of A and B horizons.

by the lower  $\frac{P}{x/m}$  values. However, the total amount of P adsorption maximum, ( $\Sigma$ b values in Table 4), which were calculated from Langmuir straight lines, showed that in corase textured soils, (Hillsdale, Locke and Miami), the B horizon has the ability to adsorb more P than surface soil, e.g. 30.8 and 32, 25.7 and 29.25, 28.6 and 31.00 for Hillsdale, Locke and Miami, A and B horizons respectively. This indicated that B horizon of coarse textured soils have the ability to adsorb more P from solution than A horizons. The greater ability is due to the accumulation of clay and Fe in B horizon. But in fine textured soils i.e. Sims and Hoytville, the total maximum adsorption are about 32.9 and 32.7 for Sims A and B and 41.7 and 40.2 mg P/100 g soil for Hoytville A and B horizon respectively. This shows that the ultimate ability to adsrob P from the solution for A and B horizons of these two soils are not different even though Figure 12, 13 showed that the B horizon of these two soils adsorbed more P than the A horizon at any given (P) under study. For fine textured soil the difference in clay content between the surface and subsoil is not as much for coarse textured soils.

The first straight line of Langmuir plotting may correspond to the steep part of the curve x/m versus (P) in Figure 9to 13, This part of the curve corresponded to the part of the soil that adsorbed P more tight-ly than that of the second part of the curve.

# 4.2.2 Phosphorus Adsorption by Flooded Soils.

## 4.2.2.1 Phosphorus Adsorption Isotherms for Flooded Surface Soils.

After flooding soil, an increase in extractable P has been found (Ponnamperuma, 1972). For the five Michigan soils under study, Srisen (1971) found that the amount of Flouride (Bray's), Sodium **bicarbonate** (Olsen's) and diluted  $H_2SO_4$  (Troug's) extractable P also increased upon flooding; (Table 1.e. in Appendix). This would suggest that the P adsorption behavior of these soils would change due to flooding and the tendency to decrease P adsorption could be anticipated since the solubility and the amount of extractable P increased.

Phosphorus adsorption by flooded and anaerobic surface soils did change upon flooding, (Table 6 and Figures 19 to 23.) But as shown in Table 6 the amount of P adsorbed (x/m) as a function of initial P concentration increased upon flooding, especially for Hillsdale A, Miami A, and Sims A soils.

For Locke A, the amount of P adsorbed after flooding is somewhat smaller than that of the air dried soil at low P concentration, but at higher P concentration(at 21.45 and 29.4 ppm P initially), the amount of P adsorbed by flooded soils become greater. On the other hand, the amount of P adsorbed by the Hoytville A horizon decreased upon submergence. These results are shown in Figures 19 to 23.

Phosphorus adsorption by flooded soils and by lake sediment has been studied by many workers who found that the disappearance of P from the solution by submerged soils was related to active Fe and  $Fe_20_3$  content of the soils (Chiang, 1963 b; De Datta et al., 1966; and Mandal and Das, 1970; Shukla et al., 1971) Shukla et al. (1971) also reported that noncalcareous lake sediment adsorbed more P than calcareous ones, and

Soll		(P) initial	Amount of P adsorbed (x/m) Incubation Time				
			0 day	1 day	3 days	7 daya	
		ppm		mg/100	g soil	*******	
Hillsdale	A	3.45 6.20 8.86 10.7 14.7 16.7 21.4 29.4	3.00 5.01 6.93 8.1 10.1 11.1 12.7 15.3	3.11 5.57 7.72 8.74 11.2 12.6 14.7 18.0	2.95 5.26 7.49 8.89 11.3 12.0 14.2 17.8	3.04 5.12 7.24 8.15 10.6  14.1 19.4	
Locke	A	3.45 6.20 8.86 10.7 14.7 16.7 21.4 29.4	3.07 5.32 7.07 7.97 9.98 10.7 12.0 13.4	2.80 4.95 6.59 7.42 9.33 10.3 12.0 15.7	3.08 5.11 6.67 7.70 10.0 10.6 12.0 15.2	2.88 4.88 6.75 6.87 8.95 12.5 19.9	
Miami	•	3.45 6.20 8.86 10.7 14.7 16.7 21.4 29.4	2.99 4.97 6.71 7.62 9.87 10.5 12.2 14.6	3.12 5.61 7.61 8.73 11.2 12.3 14.3 17.6	3.11 5.59 7.72 8.74 11.2 12.6 13.8 18.3	3.21 5.82 7.52 8.37 11.1  17.5 20.7	
Sims	•	3.45 6.20 8.86 10.7 14.7 16.7 21.4 29.4	3.14 5.56 7.68 8.89 11.5 12.6 14.9 17.9	3.28 5.81 8.17 9.67 12.8 14.4 17.7 22.7	3.30 5.95 8.38 9.94 13.3 15.1 18.3 23.8	3.27 5.89 8.48 10.0 13.3 - 18.5 24.4	
Ho <b>ytville</b>	A	3.45 6.20 8.86 10.7 14.7 16.7 21.4 29.4	3.33 5.91 8.34 9.91 13.4 14.9 18.4 23.2	3.24 5.57 7.80 9.26 12.5 14.0 16.8 22.2	3.08 5.62 8.09 9.85 12.4 13.8 16.5 21.9	2,95 5,38 7,82 9,03 12,2 13,2 17,2 23,0	

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Table 6. Amount of P adsorbed by anaerobic surface soils<sup>1</sup>.

1 average of 3 replications.

Figure 19. Amount of P adsorbed by air dried and flooded Hillsdale A soils.

Figure 20. Amount of P adsorbed by air dried and flooded Locke A soils.

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Figure 21. Amount of P adsorbed by air dried and flooded Miami A soils.

Figure 22. Amount of P adsorbed by air dried and flooded Sims A soils.

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Figure 23. Amount of P adsorbed by air dried and flooded Hoytville A soils.

oxalated soluble P played an important role in P adsorption by the lake sediments. De Datta et al. (1966) reported that there is no change in P concentration in solution during 4 days equilibrium with calcareous soils.

Greenhouse studies showed that the amount of 1 NH<sub>4</sub>OAc extractable Fe of Michigan soils under study increased considerably upon flooding (see Table 1.f. in Appendix), and reached the maxima about 3 to 6 weeks after flooding (Srisen, 1971).

For Hillsdale A, Miami A and Sims A, the amount of Fe increased greatly within 3 weeks of submergence, while for Locke A and Hoytville A, the amount of extractable Fe was also increased but the increase was much less within 3 weeks of submergence and reached the maxima slower at about 6 weeks after flooding. But in all five surface soils the extractable P increased greatly within 3 weeks of submergence, (see Table 1.e., in Appendix).

The increase in extractable Fe and extractable P upon flooding the soils should change the ability of soils to adsorb P after flooding. However, the amount of extractable Fe appears to play a more important role in this case. For Hillsdale A, Miami A and Sims A, the increase in extractable Fe within 3 weeks of submergence may cause increases in P adsorption by these soils upon flooding. However, for Locke A and Hoytville A with much lower extractable Fe within 3 weeks of flooding, (19.7, 12.0 and 38.7 ppm for those three soils compared with 1.04 and 2.73 ppm Fe for Locke A and Hoytville A), the amount of P adsorbed decreased a little in flooded treatments. This may be due to a greater increase in soluble P than could be adsorbed upon flooding within 7 days of incubation.

Therefore the P that remained in solution after shaking with the soils in flooded treatment was greater than that of air dried soils.

The adsorption of P by flooded soil would differ from that of air dried soil in this aspect. For air dried soils, the number of P adsorption sites does not change and the soil adsorbs added P from the solution. For flooded soils the number of P adsorption sites is more or less changed due to the chemical changes under anaerobic condition, e.g. extractable Fe and P increase, and flooded soil adsorbs not only applied P from the solution, but it adsorbs native P that is released into solution during chemical changes upon flooding.

As concluded by Ponnamperuma (1972) acid clay high in Fe gave a low increase in solution P while sandy soils low in Fe gave the most increase in P in the solution of flooded soils. This would indicate the importance of Fe in removal of P from solution, some of which is fixed by adsorption reaction and the other portion is precipitated.

Langmuir adsorption isotherms for flooded surfaced soils are shown in Figures 24 to 28, and P Langmuir adsorption data showed in Table 1.g. to 1.j. in Appendix. The Figures show that the longer the time of incubation the greater is the deviation from a straight line. The bonding energy constant, K, and the adsorption maximum, b, were calculated and are given in Table 7.

The strength of P adsorption in part I, indicated by  $K_1$  values, changed a little upon flooding. The tendency to decrease of the energy of adsorption in this part of the soil is shown by Hillsdale A, Locke A, and Hoytville A. However, for Miami A and Sims A soils the  $K_1$  values increased a little upon flooding.

Soil	Incubation	Par	t I	Part		
	time	к <u>і</u>	Ъ <u>1</u>	<sup>к</sup> 2	<sup>b</sup> 2	Σb
	days	x 10 <sup>-4</sup> 1/mole	mg/100 g soil	x 10 <sup>4</sup> l/mole	ng/100	g soil-
Hillsdale						
A	0	2.047	12.9	0,872	17.9	30.8
	1	2,392	15.8	0,962	21.7	37.5
	3	2,231	15.4	0.871	21.2	36.7
	7	1,880	14.0	0,663	22.9	36.9
Locke						
A	0	3.535	10.5	1,262	15.2	27.4
	1	2,200	10.8	0.748	16.9	27.7
	3	2,592	10.7	0,833	17.1	27.8
	7	2,661	8.9	0.367	21.7	30.6
Miami.						
A	0	2,593	10.7	0.734	17.9	28.6
	1	4.453	11.8	1,242	19.2	31.0
	3	3.283	14.1	0.777	24.3	38.4
	7	4.964	10.7	0.459	32.5	43.2
Sims						
A	0	3.889	12.9	1.351	20.0	32.9
	1	4.629	16.0	0,998	32.9	48.9
	3	4.167	20.0	0,961	37.1	57.1
	7	4.347	20.0	0.788	43.8	63.8
Hoytville						
A	0	7.407	15.0	2,206	26.7	41.7
	1	4.687	13.3	1.309	25.4	38.8
	3	7.778	14.3	1,267	25.4	39.7
	7	4,167	13.3	0,588	37.8	51.1

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Table 7. Langmuir adsorption parameters for anaerobic surface soils.



Figure 24. Langmuir P adsorption isotherms for flooded Hillsdale A soil.



Figure 25. Langmuir P adsorption isotherms for flooded Locke A soil.







Figure 27. Langmuir P adsorption isotherms for flooded Sims soil.

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Figure 28. Langmuir P adsorption isotherms for flooded Hoytville A soil.

The adsorption maximum in part I of adsorption,  $b_1$ , increased in Hillsdale A, Miami A and Sims A soils. While Locke A soil the adsorption maximum was relatively constant and Hoytville A soil showed a slight decrease in  $b_1$  values.

In the second part of P adsorption by soils, the bonding energy constant,  $K_2$ , decreased upon flooding, this would indicate that soils adsorb P more loosely in this part of the adsorption than in air dried soils. The adsorption became weaker when the incubation time increased up to 7 days of incubation in this study.

The ability to adsorb P, indicated by  $b_2$  values, showed that the adsorption maximum in part II increased upon flooding, e.g. from 17.9 to 21 , and from 20 to 43 mg P/100 g soil for Hillsdale A and Sims A after 3 days of incubation. However, for Hoytville A the adsorption maximum did not increase until 7 days after flooding. The increase in P adsorption maximum and the decrease in bonding energy for P adsorption in this part, associated with the small change in both b and K values in part I, indicated that the change in the behavior of P adsorption by surface soils after flooding is due to the changes in this portion of the adsorption. Generally the ability of the soil to adsorb P increased but with weaker bonding energy than those of air dried soil.

The total amount of P adsorption maximum, ( $\Sigma$ b in Table 7), increased upon submergence especially for Hillsdale A, Miami A and Sims A soils. However, the total adsorption maximum for Locke A and Hoytville A soils did not increase until after 7 days of incubation.

It should be noted that the adsorption capacity of surface soils generally increased upon flooding but the P was held with a lower bonding

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energy than in air dried soils. This change is due to the chemical changes in the soil after flooding.

In flooded soils, P became more soluble and is released in to the soil solution and could be adsorbed on the reactive sites of the soil. It has been found that (greenhouse studies) the amount of P in solution was very small compared to the extractable P for these five soils (Srisen, 1971). These showed that P was adsorbed after it was released into the solution after flooding for a period of time. This adsorbed P may account for the increase in extractable P after flooding.

It should be also noted that the break point in Langmuir curve between the two parts is between P values of 5 to 10 x  $10^{-5}$  mole P/1 (about 1.8 to 3.1 ppm P). This P concentration is somewhat higher than the amount of P in the natural lake water. Syers et al. (1973 a) concluded that the P concentration in anaerobic water at the bottom of the Lakes is about .1 to .5 ppm P. Srisen (1971) found that after 3 weeks of incubation the concentration of P in water is less than 1 ppm under greenhouse studies for Michigan soils. This means that the amount of P remained in water of flooded soils would have the possibility of removal from the solution if the contact time was longer, (e.g. by adsorption, precipitation or microbal consumption). However, under laboratory studies, the concentration of 5 to 10 x  $10^{-5}$  mole P/1 in the solution after shaking would be considered to be the concentration of P that provide loosely bound P by the soils under flooding conditions in this study.

The P adsorption reaction occurring in flooded soils should be of benefit to rice cultivation especially in the paddy field with uncontrollable water area. Phosphorus in the water which may come from native or

applied P would not be lost with drainage water. It can be adsorbed and can be used by rice during the growing season.

It should be noted that the disappearance of P from P solution occurred by the two mechanisms, chemical adsorption and precipitation. Precipitation would occur when the concentration of P and the reactive counter cations such as  $Fe^{+3}$ ,  $Fe^{+2}$ ,  $Al^{+3}$  and  $Ca^{+2}$  were sufficiently high and the solubility products are higher than the solubility product constant of the respective P compounds. Because the solubility of Fe and P in reducing conditions in flooded soil is higher than that of air dried soil, the possibility exists that P may be removed from solution by precipitation, especially when an anaerobic soil becomes aerobic. An example of this reaction is the oxidized zone in paddy rice soil (Patrick and Mahapatra, 1968). Evidence of this was found in this study during an initial experiment. When the surface soils were incubated in anaerobic chamber for 7 days and were shaken with P solution air leaks developed in the stoppers of some of the samples which then were contacted with air atmosphere during shaking periods. The loss of P from the solution in those tubes was much greater than with the other samples suggesting that precipitation occurred. The data on this investigation is shown in Table 8.

	P initial	P at	equilibriu	Lm	
Soil			replicatio	n	average
		1	2	3	
Hillsdale			ppm		,
A	3.45 6.20 8.86 10.7 14.7 16.7 21.4 29.4	0.58 1.24 1.70 2.80 4.10 <u>1.28</u> 7.25 4.00	0.42 0.91 1.54 2.33 <u>1.00 2.80</u> <u>1.90</u> <u>3.00</u>	$ \begin{array}{r} 0.30 \\ 0.27 \\ 1.03 \\ 0.40 \\ 4.00 \\ 4.00 \\ 7.15 \\ 10.0 \\ \end{array} $	0.44 0.81 1.42 1.84 3.03 2.69 5.52 5.67
Locke		_			
A	3.45 6.20 8.86 10.7 14.7 16.7 21.4 29.4	$0.64 \\ 1.31 \\ 2.11 \\ 1.72 \\ 0.73 \\ 1.00 \\ 1.60 \\ 3.30 $	0.06 1.65 0.21 3.85 5.75 1.00 1.88 7.62	0.50 0.52 0.39 0.45 1.80 5.80 8.87 9.50	0.40 1.16 0.90 2.00 2.78 2.60 4.09 6.81
Miami					•
•	3.45 6.20 8.85 10.7 14.7 16.7 21.4 29.4	0.27 0.18 1.56 0.32 3.65 0.60 3.92 9.00	0.20 0.40 <u>0.21</u> <u>0.45</u> <u>1.65</u> <u>3.63</u> <u>3.87</u>	0.05 0.35 1.11 2.35 3.36 <u>3.16</u> <u>1.10</u> 8.36	0.17 0.31 0.96 1.04 2.52 1.80 1.88 7.08
Sims					
A	3.45 6.20 8.86 10.7 14.7 16.7 21.4	0.14 0.26 0.40 0.60 1.10 <u>0.60</u> <u>1.00</u>	0,32 0,44 <u>0,07</u> 0,75 1,59 4,44 0,45	0.10 0.21 0.39 0.77 <u>0.33</u> <u>0.88</u> 3.16	0.18 0.31 0.29 0.70 1.01 1.97 1.54
Hoytville	29,4	4, 94	1,48	2.00	5.07
A	3.45 6.20 8.86 10.7 14.7 16.7 21.4 29.4	0,44 0.72 0,98 1,70 2,50 3,18 2,00 3,18	0.55 0.92 0.47 1.70 <u>1.73</u> 1.70 4.41 6.40	0.50 1.12 1.10 1.69 0.15 3.84 3.50	0.50 0.92 0.85 1.97 1.46 2.91 3.30 3.43

Table 8.	Effect	of	air	leaks	in	P	adsorption	bv	flooded	soils.
TUDTO O	THILDC C	UT.	CP 1 1	Teava	-1.64	÷.	anoutherou	-uj	TTOOTOG	

1 Underlined values were suspected of having airleaks.

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4.2.2.2 Phosphorus Adsorption Isothern for Flooded Subsurface Soils.

Chemical changes also have been found in subsoils after flooding (Srisen, 1971). The amount of extractable P increased greatly but was still smaller than that of flooded surface soils (Table i.e. in Appendix). This may be because the extractable P and organic matter content in air dried subsoils was much smaller than in surface soils (Table 1.a. in Appendix). The amount of extractable Fe in flooded subsoils also increased but the increase was much smaller than in flooded surface soils, even in Sims B and Hoytville B soils which have more extractable Fe than that of those surface soils before flooding, (Table 1.f. in Appendix). Actually the total amount of Fe in subsoils is greater than in surface soils through the process of Fe accumulation. The smaller change in the extractable Fe would indicate a lesser degree of reduction in subsoils after flooding. This may be due to more anaerobic metabolism in surface soils than in subsoils associated with higher organic matter content.

Phosphorus adsorption behavior in subsoils is also changed upon flooding, (Table 9 and Figure 29 to 33). Table 9 shows the amount of P adsorbed as a function initial P concentration. It shows that at low initial P concentrations, up to 9.6 ppm P, the amount of P adsorbed did not change upon 7 days of flooding except for Sims B soil which showed a slight increase. But at higher P concentrations, flooded subsoils adsorbed more P than unflooded ones, especially Locke B, Miami B, Sims B and Hoytville B soils. However, for Hillsdale B soil, the amount of P adsorbed was slightly decreased upon 7 days of submergence. This is shown in Figures 29 to 33.

Air dried Hillsdale B soil contained slightly higher extractable P when compared with other subsoils, (Table 1.a. in Appendix). However, the

Soil		(P) initial	Amoun	t of P adsorbed	1 (x/m)		
			Incubation Time				
			0 day	1 day	7 days		
		ppm		-ng/100 g soil			
Hillsdale	В	3.50 6.30 8.92 9.63 11.7 17.0 24.2	3.49 6.27 8.80 9.37 11.2 15.4 18.6	3.48 6.24 8.66 9.37 11.1 15.0 17.3	3.48 6.23 8.75 9.36 11.1 14.8 17.2		
Locke	B	3.50 6.30 8.92 9.63 11.7 17.0 24.2	3.48 6.23 8.69 9.32 11.0 15.8 17.7	3.47 6.21 8.66 9.32 11.1 15.8 18.7	3.47 6.20 8.69 9.35 11.2 16.0 20.4		
<b>Miami</b>	В	3.50 6.30 8.92 9.63 11.7 17.0 24.2	3.47 6.23 8.74 9.25 10.8 15.6 17.5	3.47 6.16 8.62 9.24 10.7 15.2 17.2	3.48 6.23 8.78 9.33 11.2 15.9 19.7		
Sins	B	3.50 6.30 8.92 9.63 11.7 17.0 24.2	3.32 5.96 8.19 8.52 9.86 13.3 16.5	3.38 5.86 8.15 8.57 9.67 13.3 15.2	3.48 6.15 8.92 9.20 10.9 15.9 21.7		
Ho <b>ytville</b>	В	3.50 6.30 8.92 9.63 11.7 17.0 24.2	3.48 6.25 8.83 9.48 11.3 16.2 21.3	3.49 6.27 8.84 9.49 11.4 16.3 20.7	3.49 6.28 8.85 9.51 11.4 16.4 21.3		

Table 9. Amount of P adsorbed by anaerobic subsoils  $\frac{1}{2}$ .

1/ Average of 3 replications.

. , Figure 29. Amount of P adsorbed by air dried and flooded Hillsdale B soils.

Figure 30. Amount of P adsorbed by air dried and flooded Locke B soils.

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Figure 31. Amount of P adsorbed by Miami B soil, air dried and 7 days incubation.

Figure 32. Amount of P adsorbed by Sims B soil, air dried and 7 days incubation.





Figure 33. Amount of P adsrobed by air dried and flooded Hoytville B soils.

amount of extractable Fe of this soil after 3 weeks of submergence was very small. This would account for the slight decreased in P adsorption upon 7 days of flooding. Locke B and Miami B also have a very small extractable Fe content after 3 weeks of flooding but these soils contain lower amounts of extractable P than Hillsdale B in air dried treatment. Whereas Sims B soil in which the increase in P adsorption is greater than the other subsoils after flooding, contains higher extractable Fe within 3 weeks of submergence.

The P Langmuir adsorption data for flooded subsoils are shown in Tables 1.k to 1.m in Appendix, and the plots (P)/(x/m) versus (P) are shown om Figures 34 to 38. The bonding energy constant K and the adsorption maximum were calculated and are given in Table 10.

In the part I of P adsorption, the strength of P adsorption and the ability of subsoil to adsorb P, (indicated by  $K_1$ , and  $b_1$  values in Table 10), were relatively unchanged for Hillsdale B, Locke B, and Miami B soils. However, for Sims B both  $K_1$  and  $b_1$  values increased after 7 days of flooding. While Hoytville B, soil adsorbed somewhat more P and with a little lower energy in this part of P adsorption.

In part II of P adsorption, flooded soils adsorbed P with a lower bonding energy than air dried soils, (indicated by  $K_2$  in Table 10), except for Hoytville B the  $K_2$  values increase upon flooding.

The adsorption maximum in this part of the soils was also changed upon flooding. For Locke B and Miami B soils, the b<sub>2</sub> values increased a little, whereas Sims B soil, the adsorption maximum increased considerably. However, for Hillsdale B and Hoytville B soils, the adsorption showed a slight decrease in the adsorption maximum upon flooding.

Soil	Incubation		Pa	rt I	Par		
		time	к <sub>1</sub>	<sup>b</sup> 1	к2	<sup>b</sup> 2	Σþ
		days	× 10 <sup>-5</sup>	mg/100g soil	x 10 <sup>-5</sup>	mg/100g soil	mg/100g soil
Hillsdale	в	0	8.333	12.0	.769	20.0	32.0
		1	8.392	10.8	.779	18.3	29.2
		7	8,392	10.8	.736	18.1	29.2
Locke	B	0	5.926	11.2	.694	18.0	29.2
		1	5 <b>.</b> 758	11.6	• 556	20,0	31.6
		7	5 <b>.</b> 758	11.6	.600	22.0	33.6
Miami	в	0	4.286	11.7	.431	19.3	31.0
		1	3.897	11.7	.405	19.0	30.7
		7	4.040	11.2	.458	23.0	34.2
Sims	в	0	.857	11.7	.149	21.0	32.7
		1	.884	11.3	.097	25.7	37.0
		7	1.322	13.8	<b>.</b> 139	40.0	53.7
Ho <b>ytville</b>	B	0	8,889	11.2	• 575	29.0	40.2
		1	8,000	12.2	.867	23.1	35.3
		7	7.500	13.0	.909	24,4	37.4

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Table 10. Langmuir adsorption parameters for anaerobic subsoils.



Figure 34. Langmuir P adsorption isotherms for flooded Hillsdale B soil.

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Figure 35. Langmuir P adsorption isotherms for flooded Locke B soil,

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Langmuir P adsorption isotherms for flooded Miami B soil.



Figure 37. Langmuir P adsorption isotherms for flooded Sims B soil.



Figure 38. Langmuir P adsorption isotherms for flooded Hoytville B soil.

The capacity of subsoils to adsorb P, indicated by the total adsorption maximum, ( $\Sigma$ b values in Table 10), also reflected a similar change. However, the change is not as pronounced as for surface soils except Sims B.

The change in the behavior of P adsorption by subsoils upon 7 days of flooding, both change in bonding strength and the capacity to adsorb P is similar to that of surface soils, *i.e.* generally increase the capacity of adsorption with more locsely bound P to the soil surface, and generally most of the change is in part II of adsorption. However, the degree of change is not as great as that of surface soils (See Table 7 and 10).

Because the change in the capacity of reduction in surface soils associated with high organic matter content, is greater than that of subsoils, (i.e. greater increase in extractable Fe and Mn etc.), upon flooding, the difference occurs in the P adsorption by the surface and subsoils. For Sims B soil, the amount of organic matter is somewhat greater than that of other subsoils (in air dried treatment, Table 1.a in Appendix). This may account for the faster increase in the extractable Fe content upon 3 weeks of flooding, (Table 1.f in Appendix). The higher content of extractable Fe in flooded Sims B soil may account for the much greater P adsorption with in 7 days of incubation.

It should be noted that subsoils, both flooded and air dried, adsorbed almost the same quantity of P from the solution at low P concentration. For surface soils the change in the adsorption at low P concentration is not as great as in higher P concentrations. The plots (P)/(x/m)versus (P) of flooded soils showed that the part I of P adsorption changed little upon flooding. This suggested that the adsorption sites in this

part may be due to Al or other sources which did not change upon flooding. But for the part II of P adsorption, the adsorption sites may be due to Fe or the other sources which were influenced by the reduction process. However, the further studies on the sources of the P adsorption sites in both part could give a better explanation on this matter.

The mechanism of P adsorption is not a single type of reaction. As cited by Shapiro and Fried (1959), P adsorption consists of anion adsorption on the surface of clay, adsorption on the surface of Fe and Al oxides or hydroxide and  $CaCO_3$  and indirectly anion adsorption by means of a cation bridge to the clay. Udo and Uzu (1972) noted that clay forms a part of complex gel which consists of hydrated  $Fe_2O_3$  along with small amounts of organic matter,  $Al_2O_3$  and associated  $Si(OH)_4$  and P. This complex gel is considered to be the main P adsorption site of sediments, (Shukla et al., 1971). However, Harter (1969) noted that organic matter also provides the main site of P adsorption. Therefore clay particle, oxides or hydroxide of Fe, and Al,  $CaCO_3$ , organic matter and exchangable cations i.e.  $Fe^{+2}$ ,  $Fe^{+3}$ ,  $Al^{+3}$ , and  $Ca^{+2}$  would provide directly or indirectly the sources of P adsorption sites in the soils. Some of which were influenced by reduction reactions, which account for the change in the behavior of P adsorption upon flooding.

## CONCLUSIONS

(1) Soils adsrobed more P from 0.01 M CaCl<sub>2</sub> solution than from water solution. The adsorption reaction in 0.01 M CaCl<sub>2</sub> treatment reached equilibrium faster in 24 hours, while for water solution treatment, the adsorption reaction required 48 hours or longer to reach equilibrium.

(2) Soils adsorbed more P from 0.01 M CaCl<sub>2</sub> solution adjusted to pH 6 than from unadjusted pH treatment at high P equilibirum concentrations. The adsorption reaction in the pH adjusted treatment also reached equilibrium at 24 hours of shaking.

(3) Air dried, fine textured soils adsorbed more P than coarse textured ones. Subsoils adsorbed more P than surface soils. However, for coarse textured soils, subsoils adsorbed more P than did surface soils, but for fine textured soils the difference in the amount of P adsorbed in the A and B horizons was not great.

(4) Langmuir adsorption studies showed that there are at least two different portions of the soils with respect to P adsorption, the tightly and loosely bound portions.

(5) The behavior of P adsorption changes upon flooding surface soils. The changes mostly occurred in the loosely P bound portion. The amount of adsorbed P increased with a lower bonding energy upon flooding. Extractable Fe apparently played an important role in the change in P adsorption.

(6) The increase in P adsorbed by surface soils after flooding may be responsible for the increase in the extractable P. Phosphorus adsorption by flooded surface soils, therefore, should be of benefit

for rice cultivation in lowland or paddy soils.

(7) For subsoils, the change also occurred in the loosely P bound portion of the soil upon flooding. The amount of P adsorbed increased and possessed a lower bond strength than air dried soils. However, the changes were not as great as for surface soils. LITERATURE CITED

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APPENDIX

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Soil Ty	pe	Texture	рH	Eh	Organic Matter	Extractable <sup>1/</sup> Mn	Extractable <sup>2/</sup> Fe		<u>р</u> 3/	
								Bray's	Olsen's	Troug's
				m,v,	ź	**************************************	pp <b>p</b>			
Hillsdal	e A	Sandy Loam	5.82	595	1.66	7.24	0.74	57.9	25.9	71.9
	В		5.20	660	0.41	6.05	0,44	5.3	6.5	60,8
Locke	A	Sandy Loam	6.00	536	2,72	1.59	0.15	41.7	23.7	64.3
	B		6.29	587	0.40	0,82	0,29	3.5	5.5	37.0
Miami	A	Loam	6,48	544	2.84	1.45	0.59	4.8	3.5	17.5
	В		6.52	561	0.48	1,20	0.59	2,6	4.1	5.6
Sims	A	Clay Loam	6,23	599	6.77	0,50	0,29	39.5	42.7	113.1
	В		6.54	575	0.93	0,82	0.59	2.7	1.7	80,8
Hoytville	e A	Clay Loam	6,50	599	3.16	0,50	0,29	7.5	4.5	51.6
	B		6.76	<b>52</b> 5	0,56	0.76	0,44	1.3	3,2	40.3

Table 1 a. Physical and chemical properties of air dried soils  $\frac{4}{}$ 

- 1/1 NH<sub>4</sub>OAc extractable Fe
- 2/ Saturated CaSO4 extractable Mn
- 2/ a. Bray's P, 0.03 <u>N</u> NH<sub>4</sub>F in 0.25 <u>N</u> HC1; b. Olsen's P, .5 <u>N</u> NaHCO<sub>3</sub> (pH 8.5);
  - c. Troug's P, .002 <u>N</u>  $H_2SO_4$  (buffer with  $(NH_4)_2 SO_4$ )
- 4/ From Srisen, M. 1971. M.S. Thesis, Michigan State University.

I	nit	ial	P concentration			P Ade	orbed 1/	' <u>12/</u>			
		a	nd soll	3	5	12	24	48	72 hours 3/		
	<u></u>			mg P/100 g Soil							
<u>Hc</u>	ytv:	<u>ille</u>	<u>_A</u>								
1	6	ppm	P in H <sub>2</sub> 0	4.55	4.70	4.85	5.00	5.25	5.25		
2	6		in 0.01 M CaCl <sub>2</sub>	5.76	5.87	5.88	5.82	5.75	5.72		
3	12	Ħ	in H <sub>2</sub> 0	7.85	8.20	8 <b>.76</b>	9.40	9.85	9.90		
4	12	**	in 0.01 M CaCl <sub>2</sub>	10.35	10.70	10.78	11.00	11.05	11.32		
Lo	ocke	<u>A</u>						·			
1	6	ppm	P in H <sub>2</sub> 0	2,52	2.55	2.76	3.30	3.60	4,18		
2	6	10	in 0.01 M CaCl <sub>2</sub>	3,80	4.40	4.75	5.05	5.27	5.30		
3	12	10	in H <sub>2</sub> 0	2.60	3.00	4,10	4.90	5.47	6.55		
4	12	**	in 0.01 M CaCl <sub>2</sub>	6,70	7.00	7.76	8.30	9.00	9.05		

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Table 1 b. The effect of time, CaCl<sub>2</sub> and water solution on P adsorption by air dried soils.

1/ pH of P solution was not adjusted.

2/ Average of 2 replications.

3/ Shaking Time.

Soil	·····	Unadjust pH			Adjust pH	· · · · · · · · · · · · · · · · · · ·
	Initial	Equili-	Adsorbed	Initial	Equili-	Adsorbed
	P	brium P1/	P	<u>P<sup>1</sup>/</u>	brium P	P
	ppm	x 10 <sup>5</sup> mole/1	mg/100 soil	ррт	x 10 <sup>5</sup> mole/l	mg/100 soil
Hillsdale						
A	0			3.45	1,47	2,99
	3	1.17	2.64	6,20	3.83	5.01
	6	3.89	4.98	8,85	6.21	6,94
	9	7.44	6.70	10.7	8.41	8.12
	12	12.9	8.00	14.7	14.8	10.0
	15	19.7	8.90	16.7	18.2	11.1
	20	29.1	11.0	21.4	28.2	12.7
	30	49.2	14.7	29.5	45.6	15.3
Miami A	0			3.45	1.49	2.99
	3	1,52	2.53	6,20	3.98	4.97
	6	3.94	4.78	8,86	6.94	6.71
	9	8,23	6.45	10.7	10.0	7.65
	12	12.9	8,00	14.7	15.6	9,88
	15	20.0	8.80	16.7	19.9	10.6
	20	30.0	10.7	21.4	29.7	12.2
	30	52.5	13.7	29.4	47.8	14,6
Hoytville	_			- • ···		
A	0			3.45	0.39	3.33
	3	0.40	2,88	6,20	0,95	5.91
	6	0,58	5.82	8,86	1.67	8,34
	9	2.22	8.30	10.7	2.63	9,91
	12	3.39	10.9	14.7	4.15	13.4
	15	5.33	13.3	16.7	5.79	15.0
	20	10.6	16.7	21.4	9.77	18.4
	30	23,8	22.6	29.4	20.0	23.2

Table 1 c. Effect of pH of P solution in 0.01 M CaCl<sub>2</sub> on P adsorption by soils.

1/ average of 2 replications.

Soil		Initial P	<u></u>		hours	hours			
			3	5	10	16	24	48	72
		ppm			ng	P/100 g	soil		
Sims	A	6,2	4.59	4.85	5,28	5.41	5.61	5.75	5.76
		14.7	9.10	9.76	10.67	11.31	11.68	12.54	12.68
Locke	A	6.2	4.07	4.34	5.13	5.33	5.41	5.51	5.53
		14.7	7.42	8.15	8,80	10,08	10,88	11.74	11.96

Table 1 d. P adsorption from 0.01 M CaCl<sub>2</sub>, pH 6.0 solution as a function of time.

Soil	Soil		5 P	Olsen	's P	Troug	s P	Soil water P content
	-	air dried	flooded	air dried	flooded	air dried	flooded	3 weeks of flooding
				~ <u></u>				
Hillsdale	A	57.9	109.2	25.9	41.6	71.9	133.0	0.31
	В	5.3	41.0	6.5	12.5	60.8	40.4	0,15
Locke	A	41.7	80.7	23.7	32.0	64.3	160.0	0.41
	В	3.5	52.7	5.5	7.5	37.0	68.9	0.15
Miami	A	4.8	51.3	3.5	6.0	17.5	73.2	0,22
	В	2.6	26.6	4.1	4,4	5.6	68,9	0,16
Sims	Å	39.5	65.6	42.7	55.6	113.1	214,0	0.73
	В	2.7	49.9	1.7	16.0	80,8	118.0	0.10
Hoytville	A	7.5	17.3	4.5	20,6	51.6	149.0	0.18
	B	1.3	49.9	3.2	13.3	40.3	77.5	0.14

Table 1 e. Quantity of extractable P, from air dried soils and from soils after 3 weeks of flooding  $\frac{1}{2}$ .

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1/ From Srisen, M. 1971. MS Thesis Michigan State University.

Soil			Mn		Fe	
		air	flooded soils	air	floode	d soils
		dried	3 weeks	dried	3 weeks	6 Heeks
		······································		ppm		
Hillsdal	.e A	7.24	123.00	0.74	19.70	15,30
	В	6.05	8,96	0,44	1.04	2,45
Locke	A	1.59	8.75	0.29	1.04	13.70
	В	0,82	3.40	0.15	0.20	1,22
Miami	A	1,45	81.70	0.59	12.00	9.86
	В	1,20	12,60	0.59	0,20	5.13
Sims	A	0.50	7.35	0,29	38.70	45.10
	В	0.82	9.74	0.59	4.43	7.47
Hoytvill	e A	0.50	4.05	0.29	2.73	55,80
	в	0.76	1.61	0.44	1.68	5.85

Table 1 f. Saturated  $CaSO_4$  extractable Mn, and 1 <u>N</u> NH<sub>4</sub>OAc extractable Fe from air dried and flooded soils<sup>1/</sup>.

1/ From Srisen, M. 1971 M.S. Thesis, Michigan State University.

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Soils	Initial P	Equi	Librium P <sup>1</sup> / (P)	P adsorbed $\frac{1}{(x/m)}$	<b>(</b> P)( <b>x</b> /m)
	ppm	ppm	(mole/1)X10 <sup>5</sup>	mg/100 g soil	x10 <sup>5</sup>
Hillsdale A	3.45	0.45	1.47	3.00	0.49
	6.20	1.19	3.83	5.01	0,76
	8,86	1.92	6,21	6,93	0.90
	10.7	2.60	8,41	8,12	1.04
	14.7	4.58	14.8	10.1	1.46
	16.7	5.64	18.2	11.1	1.64
	21.4	8,73	28.2	12.7	2,21
	29.4	14.1	45.6	15.3	2,98
Locke A	3.45	0,38	1.23	3.01	0.40
	6.20	0,88	2.84	5.32	0.53
	8,86	1.79	5.77	7.07	0.82
	10.7	2.75	8,88	7.97	1.11
	14.7	4.72	15.2	9,98	1.53
	16.7	6,00	19.4	10.7	1.80
	21.4	9.42	30,4	12.0	2,53
	29,4	15.5	50.1	13.9	3.61
Miami A	3.45	0.46	1.49	2.99	0.50
	6,20	1.23	3.98	4.97	0.80
	8.86	2,15	6.94	6.71	1.03
	10.7	3.10	10.0	7,62	1.31
	14.7	4,82	15,6	9,88	1,58
	16.7	6.18	20.0	10.6	1.89
	21.4	9,21	29.8	12.2	2.43
	29.4	14.8	47.8	14.6	3.27

Table 1 g. Langmuir P adsorption isotherm for air dried surface soils.

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Soils		Initial P	Equi	librium p <sup>1</sup> / (P)	P adsorbed <sup>1/</sup> (x/m)	(P)/(x/m)	
		ppm	ppm	(mole/1)X10 <sup>5</sup>	mg/100 g soil	X10 <sup>5</sup>	
Sims	A	3.45	0.31	1.00	3.14	0.32	
		6,20	0,64	2,08	5,56	0.37	
		8,86	1.18	3.81	7.68	0,50	
		10.7	1,83	5.92	8,89	0.67	
		14.7	3.17	10,2	11.5	0,89	
		16.7	4,10	13.2	12,6	1.05	
		21.4	6.52	21.0	14.9	1.41	
		29.4	11.4	37.0	17.9	2.05	
Hoytville	A	3.45	0.12	0.39	3.33	0,12	
		6.20	0.29	0.95	5.91	0.16	
		8,86	0.52	1.67	8.34	0.20	
		10.7	0,82	2.64	9 <b>. 9</b> 1	0,27	
		14.7	1.28	4.15	13.4	0.31	
		16.7	1.79	5.79	15.0	0.39	
		21,4	3.02	9.77	18.4	0,53	
		29.4	6.20	20.0	23,2	0.86	

Table 1.g. (cont'd.)

1/ Average of 3 replications.

Soils		Initial P	Equi	librium P <sup>1</sup> / (P)	P adsorbed $\frac{1}{(x/m)}$	(P)/(x/m)
		ppm	ppm	(mole)X10 <sup>5</sup>	mg/100 g soil	x10 <sup>5</sup>
Hillsdale	A	3.45	0.34	1.09	3.11	0.35
		6.20	0.63	2,03	5.57	0,36
		8,86	1.14	3.68	7.72	0.48
		10.7	1,98	6.40	8.74	0.73
		14.7	3.42	11.0	11.3	0,98
		16.7	4.17	13.4	12,6	1.06
		21.4	6.72	21.7	14.7	1.47
		29.4	11.4	36.8	18.0	2.04
Locke	A	3.45	0.65	2,09	2.80	0,74
		6.20	1.25	4.03	4.95	0,81
		8,86	2,27	7.32	6.59	1.11
		10.7	3.30	10.7	7.42	1.44
		14.7	5.37	17.3	9.33	1.86
		16.7	6.42	20.7	10.3	2.01
		21.4	9.39	30.3	12.1	2,51
		29 <b>.</b> 4	13.6	44.0	15.8	2,80
Miami	A	3.45	0.33	1.05	3,12	0.34
		6.20	0,59	1.92	5.61	0.34
		8.86	1.25	4.03	7.61	0.53
		10.7	2,00	6.45	8.72	0.74
		14.7	3.47	11,2	11.2	1.00
		16.7	4.40	14.2	12.3	1.15
		21.4	7.16	23.1	14.3	1.61
		29.4	11.7	37.9	17.6	2.15

Table 1 h. Langmuir P adsorption isotherms for flooded surface soils, incubated 24 hours.

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Soils		Initial P	Equi	(P)	P adsorbed 1/ (x/m)	(P)/(x/m)
		ppm	ppm	(mole/1)X10 <sup>5</sup>	mg/100 g soil	x10 <sup>5</sup>
Sims A	A	3.45	0.17	0.54	3.28	0,16
		6,20	0,39	1.25	5.81	0.21
		8,86	0.69	2,22	8,17	0.27
		10.7	1.06	3.42	9.67	0,35
		14.7	1.86	5.35	12.8	0.47
		16.7	2,33	7.52	14.4	0.52
		21.4	3.74	12.0	17.7	0,68
		29.4	6.63	21.4	22.8	0.94
Hoytville	A	3.45	0,21	0.69	3.24	0.21
		6,20	0.62	2.02	5.57	0.36
		8.86	1.06	3.44	7,80	0,44
		10.7	1,47	4.73	9.26	0.51
		14.7	2,16	6.97	12,5	0.56
		16.7	2,48	8,00	14.1	0.56
		21.4	4.60	14.8	16,8	0,88
		29.4	7.12	23.0	22.3	1.03

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Table 1 h. (cont'd.)

1/ Average of 3 replications.

Soils		Initial P	Equil	Librium P <sup>1</sup> / (P)	P adsorbed <sup>1</sup> / (x/m)	(P)/(x/m)	
		mqq	ppm	(mole/1)X10 <sup>5</sup>	mg/100 g soil	<b>X</b> 10 <sup>5</sup>	
Hillsdale	A	3.45	0,50	1.61	2,95	0.54	
		6.20	0.94	3.05	5.26	0,58	
		8.86	1.37	4,42	7.49	0.59	
		10.7	1.84	5.94	8 <b>.89</b>	0.67	
		14.7	3.39	10.9	11.3	0.97	
		16.7	4.68	15.1	12.1	1,25	
		21.4	7.18	23.2	14.3	1.62	
		29.4	11.5	37.2	17.9	2,08	
Locke	A	3.45	0.37	1.20	3.08	0.39	
		6,20	1.09	3.53	5,11	0,69	
		8,86	2,19	7.05	6.67	1.06	
		10.7	3.02	9.77	7.70	1.27	
		14.7	4.70	15.2	10.0	1.52	
		16.7	6.05	19.5	10.7	1.83	
		21.4	9,38	30.3	12.1	2,51	
		29.4	14.2	45.8	15.2	3.01	
Miami	A	3.45	0.34	1.11	3.11	0.35	
		6.20	0.61	1,98	5.59	0.35	
		8,86	1.14	3.67	7.72	0,48	
		10.7	1.99	6.41	8,74	0,64	
		14.7	3.49	11.3	11.2	1.00	
		16.7	4.11	13.3	12,6	1.05	
		21.4	7.58	24.5	13.9	1.76	
		29.4	11.0	35.7	18,3	1.94	

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Table 1 i. Langmuir P adsorption isotherms for flooded surface soils, incubated 3 days.

Soils		Initial P	Equi	Librium P <sup>1</sup> / (P)	P adsorbed <sup>1/</sup> (x/m)	(P)/(x/m)	
<u></u>		ppm	ppm	(mole/1)X10 <sup>5</sup>	mg/100 g soil	x10 <sup>5</sup>	
Sims	A	3.45	0,15	0,05	3.30	0.15	
		6,20	0,25	0.81	5.95	0.14	
		8,86	0.48	1.54	8,38	0,18	
		10.7	0.78	2.25	9.94	0.25	
		14.7	1.36	4,40	13.3	0.33	
		16.7	1.60	5,17	15,1	0.34	
		21.4	3.07	9 <b>. 9</b> 9	18.4	0.54	
		29.4	5.56	17.9	23.8	0.75	
Hoytville	<b>a</b>	3.45	0.37	1.18	3.08	0.38	
		6.20	0,58	1,89	5.62	0,34	
		8,86	0.77	2,48	8,09	0.31	
		10.7	0.88	2.83	9.85	0,29	
		14.7	2,25	7.25	12.4	0.58	
		16.7	2.89	9.34	13.9	0.67	
		21.4	4.94	16.0	16.5	0.97	
		29.4	7.43	24.0	22.0	1.09	

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Table 1 1. (cont'd.)

 $\underline{1}$  Average of 3 replications.

Soils	Initial P	Equilibrium P <sup>1</sup> / (P)		P adsorbed <sup>1/</sup> (x/m)	(P)/(x/m)
<u></u>		 ppm	(mole/1)X10 <sup>5</sup>	mg/100 g soil	x10 <sup>5</sup>
Hillsdale A	3.45	0,44	1,41	3,01	0.47
	6.20	1.08	3.48	5.12	0,68
	8.86	1.62	5.23	7.24	0.72
	10.7	2,58	8.32	8,15	1.02
	14.7	4.05	13.1	10.6	1.23
	16.7	-	-	-	<u> </u>
	21.4	7.33	23.7	14.1	1,68
	29.4	10.0	32.3	19.4	1,66
Locke A	3.45	0,57	1.84	2,88	0.64
	6.20	1.31	4.25	4.89	0.69
	8,86	2.10	6.79	6.76	1.01
	10.7	3.85	12.43	6.87	1.81
	14.7	5.75	18,6	8,95	2,07
	16.7	-	<b>→</b>	-	-
	21.4	8,87	28,6	12,6	2,28
	29.4	9.50	30.7	19.9	1.54
Niami A	3.45	0.24	0.77	3.21	0.24
	6.20	0.37	1_21	5.83	0,21
	8,86	1.34	4.33	7.52	0,58
	10.7	2.35	7.59	8.37	0.91
	14.7	3.50	11.6	11,2	1.01
	16.7	-	-	-	-
	21.4	3.92	12,6	17.5	0,72
	29.4	8.68	28.0	20.7	1.35

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Table 1 j. Langmuir P adsorption isotherms for flooded surface soils, incubated 7 days.

Soils		Initial Equilibrium P <sup>1</sup> P (P)		librium p <sup>1</sup> / (P)	P adsorbed <sup>1</sup> / (x/m)	(P)/(x/m)
		ppm	ppm	(mole/1)X10 <sup>5</sup>	mg/100 g soil	<b>x</b> 10 <sup>5</sup>
Sims	A	3.45	0.18	0,60	3.27	0.18
		6.20	0.31	0.99	5.89	0.17
		8.86	0,40	1,28	8,46	0.15
		10.7	0.70	2,25	10.0	0,22
		14.7	1.34	4.34	13.4	0.33
		16.7	-	-	-	-
		21.4	3.16	10,2	18.6	0.55
		29.4	4.94	15.9	34.5	0,65
Hoytville A		3.45	0.50	1.60	2.95	0,54
		6.20	0.82	2,66	5.38	0.49
		8.86	1.04	3.37	7.82	0.43
		10.7	1,70	5.47	9.03	0.61
		14.7	2,50	8.07	12,2	0,66
	16.7	3.51	11.3	13,2	0.86	
		21,4	4.41	14.2	17.2	0.84
		29.4	6,40	20.7	23.0	0,90

Table 1 j. (cont'd.)

 $\underline{1}$  / Average of 3 replications.

Soils		Initial P	Equi	librium p <sup>1</sup> / (P)	P adsorbed <sup>1</sup> / (x/m)	(P)/(x/m)
		ppm	ppm	(mole/1)X10 <sup>5</sup>	mg/100 g soil	x10 <sup>6</sup>
Hillsdale	в	3.50	0.01	0.04	3.49	0,12
		6,30	0.03	0,09	6.27	0,14
		8,92	0,12	0,40	8,80	0.45
		9.62	0,25	0,82	9.37	0.87
		11.7	0,50	1,16	11,2	1.43
		17.0	1.47	4,78	15,5	3.08
		24.2	5.62	18,1	18.6	9.76
Locke	в	3.50	0,02	0,05	3.48	0,15
		6.30	0.07	0,22	6,23	0.35
		8,92	0,23	0.76	8.69	0,87
		9.62	0.31	0.99	9.32	1.06
		11.7	0.70	2.26	11.0	2,05
		17.0	1.29	4.16	15.8	2,61
		24.2	6,50	21.0	17.7	11,8
Miami	в	3.50	0.03	0,10	3.47	0,28
		6,30	0,07	0.22	6,23	0.35
		8,92	0,18	0.57	8.74	0,65
		9,62	0.37	1.20	9.25	1.30
		11.7	0.91	2.94	10.8	2.72
		17.0	1.58	5.11	15.6	3.28
		24.2	6.70	21.6	17.5	12.3
Sims	B	3.50	0,17	0.56	3.33	1,68
		6,30	0.34	1.11	5.96	1.87
		8.92	0.73	2.37	8.19	2.89
		9.62	1.10	3.56	8,52	4.18
		11.7	1.85	5.99	9.86	6.07
		17.0	3.73	12.0	13.3	9.07
		24.2	7.72	24.9	16.5	15.1

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Table 1 k. Langmuir P adsorption isotherms for air dried subsoils.

Table 1 k. (cont'd.)

Soils	Initial P	Equilibrium P <sup>1</sup> / (P)		P adsorbed <sup>1/</sup> (x/m)	(P)/(x/m)
	ppm	ppm	(mole/1)X10 <sup>5</sup>	mg/100 g soil	x10 <sup>6</sup>
Hoytville B	3.50	0,02	0,06	3.48	0.18
	6.30	0.05	0.16	6.25	0.25
	8.92	0,09	0,28	8,83	0.45
	9.62	0,15	0,48	9.48	0.55
	11.7	0,36	1,16	11.3	1.02
	17.0	0,79	2,56	16,2	1,58
	24.2	2.89	9.33	21.3	4.37

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1/ Average of 3 replications.

Soila		Initial P	Equil	ibrium P <sup>1</sup> / (P)	$\frac{1}{(x/m)}$	(P)/(x/m)
		ppm	ppm	(mole/1)X10 <sup>5</sup>	mg/100 g soil	x10 <sup>6</sup>
Hillsda	le B	3.50	0.02	0.06	3.48	0,17
		6,30	0.06	0,19	6,24	0,30
		8.92	0.17	0.53	8,66	0.62
		9.62	0.25	0.82	9.37	0.88
		11.7	0,61	1.97	11.1	1.78
		17.0	1.11	3.58	15.9	2,25
		24.2	6.94	22.4	17.3	12.9
Locke	В	3.50	0.03	0.09	3.47	0,27
		6.30	0.09	0.31	6.21	0,49
		8.92	0.26	0.84	8.66	0.97
		9,62	0.31	0,99	9.32	1,06
		11.7	0.63	2.04	11.1	1.84
		17.0	1.23	3.97	15.8	2.52
		24.2	5.53	17.8	18.7	9.56
Miami	В	3.50	0.03	0.09	3.47	0,26
		6.30	0,14	0.44	6.16	0,72
		8,92	0,30	0.97	8,62	1.13
		9.62	0,38	1,24	9.24	1.34
		11.7	0,98	3.16	10.7	2,94
		17.0	1.80	5.83	15.2	3.83
		24,2	6,98	22.5	17.2	13.1
Sims	B	3.50	0,12	0,38	3.38	1.12
		6,30	0.43	1.40	5.87	2,39
		8.92	0.77	2,48	8.15	3.05
		9.62	1.06	3,42	8.57	3.99
		11.7	2,04	6,58	9.67	6.80
		17.0	3.67	11.8	13.3	8.89
		24.2	8,99	29.0	15.2	19.1

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Table 1 1. Langmuir P adsorption isotherms for flooded subsoils, incubated 24 hours.

Table 1 1. (cont'd.)

Soils	Initial P	Equi	Librium P <sup>1</sup> / (P)	P adsorbed $\frac{1}{(x/m)}$	(P)/(x/m) X10 <sup>6</sup>
	ppm	ppm	(mole/1)X10 <sup>5</sup>	mg/100 g soil	
Hoytville B	3.50	0.01	0,02	3.49	0.04
	6.30	0.03	0.09	6.27	0.14
	8.92	0,08	2,27	8,84	0.30
	9.62	0.14	0.45	9.49	0,47
	11.7	0.33	1.05	11.4	0.92
	17.0	0.74	2,39	16,3	1.47
	24.2	3.51	11.3	20.7	5.47

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 $\underline{1}$  average of 3 replications.

Soils		Initial P P	Equil	librium P <sup>1</sup> / (P)	$\frac{P \text{ adsorbed}^{1}}{(x/m)}$	(P)/(x/m)
		ppm	ppm	(mole/1)X10 <sup>5</sup>	mg/100 g soil	<b>X10<sup>6</sup></b>
Hillsdale	B	3.50 6.30 8.92 9.62 11.7 17.0 24.2	0.02 0.06 0.17 0.27 0.62 2.22 7.22	0.06 0.21 0.54 0.87 1.99 7.17 22.7	3.48 6.23 8.75 9.36 11.1 14.8 17.2	0.18 0.34 0.61 0.93 1.79 4.85 13.2
Locke	в	3.50 6.30 8.92 9.62 11.7 17.0 24.2	0.03 0.11 0.23 0.27 0.49 0.94 3.82	0.10 0.35 0.75 0.88 1.48 3.05 12.3	3.47 6.19 8.69 9.35 11.2 16.1 20.4	0.30 0.56 0.86 1.32 1.90 6.04
Miami	В	3.50 6.30 8.92 9.62 11.7 17.0 24.2	0.01 0.07 0.14 0.29 0.55 1.09 4.48	0.05 0.22 0.45 0.94 1.79 3.53 14.5	3.49 6.23 8.78 9.33 11.2 15.9 19.7	0.14 0.36 0.51 1.01 1.60 2.22 7.33
Sims	В	3.50 6.30 8.92 9.62 11.7 17.0 24.2	0.06 0.09 0.20 0.42 0.82 1.12 2.50	0.20 0.48 0.65 1.36 2.64 4.58 8.09	3.44 6.15 8.72 9.20 10.9 15.6 21.7	0.57 0.77 0.93 1.48 2.42 2.94 3.72
Hoytville	В	3.50 6.30 8.92 9.62 11.7 17.0 24.2	0.006 0.02 0.07 0.11 0.26 0.58 2.89	0.02 0.08 0.23 0.36 0.85 1.87 9.33	3.494 6.28 8.85 9.51 11.4 16.4 21.3	0.053 0.12 0.26 0.38 0.74 1.14 4.38

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Table 1 m. Langmuir P adsorption isotherms for flooded subsoils, incubated 7 days.

1 Average of 3 replications.