STUDIES ON PHOSPHATE SORPTION IN TANZANIAN HAPLUSTOX AND VITRANDEPT SOILS

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DECLARATION

I, Benjamin Michael Gama hereby declare to the Senate of the University of Dar es Salaam that this thesis is my original work and that it has never been submitted for a degree in any other University.

Signature: [signature]

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Date: 19th May, 1979

A C K N O W L E D G E M E N T S

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ABSTRACT

Two virgin soils, a Haplustox with appreciable amounts of kaolinite, amorphous ferrialumino silicate (AFAS), and oxides and hydrous oxides of iron, and a Vitrandept dominant in AFAS with very little crystalline minerals, were chosen for this project. Phosphate sorption in these soils were investigated with respect to length of equilibration, initial solution concentration and pH, organic matter content, and amount and nature of extractants. It was also attempted to assess the equilibrium-P required for near maximum growth of maize (Zea mays L. var. Ilonga composite) and bean (Phaseolus vulgaris L. var Canadian wonder) in the greenhouse.

With respect to the length of equilibration, rapid P sorption was observed initially in both the soils but near equilibrium condition was obtained only after 24 hours. The magnitude of sorbed-P increased with increasing initial P concentration in the equilibrating solution. The initial solution pH had no effect on P sorption. Destruction of organic matter led to over three fold increase in P sorption in both the soils.

The amount of desorbed-P increased with increasing volumes of water, 1M KNO_3 or 1M K_2SO_4 solution. The SO_4^{2-} ion desorbed more P than the NO_3^- or OH^- ion.

Studies in the greenhouse showed that dry matter yield, percent P in plant tissues and total P uptake for both the crops grown on either soil increased with increasing equilibrium-P up to certain concentration beyond which these parameters tended to reach a plateau. On the Haplustox soil, 95 percent of the maximum maize yield was obtained at an adjusted P concentration of 9.7 µg P/ml while 2.6 µg P/ml was adequate on the Vitrandept soil. For bean, 95 percent of the maximum yield was obtained at 9.5 and 5 µg P/ml adjusted P concentration in the Vitrandept and Haplustox soils, respectively. From economic considerations, however, an adjusted P concentration lower than that required for 95 percent of the maximum yield is suggested.

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INTRODUCTION

The term "adsorption" - accumulation on surface - is appropriate to describe the process of retention of non-specifically adsorbed anions such as NO_3^- or Cl^- on colloidal surfaces in soils. However, it is misappropriate if employed to describe retention of specifically adsorbed anions such as phosphate because both adsorption and absorption processes are suspected to be involved. The term "sorption" as suggested by McBain (quoted by Bikerman, 1958) has, therefore, been used throughout this thesis to describe the phosphate retention in the experimental soils.

Uriyo and Kesseba (1973, 1975) have done extensive work on amounts and distribution of various forms of P in Tanzanian soils. Also, they (1972, 1973) have attempted to modify the method of Chang and Jackson (1957) for fractionation of P to suit the soils of Tanzania. Phosphate sorption characteristics of Tanzanian soils, however, have never been investigated.

Phosphate sorption reactions in tropical soils, especially the highly weathered ones, are of significance as they affect the concentration of P in soil solution ("intensity" of P nutrition) and the amount of P retained on the colloidal surfaces ("capacity" for P nutrition). Such soils usually possess a large number of positive charges, and, particularly under acidic conditions, therefore, have opportunities for

ligand exchange on their extensive surfaces. In fact, Fox et al. (1968) demonstrated that phosphate sorption maxima for highly weathered tropical soils from Hawaii were 10-20 times greater than those usually reported for the temperate zone soils.

Studies with the tropical soils from Hawaii (Fox et al., 1971, 1974; Rajan and Fox, 1972; Rajan, 1975; Silva and Fox, 1974; Nishimoto et al., 1975), Fiji Islands (Chee et al., 1978), Papua New Guinea (Parfitt and Mavo, 1975; Parfitt, 1977), and Sierra Leone (Rhodes, 1975) have shown that phosphate sorption in these soils is affected by such factors as solution P concentration, soil or equilibrating solution pH, and contents of organic matter and silica-sesquioxides. These factors influence both the intensity of and capacity for P nutrition in the soil. Effects of some of these factors on P sorption characteristics of the Tanzanian soils warrant investigation.

Several theories have been proposed in the past to describe the mechanisms of phosphate sorption in soils based on investigations under simulated field conditions using synthetic colloidal materials. In this respect, the work of Rajan and Perrott (1975) involving synthetic alumino-silicate gels deserves mention. According to them, phosphate

exchanges mainly with aquo $(Al-H_2O)^+$ and hydroxo $(Al-OH)^o$ ligands at concentrations below 10 µmole/ml. In fact, the ligands exchanged are aquo $(-H_2O)$ and hydroxo $(-OH)$ groups, and not $(Al-H_2O)^+$ and $(Al-OH)^o$ as mentioned by Rajan and Perrott (1975). At higher concentrations, P is sorbed (i) on sites arising from disruption of hydroxy aluminium polymers and (ii) by displacement of structural silicate. Exchange of phosphate with anions, such as SO_4^{2-}, Cl^-, and NO_3^-, retained on highly reactive sites is also possible. A knowledge of possible mechanisms of P sorption in Tanzanian soils may help in manipulating the agrotechnology to keep most of the applied P in soil solution for maximum utilization by plants.

Majority of the highly weathered soils and those derived from volcanic ash are deficient in P; therefore, they need to be fertilized. This would require a careful assessment of the amount of P to be applied to these soils for economic crop yield. Phosphate sorption isotherm may be useful in this respect because it takes into account both the intensity and capacity factors. Silva and Fox (1974) pointed out that the use of sorption isotherm for estimating P requirement may reduce the amount and increase the efficiency of P fertilization because the method takes into account the ability of a soil to sorb and maintain P in soil solution. The amount of P sorbed by a soil at an equilibrium P concentration

associated with any given yield is an estimate of the P requirement for that yield (Rajan and Fox, 1972). The equilibrium P concentration is expected to vary from soil to soil and from crop to crop. Beckwith (1965), working with humic gley, podzolic, Kraznozem and lateritic red earth soils from South-East Queensland (Australia) reported an equilibrium concentration of 0.2 ppm P for optimum growth of most plants. Silva and Fox (1974) reported that maize required 0.06 ppm equilibrium-P concentration to attain 95 percent of the maximum yield while sweet potatoes and lettuce needed 0.1 and 0.04 ppm P, respectively.

In view of the above, the project was undertaken with the following major objectives:

1. To study phosphate sorption in the Vitrandept and Haplustox soils as affected by:
   - (i) length of equilibration,
   - (ii) initial P concentration in the equilibrating solution,
   - (iii) initial pH of the equilibrating solution, and
   - (iv) destruction of organic matter.
2. To investigate the effect of amount and nature of extractants on desorption of sorbed-P
3. To predict external P requirement of maize (Zea mays L. var. Ilonga composite) and bean (Phaseolus vulgaris L. var. Canadian wonder) using P sorption isotherms.

REVIEW OF LITERATURE

Extensive information is available on phosphate sorption in pure clay minerals and in temperate soils. But relatively little work has been done on this aspect with tropical soils and virtually nothing with Tanzanian soils. In the following sections, efforts have been made to review critically some of the past reports on phosphate sorption, particularly those with respect to tropical soils.

Effect of Length of Equilibration on Phosphate Sorption

Phosphate sorption reaction in soils is invariably fast initially and slows down later to the extent that near complete equilibration state may take several days or weeks. For instance, Fox and Kamprath (1970), working with Ultisol and Histosol soils from Central and Eastern North Carolina, and Rajan and Fox (1972), with calcareous and latosol soils from India and Hawaii, were able to obtain a reasonably stable level of P in soil solution only after 6 days of equilibration. The fact that a long period of equilibration is needed to attain equilibrium is important from view point of phosphate fertilization as it gives an idea of the residual effect. Munns and Fox (1976) while investigating the slow reaction which continued during the process of phosphate sorption, observed that equilibrium was achieved in 50 days in an Andept and as much

as 100-120 days in Oxisol soils. They estimated labile phosphate in order of 30-50 percent of what was added. This implies that there may be substantial residual effect of applied P which is likely to be permanent except for removal by crops and erosion.

Substantially long period required to attain equilibrium during phosphate sorption could be attributed to the nature of reactions taking part in the process. Several workers (Bache, 1963; Muljadi et al., 1966 ; Ryden and Syers 1977) working mainly with synthetic materials suggested that the first fast phosphate sorption reaction is essentially a physical process that transports phosphate ions from the outer solution (equilibrating solution) to the colloidal surface. According to Bache (1963), this process occurred within the first day. Ryden and Syers (1977), however, observed that the fast reaction with soil and iron gel took 48 hours and this was followed by a slow reaction between 48 and 192 hours. But in synthetic goethite, the equilibrium was reached within 48 hours. The second reaction subsequent to the initially fast physical process is essentially a chemisorption which involves diffusion of P into either structurally porous soil colloidal material or colloidal imperfections.

Duration of the above mentioned phosphate sorption processes depends on pH of the system, solution/solid ratio and mineralogy of the adsorbent material. Equilibrium is achieved fairly rapidly at low solution/solid ratio and low pH. In his study with synthetic variscite and strengite, Bache (1963) postulated that equilibrium is established fairly rapidly at low pH as well as at low solution/solid ratio. The reason given was that at low pH the solvent action on the mineral releases both metal and phosphate ions into solution, thereby, creates crystal imperfections and exposes underlying layers. At high pH, however, where one of the reaction products is almost insoluble, the underlying layers are protected and the reaction may continue at a very slow rate for a long time.

As far as routine analysis is concerned, it is not practical to equilibrate soils for a long time. Rhodes (1975) felt that equilibrating soils for several days was unnecessary for highly weathered soils of Sierra Leone. He suggested that continuous shaking of a soil sample sieved through 0.2 mm with added P for 24 hours was adequate to obtain near complete equilibrium.

Effect of Phosphate Concentration on its Sorption

There is well documented evidence (Olsen and Watanabe, 1957; Rajan and Fox, 1975; Ryden et al., 1977a; Parfitt, 1977;

Taylor and Ellis, 1978) to support the statement that phosphate sorption increases with its increasing concentration in the solution. Scientists (Low and Black, 1950; Olsen and Watanabe, 1957; Woodruff and Kamprath, 1965; Rajan, 1975; White and Taylor, 1977; Taylor and Ellis, 1978) have tried to explain the relationship between phosphate sorption and equilibrium P concentration in terms of the Langmuir and Freundlich adsorption models. The linear form of the Langmuir model usually fits the experimental data at low equilibrium P concentrations only. Rajan (1973) working with the Hawaiian soils found that the isotherms of all the soils investigated obeyed the Langmuir equation at concentrations less than 5 μg P/ml. Similarly, Rhodes (1975) working with Sierra Leone soils observed that the Langmuir plot was approximately linear over a small range of phosphate concentrations in the region of 0-25 μg P/ml.

In a study with Hawaiian soils, Rajan and Fox (1975) obtained an abrupt increase in phosphate sorption at high phosphate concentrations. Parfitt (1977), while working with an Oxisol soil in Papua New Guinea, observed high sorption affinity at low concentrations and a linear increase in sorption at high concentrations. Further, phosphate was strongly sorbed up to 7 μmol/g in a sample from A horizon and 18 μmol/g in that from B horizon of the Oxisol soil when equilibrated with P solution prepared in 0.01M $CaCl_2$ and adjusted to pH 5.5.

The increase in P sorption with increasing solution P concentration has been ascribed to the mechanisms involved in the sorption at various equilibrium concentrations as well as to the energetics of sorption reactions. It is generally accepted that the initial fast reaction during P sorption is of high energy involving transport of ions from the outer solution (equilibrating solution) to the colloidal surface. This reaction is mainly physical in nature (Bache, 1963). The second reaction which is even more marked at high solution P concentration is essentially chemical involving the exchange of phosphate with anions, such as hydroxyl, silicate and sulphate retained on the surfaces. At high P solution concentration and with time, diffusion of P ions between surface and interior of the crystal or soil colloids also takes place (Bache, 1963; Ryden and Syers 1977).

Several hypotheses have been proposed (Kuo and Lotse, 1972; Parfitt and Atkinson, 1976; Taylor and Ellis, 1978) on the nature of compounds formed (discussed later in this section and in the section on mechanisms of phosphate sorption) and on the kinds of bonds by which phosphate is linked with Fe and Al atoms on the colloidal surfaces. Kafkafi et al. (1967) hypothesised that the bond between phosphate and colloidal surfaces is, at least partly, covalent due to the fact that there is a sharing of a

proton with the surface, leaving an additional negative charge on $H_2PO_4^-$ grouping. Kuo and Lotse (1972) have proposed another hypothesis. They believed that the link of phosphate with the surface is in effect a surface neutralization reaction. They suggested that a covalent bond is formed between aluminium of the surface and oxygen of phosphate ion, rather than between aluminium and hydrogen.

Parfitt and Atkinson (1976) while working with wet synthetic goethite films using infrared spectroscopic technique demonstrated the formation of a binuclear surface complex of the type Fe-O-P-O-Fe whereby two of the oxygen atoms of the phosphate ion are coordinated, each to a different Fe^{3+} ion when phosphate reacts with Fe oxide. In their studies with soil and anion exchange resin, Taylor and Ellis (1978) postulated a two point attachment of phosphate on the colloidal surface. This mechanism is elaborated later in the section on mechanisms of P sorption.

Effect of pH of the Equilibrating Solution on Phosphate Sorption

The highly weathered tropical soils are usually characterized by surfaces having a constant surface potential determined by H^+ and OH^- ions which are called potential determining ions (van Raij and Peech, 1972). The surfaces are usually positively charged at low pH which is manifested by the presence of hydrated iron and aluminium oxides. (White and Taylor, 1977).

The pH effect is less on sorption of phosphate than other anions such as sulphate (Fox et al., 1971). Studies (Muljadi et al., 1966; Gebhardt and Coleman, 1974; Chen and Hwang, 1974; White and Taylor, 1977) have shown a linear increase in phosphate sorption with decreasing pH. In studies with synthetic kaolinite, gibbsite and pseudoboehmite, Muljadi et al. (1966) observed that at low pH positively charged sites are available for P sorption. The H^+ ions are potential determining ions at low pH values. At high pH, however, hydroxyl ions compete with phosphate ions for sorption sites resulting in a decline in the magnitude of P sorption. It was also pointed out that there is an increase in the amount of negative charge on the colloidal surfaces at high pH due to dissociation of edge hydroxyls. This caused a decrease in the magnitude of phosphate sorption.

Affinity of phosphate for sorption is usually reported to increase with decreasing pH. This, however, may not always hold true. White and Taylor (1977), while working with acid soils, found that sorption of P was substantial between pH 5.2-5.5 when the phosphate concentration initially was low (1-100 μM P). At the highest P concentration (1000 μM P) sorption of P was least between pH 5.2-5.5. These results are in agreement with those of Lopez-Hernandez and Burnham (1974) who observed a significant decrease in phosphate sorption with increasing pH at high P concentrations. The

decrease in sorption was partly attributed to the reduction of exchangeable aluminium which was found to be essential for P sorption.

Effect of Organic Matter on Phosphate Sorption

Conflicting reports are available regarding the effect of organic matter on phosphate sorption. Some workers (Williams et al., 1958; Harter, 1969; Singh and Jones, 1976) showed that addition of organic matter to a soil increased phosphate sorption while others (Dalton et al., 1952; Larsen et al., 1959; Udo and Uzu, 1972; Brown and Loewenstein, 1978) obtained no correlation or even negative correlation between organic matter and phosphate sorption.

Organic matter has a protective function in phosphate sorption phenomena in acid tropical soils. This statement may be substantiated by the work of Bhat and Bouyer (1968) who observed that organic matter decreased phosphate sorption in ferruginous but not in illuvial hydromorphic soils in Senegal.

During their studies on phosphate sorption in Hawaiian soils, Fox et al. (1971) made interesting observations concerning the influence of organic matter on phosphate sorption. They observed that a recently sampled original phosphated sub-soil sorbed much more phosphate than a

non-phosphated sub-soil which had very little forage grown on it for 12 years. The non-phosphated sub-soil in turn sorbed more P than the unfertilized top soil. It was postulated that organic anions in the soils were responsible for blocking the phosphate sorption sites leading to less sorption capacity in soils which were relatively high in organic matter.

Several workers (Williams et al., 1958; Larsen et al., 1959; Brown and Loewenstein, 1978) tried to explain the linear relationship between phosphate sorption and organic matter content. They attributed the effect as being due to the presence of Fe and Al particularly in tropical soils. For example, Williams et al. (1958) while studying the effect of several soil properties on phosphate sorption, argued that high sorption capacity observed was a result of iron and aluminium which were present as humate complexes in the organic fraction of the soils. These humates were known to sorb a lot of P over a large range of pH in soils (Mattson et al., 1950).

Brown and Loewenstein (1978) obtained highly significant correlation between organic matter and aluminium sorption but not phosphate sorption in the volcanic soils of Idaho (U.S.A.). They argued that due to large exchange capacity of organic matter and abundance and reactivity of aluminium the organic

matter would be much more likely to sorb more aluminium than phosphate ions because direct sorption of phosphate ions on organic matter would be prevented. Larsen et al. (1959) while studying the effect of Fe, Al and humic acid on phosphate sorption in organic soils, observed that addition of Fe and Al increased phosphate sorption while that of humic acid reduced it. In fact, negative sorption of P was observed.

Stage of decomposition of the organic matter also affects the amount of P sorption. Singh and Jones (1976) observed that organic residues including saw dust (mixed conifer), barley (Hordeum vulgare) straw, wheat (Triticum aestivum) straw, alfalfa (Medicago sativa) hay, corn (Zea mays) stalks, bean (Phaseolus vulgaris) straw and poultry manure decreased P sorption when decomposed for only 30 days. Decomposition of the residues for periods more than this and up to 150 days significantly increased P sorption. Further, they noted that 0.3 percent P in the residues was a critical value below which sorption of P in the soil increased.

Mechanisms of Phosphate Sorption

Mechanisms of phosphate sorption in soils as well as in synthetic minerals have not been explained exclusively in the literature. However, several hypotheses have been proposed. General consesus of opinion (Stout, 1939; Low and Black, 1950;

Kuo and Lotse, 1972; Rajan and Perrott, 1975; Ryden et al., 1977a; Taylor and Ellis, 1978) is that phosphate ions replace exposed OH^- groups and/or other sorbed anions such as SO_4^{2-}, SiO_4^{4-} or H_2O on the clay or sesquioxide mineral surface. This mechanism has been used to explain phosphate sorption mainly at low equilibrium P concentration and at the beginning of the reaction (Muljadi et al., 1966; Rajan and Perrott, 1975; Rajan, 1975). At higher solution P concentrations and with increasing time, phosphate reacts with structural components of the adsorbent to form complex compounds releasing some of the structural elements (Stout, 1939; Low and Black 1950; Muljadi et al., 1966; Rajan and Perrott, 1975; Rajan, 1975; Ryden et al., 1977a)

Low and Black (1950), while investigating reactions of phosphate with kaolinite showed that silicon was released and aluminium was changed to a form extractable with aluminium complexing reagents. Similar results were obtained when pure hydrous alumina (Rajan et al., 1974), synthetic amorphous alumino-silicates (Rajan and Perrott, 1975) and clays from volcanic ash soils (Rajan, 1975) were used. Rajan and co-workers (1974, 1975) specified that at low phosphate concentrations, phosphate is sorbed on hydrous oxides by exchange with aquo $(Al-H_2O)^+$ and hydroxo $(Al-OH)^o$ ligands and with other weakly held but specifically sorbed anions such as SO_4^{2-} and SiO_4^{4-}. At higher concentrations, phosphate is

sorbed (i) on sites arising from disruption of hydroxy aluminium polymers in the gels and (ii) by distruction of structural silicate. This mechanism is illustrated below:

$$Al\text{-}H_3SiO_4\rceil^{o} + H_2PO_4^{-} = Al\text{-}H_2PO_4^{-}\rceil^{o} + H_3SiO_4^{-} \quad (1)$$

$$Al\text{-}H_2O\rceil^{+} + H_2PO_4^{-} = Al\text{-}H_2PO_4^{-}\rceil^{o} + H_2O \quad (2)$$

$$Al\text{-}OH\rceil^{o} + H_2PO_4^{-} = Al\text{-}H_2PO_4^{-}\rceil^{o} + OH^{-} \quad (3)$$

The actual type of bonding between phosphate ion and Al^{3+} is not known. It is not clear whether the bond is ionic covalent or coordinate covalent (Taylor and Ellis, 1978). Some workers such as Kuo and Lotse (1972), in fact, have disagreed with the hypothesis that phosphate replaces sorbed OH^{-} on the clay mineral surface. They suggested that a coordinate covalent bond is formed between Al^{3+} of the surface and O^{2-} of the phosphate ion by replacement of coordinated-H_2O or another anion.

Phosphate sorption isotherm, to a limited extent, gives an idea of the mechanisms involved in phosphate sorption. A number of researchers (Chen and Hwang, 1974; Rajan and Perrott, 1975; Taylor and Ellis, 1978; Chao *et al.*, 1978) observed that the Langmuir sorption isotherm deviates from linearity at high equilibrium P concentration. Griffin and Jurinak (1973) observed the deviation at low concentration.

Muljadi et al. (1966) distinguished three regions in the P sorption isotherm. The first region at low concentrations of the order of 1×10^{-4} MP where adsorption isotherm rises steeply and remains close to the y-axis. This was suggested to represent sites with a very high affinity for phosphate. Region II commenced at about 1×10^{-4} MP where the isotherm becomes convex to the y-axis while region III is linear occurring at medium to high concentrations 10^{-3}–10^{-1} MP. They argued that regions I and II were governed by the Langmuir isotherm while region III was not. They gave the following equations to describe the reactions in regions I and II:

$$(\text{Step. I}) \quad \text{>AlOH} + H^+ + OH^- \underset{}{\overset{K_1^-}{\rightleftharpoons}} \text{>Al}^+ \begin{matrix} \swarrow (H_2O) \\ \cdots (OH^-) \end{matrix} \qquad (4)$$

$$(\text{Step. 2}) \quad \text{>Al}^{+} \begin{matrix} \swarrow H_2O \\ \cdots OH^- \end{matrix} + H_2PO_4^- \underset{}{\overset{K_2^-}{\rightleftharpoons}} \text{>Al}^{+} \begin{matrix} \swarrow (H_2O) \\ \cdots (H_2PO_4^-) \end{matrix} + OH^- \qquad (5)$$

where K_1^- is the equilibrium constant for hydrolysis of OH^-

K_2^- is the equilibrium constant for the exchange reaction

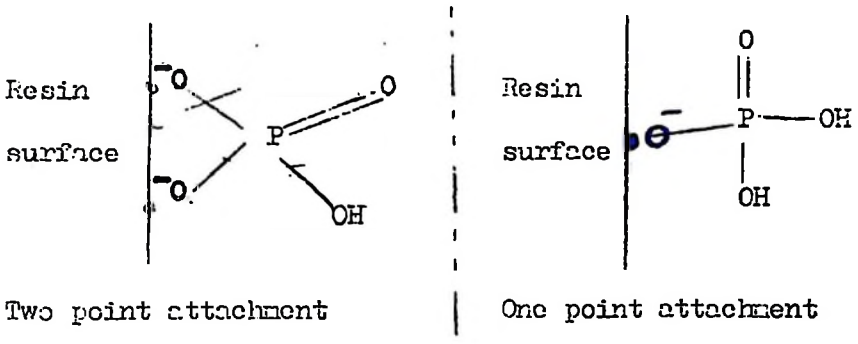
$\swarrow$ symbol denotes a coordinate link, and

$\cdots$ denotes an electrovalent link.

The above equations show a reaction involving the exchange of phosphate ion for OH^- counter-ion of a positively-charged

edge Al atom which is formed by surface hydrolysis of an OH^- group. The OH^- counter ion is held near the surface until exchange occurs with some other ion from solution.

Taylor and Ellis (1978) working with soil and synthetic material distinguished two distinct regions in the sorption isotherm. They gave an explanation similar to that of Muljadi et al. (1966). According to them, the slopes on the phosphate sorption isotherm which led to two regions might be due to sorption taking place at energetically different sites on the surface; i.e. sorption occurring in layers and precipitation of phosphate ion on the surfaces. They proposed that at low concentrations, P was bonded by two points of attachment after deprotonation of $H_2PO_4^-$ ion followed by one point attachment at higher P concentrations during adsorption on the resin surface as shown below:



Two point attachment | One point attachment

Chee et al. (1978) in their recent work with Fijian soils warned on the indiscriminate use of Langmuir sorption isotherms. They pointed out that it is essential to have sufficient data to distinguish the various regions as the number of discontinuities on the curve varies among different soils. They, however, concluded that in most cases 2 to 3 regions can be distinguished for many soils each corresponding to an increase in fixation of phosphate by the soil and perhaps to a different sorption mechanism.

Desorption of Phosphate

Researchers (Fox and Kamprath, 1970; Rajan, 1973; Barrow and Shaw, 1975; Ryden et al., 1977b)have pointed out that desorption of phosphate from a soil depends on factors such as period of contact between soil and extracting solution, physico-chemical and mineralogical properties of the soil, and soil: solution ratio. Barrow and Shaw (1975) while investigating the effect of prior contact on desorption of phosphate from soils observed that when gentle shaking was done, desorption was complete within a few hours when the solution: soil ratio was small but took as long as 96 hours when the ratio was large. Further, they observed that the amount of phosphate desorbed decreased as the period of prior contact between soil and phosphate solution increased.

Ryden et al. (1977b) obtained results similar to that of Barrow and Shaw (1975) in their study with synthetic hydrous ferric oxide. They observed resorption of phosphate after 30 hours of desorption. These results suggested that physically-sorbed phosphate was reversible with respect to changes in ionic strength and cation species of the desorbing solution. It was further noted that isotopic exchangeability of physically-sorbed P was at least ten times greater than the chemisorbed P.

Studies (Fox and Kamprath, 1970; Rajan, 1973) have shown that P desorption characteristic of a soil has considerable effect on P supplying capacity of that soil. Fox and Kamprath (1970) pointed out that desorption isotherms are necessary for the assessment of P solubility particularly after large amount of phosphate fertilizer is applied because concentration of P in solution is a good indicator of P nutritional status of the soil since concentration gradients provide the driving force for moving P from solution to roots.

Rajan (1973) while working with highly weathered soils of Hawaii observed that soils with high P buffering capacity such as the highly weathered Inceptisols were more capable of maintaining P in solution, hence had better P nutrition status than the Oxisols. He further observed that there was an increase in desorption of P with increasing volume of 0.01M

$CaCl_2$ solution suggesting that more anions were available for desorption of sorbed-P at higher than lower volumes.

Use of Phosphate Sorption Isotherms for Assessing Fertilizer-P Requirement

The phosphate sorption isotherm has recently been employed for estimating fertilizer-P to be added to a soil relative to the requirement of a crop. The rationale of using phosphate sorption isotherms for predicting fertilizer-P need of crops is that the method takes into account the P concentration in solution ("intensity" of P nutrition) as well as the quantity of phosphate retained by soil colloids ("capacity" for P nutrition).

The idea of using phosphate sorption isotherms for assessing fertilizer-P requirement was first advanced by Beckwith (1965). While working with some soils of South-East Queensland (Australia), he concluded that an equilibrium concentration of 0.2 ppm P was adequate for optimum growth of most plants.

Subsequent studies have shown that external P requirement of crops depends on a variety of factors such as moisture condition of soil, mineralogy, chemistry and management of soil, kind of crops to be grown, and the growth stage of the crop at which harvesting is derired.

In their studies with millet (Pennisitum typhoides var. Gahi-1) on Ultisol, a sandy soil, and a Histosol of Central and Eastern North Carolina, Fox and Kamprath (1970) obtained yield that approached 95 percent of maximum when phosphate in soil solution was adjusted to 0.2 ppm. Silva and Fox (1974) obtained yields which were 92 to 99 percent of the maximum with 0.2 ppm adjusted P in solution under similar conditions as for the above mentioned study. They observed that with corn (Zea mays) grown in the field at two different locations of varying soil and climatic conditions, a range of 0.05 to 0.07 ppm P was required for attainment of 95 percent of the maximum yield. On the other hand, Chinese cabbage (Brassica pekinensis) had an external P requirement of 0.2 ppm P while lettuce (Lactuca sativa) needed 0.3 ppm P in the equilibrium solution to attain 95 percent of maximum yield. Sweet potatoes (Ipomea batatas), however, needed only 0.003 ppm P in solution for 75 percent of maximum yield but as much as 0.1 ppm P in solution for 95 percent of maximum yield.

Fox et al. (1974), working with Inceptisol and Oxisol soils of Hawaii obtained differences in external P requirements of different crops. They found that maize (Zea mays) required 0.06 ppm P in solution to attain 95 percent of the maximum yield while sweet potatoes (Ipomea batatas) and lettuce (Lactuca sativa) required 0.1 and 0.4 ppm P, respectively.

Nishimoto et al. (1975) showed that flower diameter and stem length in Chrysanthemum morifolium were less affected by external P concentration than the total fresh weight. For cut flower production, 95 percent of maximum yield was obtained at 0.05 ppm P in the equilibrium solution while for total fresh weight 0.16 ppm P was needed.

MATERIALS AND METHODS

The Soils

Two extensively occurring soils belonging to the great groups Haplustox and Vitrandept according to the Soil Taxonomy (Soil Survey Staff, 1975) were chosen for this study. For each soil, a surface (0-15cm) sample was collected from the virgin land. The samples were dried in air and passed through a 60-mesh sieve. About 200 kg of each soil were also collected for the greenhouse experiments. Description of place of sampling, profile characteristics and mineralogy of each soil are given in Table 1 and Appendices 1-3.

General Experimental Procedures for Sorption Studies

In all experiments involving equilibration, 30 ml of the equilibrating solution were added to 3 g (oven-dry weight basis) soil in 100-ml plastic centrifuge tube. Three drops of toluene were added to arrest microbial activity. The tube with its content was shaken on a mechanical shaker in an air-conditioned room at 25°C for 24 hours except in Experiment I where different periods of equilibration were evaluated. The equilibration period of 24 hours was chosen on the basis of the results of Experiment I. This period was found adequate for near complete equilibrium. The content in the tube were then centrifuged at 3×10^3 revolutions per minute

until a clear supernatant was obtained. The supernatant solution was filtered through a Whatman No. 42 filter paper. The clear supernatant and the equilibrating solution were analysed for P and other parameters as required.

Each treatment was run in duplicate and all the solutions were prepared using the analytical grade reagents. The glasswares were washed with dilute HCl and rinsed 3 times with tap water and finally twice with distilled water. Any deviation from this standard procedure is indicated at appropriate places.

The amount of P sorbed by a soil was the difference in the initial concentration of P in the equilibrating solution and that in the supernatant. The concentration of P in the supernatant has been referred to as "equilibrium-P" in the text.

Experiment I. Effect of the Length of Equilibration on Sorption

Equilibration periods of 0.5, 1, 4, 8, 12, 24, 48 and 72 hours were tested in this experiment. The soil samples were equilibrated with 5 and 50 μg P/ml solutions prepared in 0.01M $CaCl_2$. For equilibration periods of 0.5 to 12 hours, shaking was done continuously. For periods from 24 to 72 hours, the samples were shaken for 1 hour twice daily, once in the morning and again in the evening. The content in the tube was centrifuged immediately after removal from the shaker and the clear supernatant was analysed for P. Shaking period beyond which

no significant change in phosphate sorption occurred was considered as one that was adequate for near complete equilibration.

Experiment II. Effect of Initial P Concentration in the Equilibrating Solution on Sorption

The initial concentrations of the equilibrating solutions were 0, 0.05, 0.1, 0.5, 1.0, 5.0, 10.0, 25.0, 50.0 and 100.0 µg P/ml. The soil samples were equilibrated for 24 hours. At the end of equilibration, the content in the tube was centrifuged, filtered and analysed for P.

Experiment III. Effect of the initial pH of the Equilibrating Solution on Sorption

Equilibrating solutions of initial concentrations 0.5 and 5 µg P/ml were adjusted to pHs 2,3,4,5 and 6 using HCl or KOH as required.

After equilibration, the content in the tube was centrifuged, filtered and analysed for P.

Experiment IV. Effect of Destruction of Organic Matter on Phosphate Sorption

Four 100-ml centrifuge tubes, two for each soil, were numbered and weighed. In each tube, 1g soil was treated with 5 ml of 30 percent H_2O_2 and left overnight which was found to be adequate for complete destruction of organic matter. Subsequently, 10ml of distilled watter was added to the tube and the content

centrifuged. The supernatant was discarded and the above process was repeated one more time. The tube was weighed again to estimate the amount of entrapped liquid. After destruction of the organic matter, 10 ml of a 50 µg P/ml solution was equilibrated with the content in the tube for 24 hours. P was then determined in the supernatant. The amount of entrapped liquid in the tube was taken into account while calculating the amount of P in the supernatant.

Experiment V. Desorption Studies

For each soil, 14 plastic centrifuge tubes were weighed and numbered. In each tube 3g soil was equilibrated with 30 ml of a 50 µg P/ml solution for 24 hours. At the end, the content in the tube was centrifuged. While the supernatant in tubes 1 and 2 was analysed for P to obtain data on the amount of P sorbed, that in the others was discarded. While discarding the supernatant, extreme care was exercised so as to leave as little liquid in the tubes as possible. The tubes were weighed again. The difference between this and the initial weight of the tube plus 3 g soil gave the weight of the entrapped liquid of which the concentration was known from the sorption data obtained after P determination in the supernatants in tubes 1 and 2.

1. Desorption of the sorbed-P with water

The content of the tube was transferred quantitatively to a 500-ml plastic bottle. These bottles were numbered in the same way as the centrifuge tubes. For desorption, the following water treatments were applied:

Bottle No:	Water added (ml)
1 - 2	50
3 - 4	100
5 - 6	150
7 - 14	200

The bottles were shaken for 24 hours. The supernatant solutions in bottles 1 - 6 were analysed for P while those of others were discarded.

2. Desorption with 1M solutions of KNO_3 or K_2SO_4 after desorption with water

In this study, the following treatments were applied:

Bottle No.	Treatment
7 - 8	100 ml 1M KNO_3 solution
9 - 10	200 ml 1M KNO_3 solution
11 - 12	100 ml 1M K_2SO_4 solution
13 - 14	200 ml 1M K_2SO_4 solution

The bottles were then shaken for 24 hours, centrifuged and the supernatant analysed for P. While calculating the amount of P desorbed by water and salt solutions, the amount

of P entrapped in the liquid after the first step of equilibration was taken into account.

Experiment VI. Greenhouse Studies

A greenhouse experiment involving both the soils was set up to determine the external P requirement for near maximum growth of maize (Zea mays L. var. Ilonga composite) and bean (Phaseolus vulgaris L. var. Canadian wonder) based on the phosphate sorption isotherms determined in the Experiment II. The solution P concentrations chosen were 0, 0.3, 0.5, 1.0, 2.5, 5.0, 10.0 and 15.0 µg P/ml. The corresponding amount of P to be added to obtain the respective adjusted P concentration in the soil solution was obtained from the sorption isotherms.

For the pot experiment, 3 kg (on oven-dry weight basis) of soil, previously screened through a 2mm sieve, was spread on a clean plastic sheet. This soil sample received a basal application of 200 kg N/ha and 50 kg K/ha. A stock solution of N and K was prepared whose concentration was such that the volume of the liquid equivalent to the field capacity of the soil contained these two nutrients at the above rates. The required amount of KH_2PO_4 to obtain a particular adjusted P concentration in the soil solution was added to the measured amount of the above solution, dissolved by stirring, then mixed

thoroughly with the soil on the plastic sheet. The soil was then transferred to a plastic bag and equilibrated for two weeks with mixing every alternate day.

After equilibration, the soil was transferred to a 4 kg pot. The pots with soil were weighed and the loss of moisture was made up subsequently to maintain the soil at the field capacity throughout the growth of the crop. Two such sets were prepared - one for maize and the other for bean. In each pot, two seeds were planted but only one was maintained after germination.

After 7 weeks of growth the crops were harvested. To remove any adhered dust and other contaminants, the plants were washed in a sequence; twice in tap water and twice in distilled water. Great care was taken during this process to avoid loss of any plant material. The plants were then left in sun for free water to evaporate and then dried in oven at 60°C to constant weight. The dry weight was recorded. The plants were ground and wet-ashed for P determination following the method as described by Chapman and Pratt (1961).

The external P requirement for the two crops was determined by plotting the dry matter yield as a function of adjusted P concentration.

Analytical Methods

Soil pH

Soil pH was determined on a Corning Model 12 Expanded Scale Research pH meter using Corning glass and calomel reference electrodes. The pH was measured in water, 1N KCl, 0.1N KCl, 0.1N KH_2PO_4 and 0.01M $CaCl_2$ solutions at a soil-solution ratio of 1:1.

Soil texture

Particle size analysis was performed by the sedimentation method (Jackson, 1967) after removal of organic matter and free iron oxides. Soil textural class was determined by using U.S.D.A. textural class triangle.

Organic carbon

Organic carbon in the soils was determined by the Walkeley and Black method (Allison, 1965). Normal $K_2Cr_2O_7$ and concentrated H_2SO_4 were used to oxidise the organic carbon. The amount of 1N $K_2Cr_2O_7$ used was taken as a measure of the organic carbon content. A correction factor of 1.33 was used.

Total nitrogen

Total nitrogen in the soils was determined by the macro-Kjeldahl digestion-distillation method (Bremner, 1965). The soil sample was digested with concentrated sulphuric acid in the presence of a $K_2SO_4.5H_2O$: $CuSO_4.5H_2O$: selenium powder salts mixture in the ratio of 10:1:0.1 by weight. The clear digest was distilled after addition of 40 percent NaOH to change NH_4^+ to NH_3 which was received in boric acid-mixed indicator solution and titrated with standard H_2SO_4. The acid titre was a measure of total N in the digest, hence, in the soil sample.

Available phosphorus

Available phosphorus in the soil was extracted with 0.03N NH_4F + 0.02N HCl as described by Bray and Kurtz (1945). P in this extract as well as in the supernatant solution from the sorption studies was determined by the chlorostannous-reduced molybdophosphoric blue colour method as described by Jackson (1958). The pH of the system was maintained at 5.0 with 4N NH_4OH or 4N HCl as required; 2, 4-dinitrophenol was used as indicator.

Ion exchange properties

Cation exchange capacity was determined by the ammonium saturation method (Chapman, 1965). The soil was saturated with neutral normal ammonium acetate and then filtered. The

residue was washed with methyl alcohol, subsequently shaken with 4 percent KCl solution and filtered. The NH_4-N in the filtrate, which is a measure of the CEC of the soil, was determined on a Markham distillation apparatus.

Exchangeable acidity was determined by the method of Peech et al. (1962). In the procedure, 10g soil was taken in a 125-ml conical flask. 100ml of 0.5N $BaCl_2$-0.055 N triethanolamine extracting solution was added to the content, mixed and left overnight. The content was then leached through a Pyrex buchner funnel by adding small portions of extracting solution until 225 ml of the extract had been collected. The leachate was quantitatively transferred to a 250-ml volumetric flask and made to the volume with the extracting solution. Subsequently, the leachate was transferred to a 500-ml conical flask and titrated against standard HCl to a pink end point using a mixed indicator solution of bromocresol green and methyl red.

Free iron oxide

Free iron oxide content of the soil was determined by the citrate-bicarbonate - dithionite method (Jackson, 1967) after removal of carbonates and organic matter. Iron in the extract was determined on a Pye Unicam SP191 Atomic Absorption Spectrophotometer.

Amorphous ferrialumino silicate (AFAS)

The soil sample from which free iron oxides have been removed was used for estimating amorphous ferrialumino silicate by the method of Alexiades and Jackson (1966) as modified by Mengasamy et al. (1975). The soil was suspended in a 1000-ml cylinder after removing particles 50 um in size by sieving. A suitable aliquot from the suspension, whose concentration was previously determined, was transferred to a stainless steel beaker. To the beaker, 100ml of 0.5 N NaOH was added and the content boiled for 2.5 minutes. The content in the beaker was cooled at once to room temperature in a water bath. Subsequently the supernatant liquid was removed by centrifugation and analysed immediately for Si, Al and Fe.

Silicon was estimated colourimetrically following the procedure described by Kilmer (1965). Ten ml aliquot of the solution was transferred to a 100-ml volumetric flask. One ml of ammonium molybdate was added while swirling the flask and the content allowed to stand for ten minutes. Thereafter, 4 ml of tartaric acid followed by 1 ml of a reducing solution (sodium sulphite + 1-amino-2 naphthol-4-sulphonic acid) were added. The content was made to the volume with distilled water. After thirty minutes, colour intensity was measured on EEL model 197 colourimeter at 650 mu. A standard curve was constructed.

Aluminium in the supernatant was determined by the aluminon method as described by McLean (1965). An aliquot of 5 ml was taken into a 50-ml volumetric flask. After adding 25 ml water, 2 ml thioglycolic acid and 10 ml aluminon reagent, the flask was heated on a water bath for 16 minutes, cooled for 1.5 hours and the volume made to the mark before reading the transmittance on an EEL model 197 colourimeter at 530 mu. A standard curve was also prepared.

Iron content in the structure of AFS was determined by extracting the residue obtained after centrifugation using citrate-bicarbonate dithionite reagent as described by Jackson (1967). The iron in the extract was determined on a Pye Unicam SP 191 atomic absorption spectrophotometer.

Defferential thermal analysis (DTA)

Differential thermal analysis of the whole soil (ground and passed through a 60 mesh sieve) was done following the details given by Barshad (1965) on a Dupont Thermal Analyser Model 990.

RESULTS AND DISCUSSION

The soils, one belonging to the Great group Haplustox and the other to Vitrandept according to the Soil Taxonomy (Soil Survey Staff, 1975) were selected for this project. Some characteristics of the profiles are given in Appendix 1. Description of the sampling sites, origin and mineralogy of the two soils are included in Table 1. Henceforth, these soils will be referred to as Haplustox and Vitrandept. Differential thermal analysis revealed that the Haplustox soil (Appendix 2) dominantly contained hydrous oxides of iron and kaolinite. The Vitrandept soil (Appendix 3) contained amorphous minerals and hydrous oxides of iron. As reported by Parmar (1978) based on her x-ray analysis results, the soil predominantly contained x-ray amorphous materials with traces of illite of micaceous origin. Chemical analysis (Jackson, 1967) revealed that both the soils contained free iron oxides, crystalline and amorphous, and amorphous ferrialumino silicate (Table 2).

Some physico-chemical properties of the soils are given in Table 2. The Δ pH = $pH_{1N\ KCl} - pH_{H_2O}$ value which is a measure of net surface charge, was negative for both the soils. Thus, the soils had net negative charge, the ΔpH = $pH_{0.1N\ KH_2PO_4} - pH_{0.1N\ KCl}$ which is a measure of the extent to which phosphate displaces OH^- ions, was positive for the Haplustox soil but negative for the Vitrandept soil.

Table 1. Description of sampling sites, origin and mineralogy of the soils

Soil	Location	Elevation (m)	Average annual rainfall (mm)	Origin, mineralogy and dominant vegetation
Haplustox	Mzumbe Secondary School, Morogoro	520	670	Metasediments of the Usagaran System; dominantly hydrous oxides of iron and kaolinite; major vegetation - maize
Vitrandept	Olmotonyi Forest, Arusha	1600	950	Basic volcanic ash; predominantly x-ray amorphous, traces of illite of micaceous origin; major vegetation - Pinus patula Schl & Cham.

Table 2. Physico-chemical properties of the soils

Parameters	Soil	
	Haplustox	Vitrandept
pH_{H_2O}	5.0	7.0
$pH_{1\underline{N}\ KCl}$	4.0	5.9
Δ $pH=pH_{1\underline{N}\ KCl}-pH_{H_2O}$	-1.0	-1.1
$pH_{0.1\underline{N}\ KCl}$	4.2	6.1
$pH_{0.1\underline{N}\ KH_2PO_4}$	4.4	5.6
Δ $pH=pH_{0.1\underline{N}\ KH_2PO_4}-pH_{0.1\underline{N}\ KCl}$	+0.2	-0.5
$pH_{0.01\underline{M}\ CaCl_2}$	4.5	6.3
Organic C (%)	2.4	4.5
Total N (%)	0.13	0.40
C:N ratio	18	11
CEC (me/100g soil)	23	39
Bray No. 1-P (ppm)	20	23
Particle-size-analysis (%):		
Sand	24	50
Silt	27	26
Clay	49	24
Textural class	Clay	Sandy loam
Free Fe_2O_3 (dithionite soluble) (%)	2.3	0.3
Amorphous Fe_2O_3 (oxalate soluble) (%)	0.3	0.2
Crystalline Fe_2O_3 (by difference) (%)	2.0	0.1
Amorphous ferrialumino silicate (AFAS) (%)	23.6	13.9
% AFAS content on clay basis	48.3	58.1

Thus, the Haplustox soil appears to have more phosphate-replaceable OH^- groups than the Vitrandept soil. This contention finds further support from the fact that on soil basis the Haplustox contained more amount of AF.S than the Vitrandept (Table 2).

Experiment I. Effect of Length of Equilibration on Phosphate Sorption

The data on P sorption in the soils as a function of length of equilibration at two concentrations of the equilibrating solution are given in Table 3. The magnitudes of P sorbed and that remaining in the solution during equilibration for the various lengths of time are depicted in Fig. 1 and 2.

The magnitude of sorbed-P increased with increasing length of equilibration. The effect of time was more pronounced at 50 than 5 ppm P in the equilibrating solution (Table 3). A length of 24 hours appeared adequate for near complete equilibration as beyond this period the increase in the magnitude of sorbed-P was not appreciable (Table 3, Figs. 1 and 2). Rhodes (1975) while working with highly weathered acidic soils of Sierra Leone, concluded that an equilibration time of 24 hours was adequate for near equilibrium condition.

Equilibrium-P concentration dropped down rather drastically during 24 hours of equilibration and was more or less stabilised thereafter (Figs. 1 and 2). A completely stable

Table 3. Effect of length of equilibration on phosphate sorption in the soils

Soil	Initial P concentration (ppm) of equilibrating solution	Time of equilibration (hr)							
		0.5	1	4	8	12	24	48	72
		μg P/g							
Haplustox	5	43	43	43	45	45	46	46	48
	50	410	419	419	423	437	444	454	454
Vitrandept	5	42	43	45	46	47	48	48	48
	50	387	391	395	419	421	428	448	447

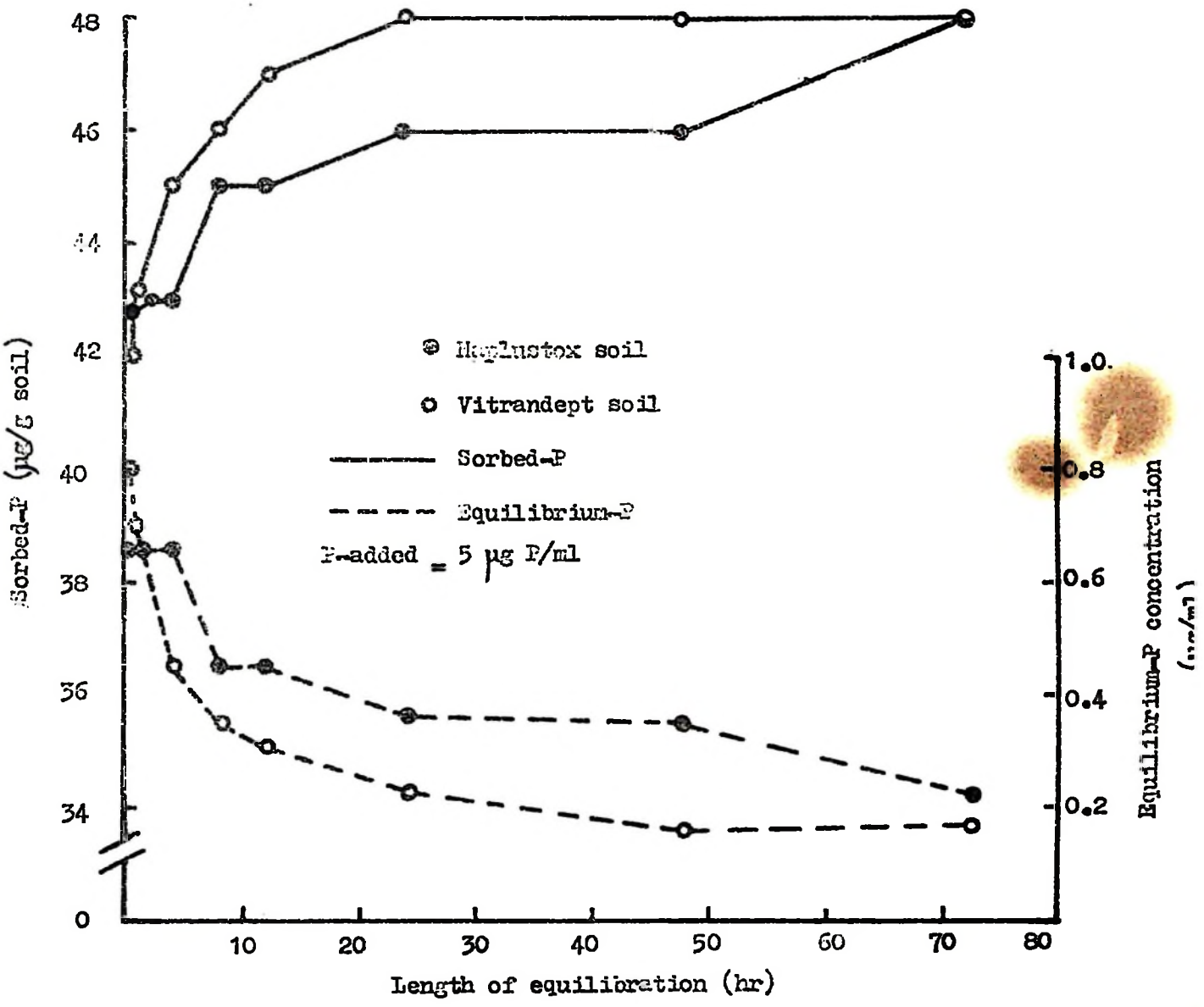


Fig. 1. Effect of length of equilibration on P sorption and equilibrium-P concentration in the soils

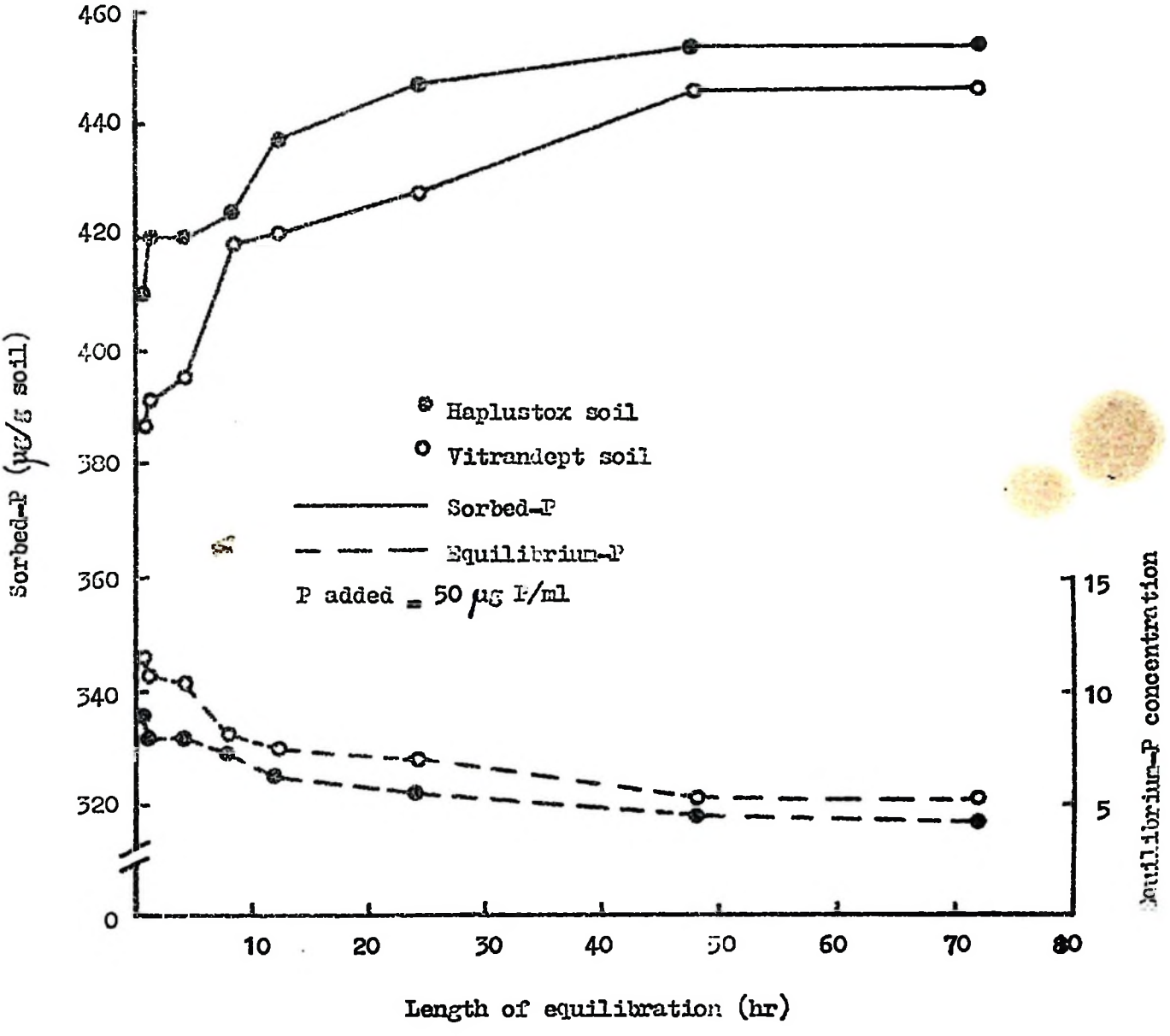


Fig. 2. Effect of length of equilibration on P sorption and equilibrium-P concentration in the soils

level of equilibrium-P, however, was not attained during the periods included in the text. Perhaps, equilibration time longer than 72 hours was required. Fox and Kamprath (1970), Rajan and Fox (1972), and Chae et al., (1978) obtained equilibrium condition only after six days of equilibration.

The P sorption was rapid in the first half hour but slowed down with passage of time. In their investigation of P sorption in Latosol from Hawaii and montmorillonitic soils from India, Rajan and Fox (1972) observed that 85 percent of P sorption was complete during 24 and 48 hours of equilibration in the respective soils (based on 10 days = 100 percent). Data obtained in this study (Table 3) indicate that over 90 percent of P sorption took place within 24 hours of equilibration. For example in the Kaplustox soil, 92 and 98 percent of sorption at 5 and 50 µg/ml P added took place during 24 hours of equilibration (based on 72 hours = 100 percent). In the Vitrandept soil, 98 and 96 percent of sorption respectively for 5 and 50 µg/ml P added took place during 24 hours of equilibration.

Several investigators have attempted to explain the nature of reactions taking place during P sorption as a function of time. The initial fast reaction is believed (Bache, 1963; Muljadi et al., 1966 ; Hyden and Syers, 1977)

to be essentially physical involving movement of P from the equilibrating solution to the colloidal surface. This subsequent slow reaction according to Bache (1963) and Ryden et al. (1977a) is essentially chemical involving diffusion of P into colloidal material. This process is slow and may take days or even weeks (Munns and Fox, 1976). Bache (1965) pointed out that the period required to attain equilibrium is dependent upon the pH of the system, solution/solid ratio and mineralogy of the adsorbent material.

Experiment 11. Effect of Initial P Concentration of Equilibrating Solution on its Sorption

It is evident from the data in Table 4 and the P sorption isotherms in Fig. 3 that the magnitude of sorbed-P in both soils increased consistently with increasing initial P concentration in the equilibrating solution. This is consistent with reports from elsewhere in the tropics (Rajan, 1973; 1975; Parfitt and Mayo, 1975; Chee et al. 1978). Appreciable P sorption occurred at 5 µg P/ml or higher initial P concentration in the equilibrating solution. Both soils sorbed substantial amounts of added P. Parfitt (1977) believed that P sorption in Oxisols was mainly due to oxides of iron and aluminium. Rajan (1973), and Gebhardt and Coleman (1974)

Table 4. Effect of the initial P concentration of equilibrating solution on its sorption in the soils

Soil	Initial P concentration (ppm) of the equilibrating solution									
	0	0.05	0.1	0.5	1.0	5.0	10.0	25.0	50.0	100.0
	μg P/g									
Haplustox	-3	-2	-2	2	5	45	95	212	423	824
Vitrandept	-2	-2	-1	2	5	45	93	235	431	792

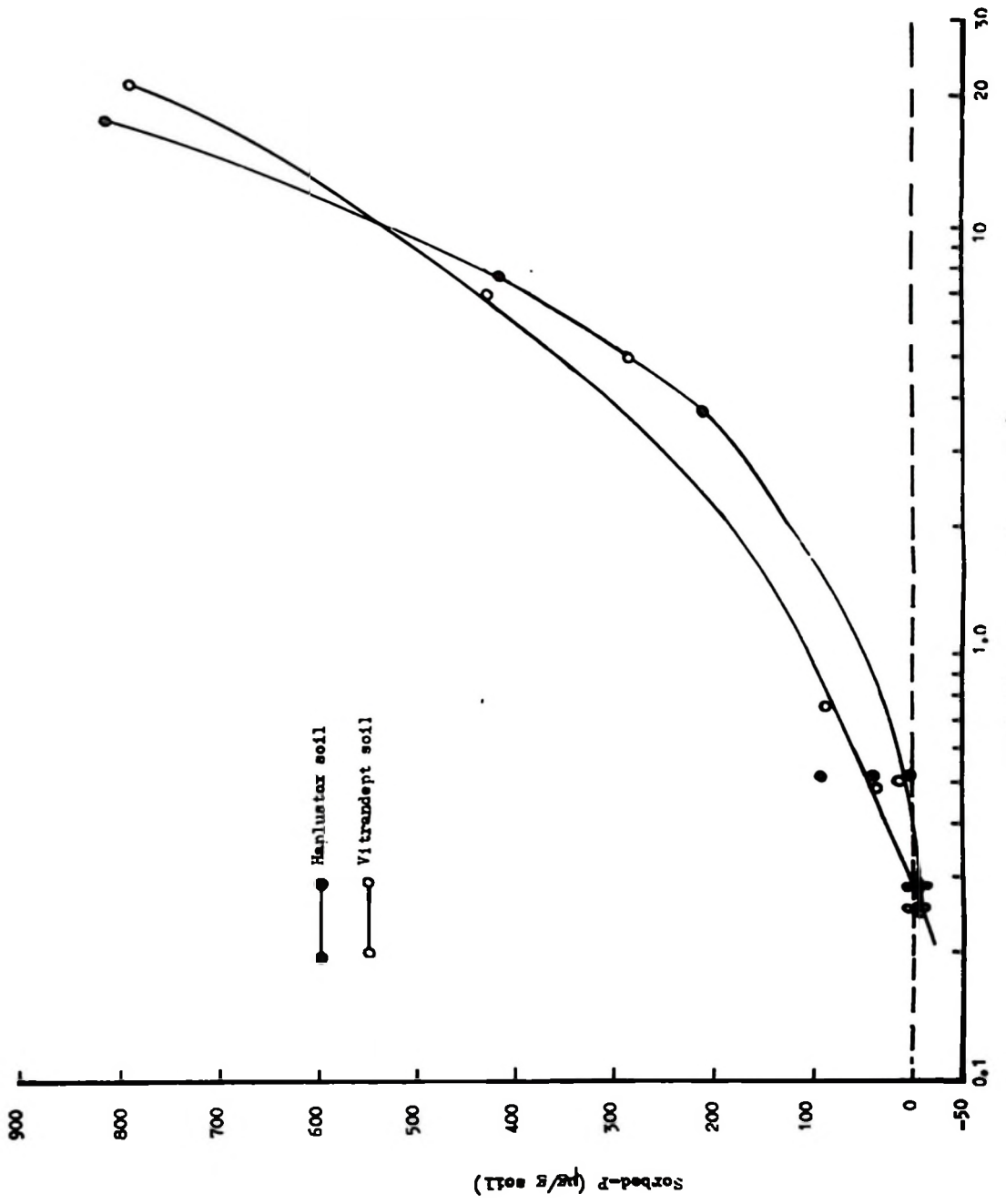


Fig. 3. Phosphate sorption isotherms for the soils

advocated that Andept soils sorbed substantial amount of P on their extensive surfaces due to presence of amorphous materials. It should be noted, however, that at any one concentration, the amount of sorbed-P in the two soils did not differ to any appreciable extent (Table 4). Further, the Vitrandept soil sorbed somewhat less P (Table 4) at the highest initial P concentration of 100ppm. This can be explained on the basis of mineralogy of the two soils. Even though the Vitrandept is expected to be mostly amorphous, selective dissolution analysis (Table 2) revealed that both the soils contained appreciable and nearly equal amounts of AFAS in their clay fractions. Hence they sorbed substantial amounts of added P. The presence of AFAS in tropical ferruginous soils similar to the Haplustox, and their influence on soil properties have been reported by Rengasamy et al.(1978). The slightly higher sorption of P in the Haplustox can probably be explained on the basis of its higher AFAS content on soil basis.

Some investigators (Muljadi et al., 1966; Rajan and Perrott 1975; Taylor and Ellis, 1978) believe that energetically different sorption sites exist at colloidal surfaces. They have shown that at low concentrations P exchanges with sorbed ions such as SO_4^{2-}, SiO_4^{4-} and OH^-. At high concentrations and with increasing time P exchanges not only with the sorbed ions but also with structural materials of the soil colloids or any other adsorbent. The movement of P into these materials is mainly by diffusion.

Experiment III. Effect of Initial pH of the Equilibrating P Solution on Phosphate Sorption

The data in Table 5 show that the Initial pH of the equilibrating solution had virtually no effect on P sorption in either soil. This observation is contrary to that of others (Muljadi et al., 1966; Lopez-Hernandez and Burnham, 1974) who observed increased P

Table 5. Effect of initial pH of the equilibrating P solution on its sorption in the soils

Soil	Initial P concentration (ppm) of the equilibrating solution	Initial pH of the equilibrating P solution				
		1.0	3.0	4.0	5.0	6.0
		μg P/g				
Haplustox	0.5	-0.9	-0.9	-0.9	-1.1	-1.4
	5.0	47	47	48	48	48
Vitrandept	0.5	-1	-1	-1	-1	-1
	5.0	46	46	45	45	45

sorption with increasing pH of the equilibrium solution. The reason for the lack of effect due to initial pH of the solution in the present study may be the high buffering capacity of these soils. It is possible that the solutions of different pH values failed to change the pH of soil-solution suspension to the extent that may cause change in the magnitude of P sorption.

Experiment IV. Effect of Destruction of Organic Matter on Phosphate Sorption

In both soils, substantial increase in phosphate sorption was observed after the destruction of organic matter(Table 6). The magnitude of increase in P sorption due to destruction of organic matter as compared to when it was present was over three fold. Bhat and Bouyer (1968) observed a marked decrease in the phosphate sorption with addition of organic matter in a ferruginous tropical soil of Senegal but not in a hydromorphic soil. Fox et al. (1971) while working with the Hawaiian tropical soils observed that soils high in organic matter sorbed less P than those low in its content. The reason given was that organic anions blocked P sorption sites in the soils high in organic matter. These observations support the results obtained in the present study.

Table 6. Effect of destruction of organic matter on P sorption in the soils

	Initial P concentration (ppm) of the equilibrating solution	Soil	
		Haplustox	Vitrandept
		μg P/g	
Present	5	45	45
	50	423	421
Destroyed	5	149	149
	50	1496	1489

Contrary to the discussions above, some workers (Williams et al., 1958; Porter, 1969; Singh and Jones, 1976) obtained increased sorption of phosphate subsequent to addition of organic matter to soils. Williams et al. (1958) argued that the high P sorption in organic matter rich soils is due to iron and aluminium present as humate complexes in the organic fraction. These humates are capable of sorbing a lot of P over a wide range of pH in the soils (Hattson et al., 1950).

Experiment V. Desorption Studies

This experiment was designed to study the relative ability of the experimental soils to maintain P concentration in the soil solution when subjected to various environmental conditions with respect to amounts and nature of anions. After allowing P sorption to take place, the soils were treated with water and then with 1N KNO_3 and 1N K_2SO_4 solutions.

The amount of phosphate desorbed increased with increasing volumes of water as well as the salt solutions (Fig.4). Similar observations were made by Rajan (1973) while working with highly weathered Hawaiian soils. It is possible that more anions were available to cause P desorption when large volume of the extractant was used.

It was further observed that more phosphate was desorbed by SO_4^{2-} than NO_3^- ions (Fig.4). The difference in sorption

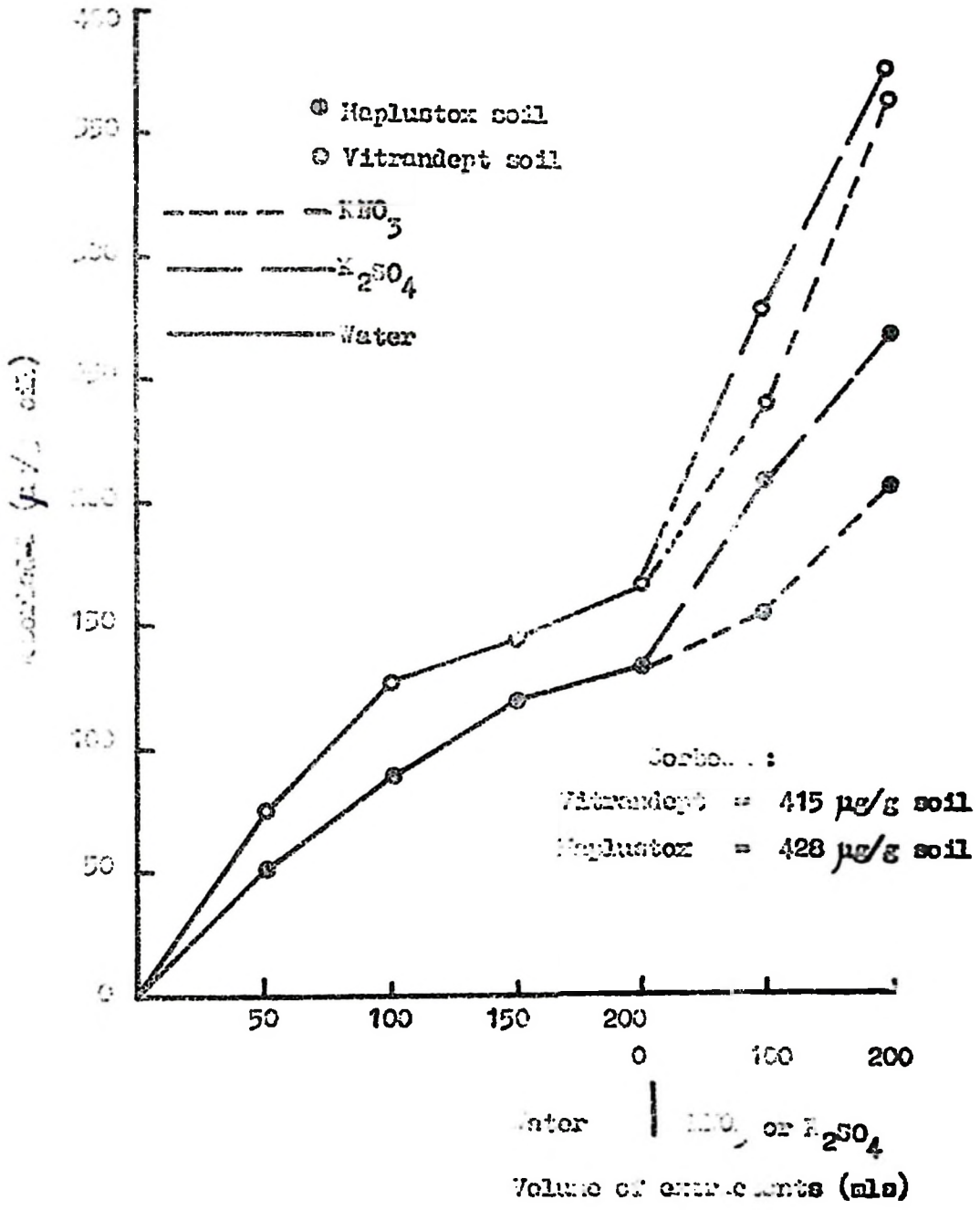


Fig. 4. Desorption of P as affected by the nature of anions and volume of the extracting solution. (The curve due to a salt solution is additive to that of water on the assumption that the amount desorbed by the latter would also be desorbed by the former).

mechanisms between NO_3^- and SO_4^{2-} may have led to the above observation. While SO_4^{2-} and phosphate ions are "specifically sorbed" on colloidal surfaces, NO_3^- ion is "non-specifically sorbed" (Hingston et al., 1968). It is, therefore, possible that SO_4^{2-} ions were able to desorb more phosphate from the colloidal surfaces than NO_3^- ion because of similarity in the sorption mechanisms of phosphate and SO_4^{2-} ions.

It is interesting to note in Fig. 4 that more phosphate was desorbed by all the extractants from the Vitrandept than Haplustox soil. A similar observation was made by Rajan (1973) with Hawaiian soils. Apparently the Vitrandept soil had higher P buffering capacity than the Haplustox soil. Consequently, the Vitrandept is capable of rendering more P available to plants than the Haplustox soil. The concentration of P in the soil solution gives useful indication of P nutrition due to the fact that concentration gradient provides the driving force for P to move to roots, and that P uptake by roots is concentration-dependent (Fox and Kamprath, 1970).

Experiment VI. Greenhouse Studies

Studies (Fox and Kamprath, 1970; Rajan, 1973) have shown that P sorption isotherms can be used for predicting P requirement of soils and its availability to plants. It has been pointed out (Rajan and Fox, 1972) that the amount of phosphate

sorbed by a soil at an equilibrium P concentration associated with any given yield is an estimate of the P requirement for that yield.

1. Dry matter yield of maize and bean as affected by the adjusted P concentration in soil solution

On either soils, the dry matter yield of both maize and bean initially increased rapidly then gradually as the adjusted soil solution P concentration increased (Table 7; Figs. 5 and 6). To some extent this growth pattern may be seen in plates 1-4. Phosphorus deficiency symptoms were seen in the control treatment on both soils. The symptom appeared as purple colouration on lower leaves in maize (Plate 5).

On Haplustox soil, 95 percent of the maximum yield of maize was obtained at an adjusted P concentration of 9.7 µg P/ml (indicated by arrows in Fig. 5). On the Vitrandept soil, an adjusted P concentration of 2.6 µg P/ml was adequate for obtaining 95 percent of the maximum yield (indicated by arrows in Fig.5).

For bean, 95 percent of the maximum yield was obtained at 9.5 and 5 µg P/ml adjusted P concentration in the Vitrandept and Haplustox soil, respectively (Fig. 6). From economic considerations, however, adjusted P concentrations lower than that required for 95 percent of the maximum yield may be chosen so long as a reasonable yield is obtained.

Table 7. Dry matter yield (g/pot) of maize and beans as a function of the adjusted P concentration in the soil solution

Adjusted P concentration (µg/ml)	Yield of Maize		Yield of Beans	
	Kaplustox	Vitrandept	Kaplustox	Vitrandept
0	7.1	2.9	5.4	4.3
0.3	8.5	3.7	5.5	4.3
0.5	10.7	6.8	6.5	6.9
1.0	10.4	8.3	6.5	8.4
2.5	10.0	10.0	7.9	8.7
5	11.3	10.9	9.2	9.5
10	14.1	10.9	9.1	11.0
15	14.4	11.1	9.5	11.0

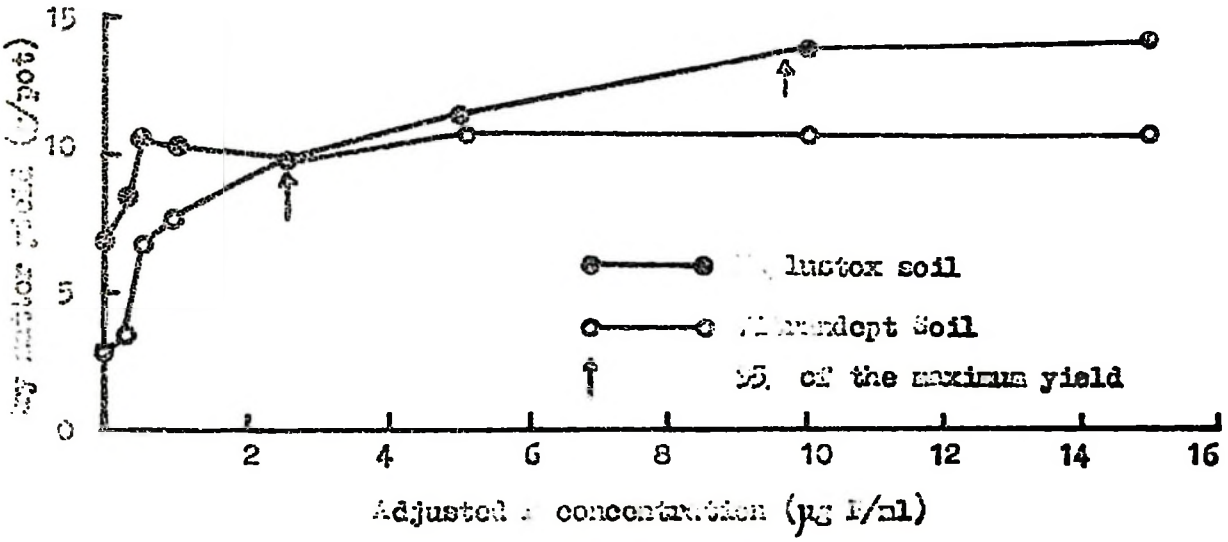


Fig. 5. Dry matter yield of maize as a function of adjusted P concentration in the soil solution

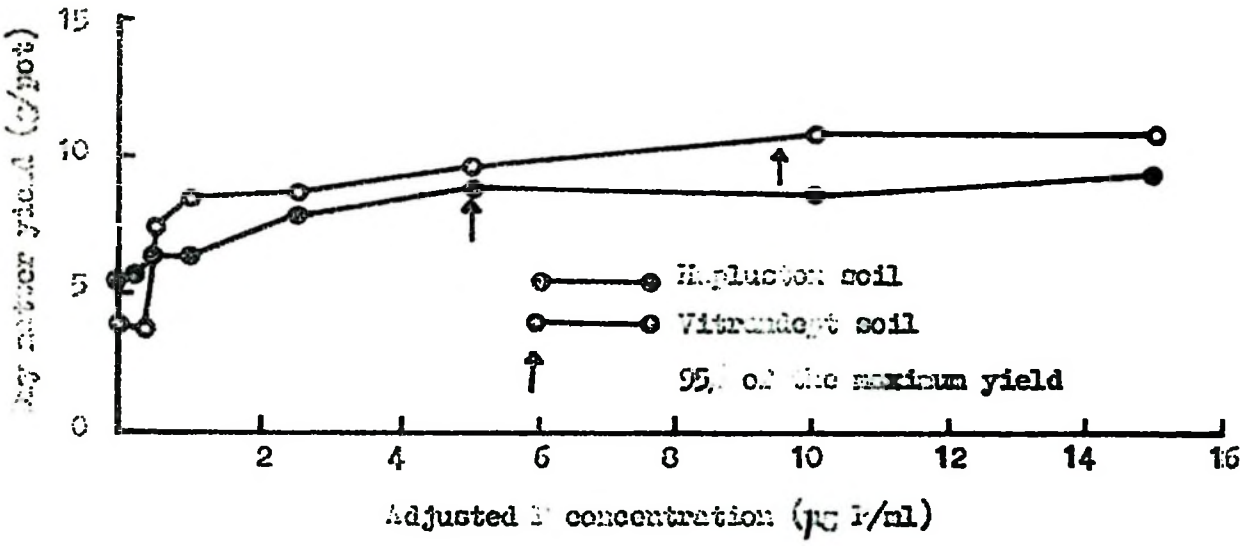


Fig. 6. Dry matter yield of bean as a function of adjusted P concentration in the soil solution

Plate 1. Growth pattern of bean in the Asplustox soil.

Plate 2. Growth pattern of bean in the Vitrandept soil.

Plate 3. Growth pattern of maize in the Haplustox soil.

Plate 4. Growth pattern of maize in the Vitrandept soil.

Plate 5. Phosphorus deficiency symptoms in maize grown in the Vitrandept soil.

Results obtained in this investigation apparently differ from those reported from elsewhere. Beckwith (1965) proposed a 0.2 µg/ml equilibrium-P concentration as being adequate for optimum growth of most plants. Silva and Fox (1974) reported an adjusted P concentration of 0.06 µg P/ml for the maximum yield of maize on Hawaiian soils. The data obtained in this study (Table 7; Figs. 5 and 6) show that much higher levels of adjusted P in solution than reported by Beckwith (1965) and Silva and Fox (1974) are required for maximum growth of maize and beans in the P maximum soils. Similar was the opinion of Mrema (1978). Based on his studies with an acid sandy loam soil in Reading (Britain), he felt that the equilibrium-P concentration of 0.2 µg/ml recommended by Beckwith (1965) and Fox and Kamprath (1970) cannot be generalised as it is dependent on environmental conditions such as climate, and soil factors such as mineralogy, chemistry and management as was also argued by Silva and Fox (1974) and Nishimoto et al. (1975). He observed that an equilibrium-P concentration of 0.61 µg P/ml was not adequate for attainment of maximum yield of cowpea (Vigna unguiculata).

The variation in the adjusted equilibrium-P requirements of the two soils is also of interest. Less equilibrium-P was needed for the Vitrandept soil for maximum growth of maize than for the Haplustox soil (Fig. 5). It has been argued (Fox and Kamprath, 1970; Mejan, 1975) that soils with higher capacity

of maintaining P in solution (higher P buffering capacity) are more efficient in supplying P to the plants than those with lower capacity. Apparently the Vitrandept soil was of higher P buffering capacity than the Haplustox soil and hence less P was required in the solution of this soil for rendering maximum yield of maize than that of the Haplustox soil.

2. Percentage P in Plant Tissues and its Uptake in Maize and Bean as Affected by the Adjusted P Concentration in the Soil Solution

There was a rapid linear increase in percent P in plant tissues as well as P uptake with increasing levels of adjusted P concentration, followed by a flat portion or plateau beyond certain concentrations which varied from soil to soil and crop to crop (Figs. 7 and 8). Similar observations were made by Mann (1979) in his studies with cowpea (Vigna unguiculata) grown on a sandy acidic soil at Reading (Britain). He observed an increase in P uptake with increasing levels of equilibrium-P up to 0.61 µg P/ml, the highest adjusted P concentration included in the test. The maximum level after which the curve flattened as observed in this investigation was not reached in his study. Olsen et al. (1961) also observed a linear increase in P uptake with increasing P concentration in the soil solution. They, however, did not reach a level where a decline occured.

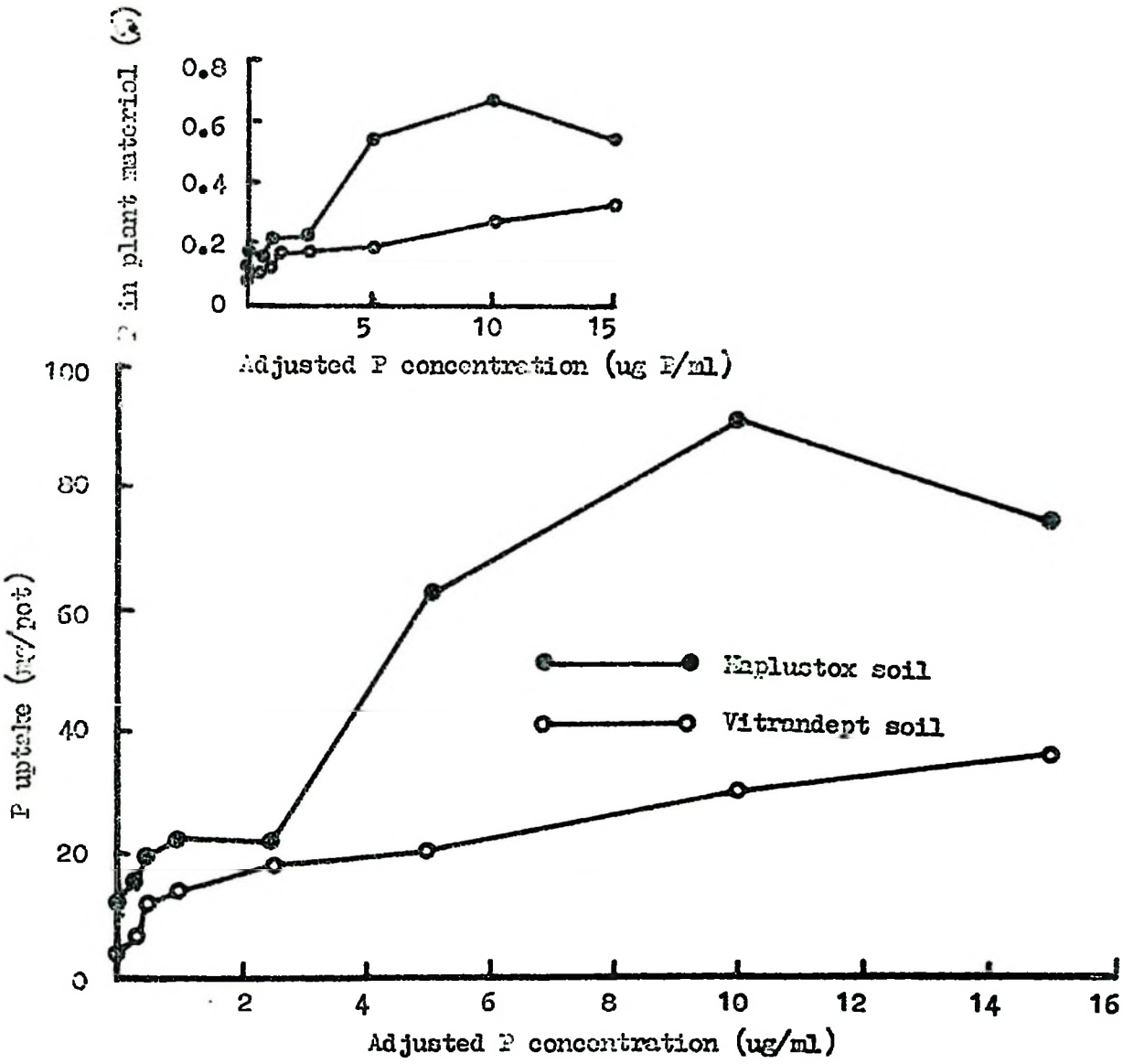
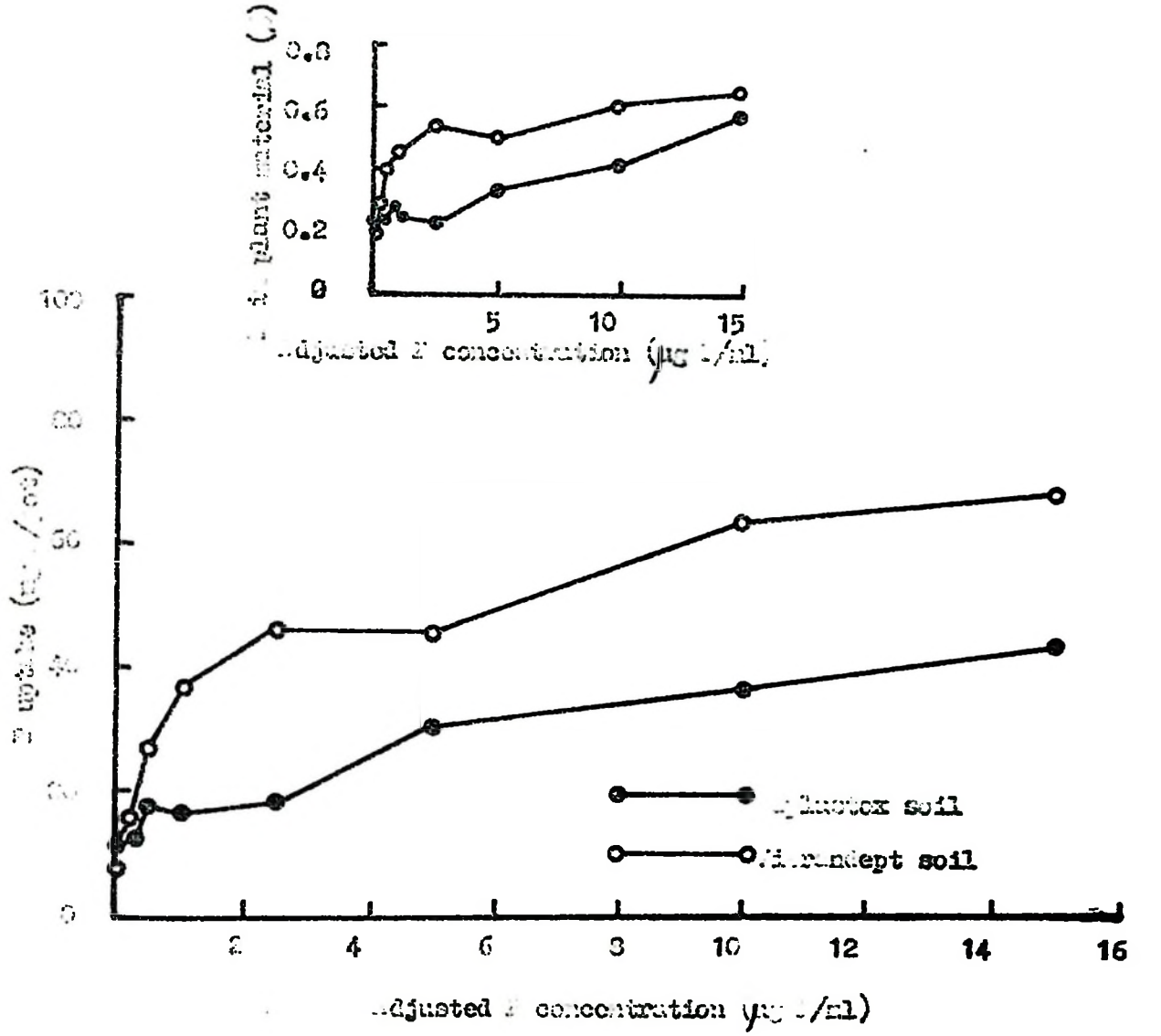


Fig. 7. Phosphorus uptake by maize as a function of adjusted P concentration in the soil solution



F. 3. Phosphorus uptake by bean as a function of adjusted P concentration in the soil solution

SUMMARY AND CONCLUSIONS

Sorption of phosphate in virgin Tanzanian soils belonging to the Great group Haplustox (kaolinite, AlOOH and hydrous oxides of iron as dominant minerals) and Vitrandept (mostly Al_2O_3) were investigated with respect to length of equilibration, initial concentration and pH of the equilibrating solution, organic matter content, and volume of equilibrants and their anionic composition. An attempt was also made to elucidate the equilibrium-P required for near maximum growth of maize (Zea mays L.) and bean (Phaseolus vulgaris L.).

There was rapid P sorption in both soils in the first half hour which slowed with increasing length of equilibration. Complete equilibration did not take place within the period tested, but a length of 24 hours appeared adequate for near complete equilibration. Beyond this period, the increase in the magnitude of sorbed-P was not appreciable.

The magnitude of sorbed-P increased consistently with increasing P concentration in the equilibrating solution. Appreciable P sorption occurred at concentration of 5 µg P/ml or higher in the equilibrating solution. No appreciable difference in P sorption was observed in the two soils at any one concentration. Selective dissolution analysis revealed that both soils contained appreciable and nearly equal amounts of AlOOH, indicating that P sorption was

mainly by displacement of - OH groups in [illegible] of these soils.

The initial pH of the equilibrating solution had virtually no effect on P sorption in both soils. It was attributed to high buffering capacity of the soils which resisted any appreciable change in the pH of the soil-solution suspension when solutions of different pH values were added.

In both soils, there was substantial increase in the phosphate sorption after destruction of the organic matter. The magnitude of increase due to destruction of organic matter was over three fold compared to that when it was not destroyed. Probably the sorption sites blocked by organic matter became available after its destruction.

The amount of desorbed-P increased with increasing volume of water, 1N KNO_3 or 1N K_2SO_4. The increase was probably due to more anions being available to desorb the sorbed-P at high than at low volume of the extractants. It was further observed that more phosphate was desorbed by SO_4^{2-} than NO_3^- ions. This was attributed to the fact that phosphate and SO_4^{2-} ions are "specifically sorbed" while NO_3^- ion is "non specifically sorbed". It was, therefore, possible that SO_4^{2-} ions were able to desorb more phosphate from the colloidal surfaces

than NO_3^- ions because of similarity in the sorption mechanism of phosphate and SO_4^{2-} ions. It was further noted that more phosphate was desorbed by all the extractants in the Vitrandept soil than in the Haplustox soil. It appeared that the Vitrandept soil had higher P buffering capacity than the Haplustox soil. The former soil may be capable of rendering more P available to plants than the latter.

Greenhouse studies revealed that in both soils, the dry matter yield of maize had been initially increased rapidly then gradually as the adjusted soil solution P concentration increased. On Haplustox soil, 95 percent of the maximum yield of maize was obtained at an adjusted P concentration of 9.7 μg P/ml. On the Vitrandept soil an adjusted P concentration of 2.6 μg P/ml was adequate for obtaining 95 percent of the maximum yield. For bean 95 percent of maximum yield was obtained at 9.5 and 5 μg P/ml adjusted P concentration in the Vitrandept and Haplustox soil, respectively. From economic considerations, however, adjusted P concentrations lower than that required for 95 percent of the maximum yield may be chosen so long as a reasonable yield is obtained.

The percentage P in the plant tissues and P uptake initially increased rather rapidly with increasing levels of adjusted P concentration. The rapid increase was followed by a flat portion or plateau beyond certain concentrations which varied

from soil to soil and crop to crop.

The following conclusions and recommendations can be made in view of the findings in this investigation:

1. Equilibrating the soils for P sorption for several days is unneccessary.

   A length of 24 hours appears to be adequate for routine work.

2. Further investigation is required on the effect of pH on P sorption in the soils as this study showed no effect contrary to most reports in the literature.

3. Addition of organic matter to the soils could be a necessary amendment measure as the study has clearly demonstrated that its removal from the soil led to substantial sorption of P.

4. In view of the prevailing and ever increasing high costs of phosphatic fertilizers, equilibrium-P concentrations less than those necessary for maximum yields of maize and bean could be recommended. This is suggested in view of the high adjusted P concentrations found necessary for attainment of the maximum yield of the crops in this investigation.

REFERENCES

Alexiades, C.A. and Jackson, M.L. (1966). Quantitative clay mineralogical analysis of soils and sediments. Clays and Clay Minerals. 14: 35-52.

Allison, L.E. (1965). Organic Carbon. In Black, C.A., Evans, D.D., Ensminger, L.E., White, J.L. and Clark, F.E. (eds.) Methods of Soil Analysis. pp. 1367-1379. American Society of Agronomy, Madison, Wisc.

Bache, B.W. (1963). Aluminium and iron phosphate studies relating to soils. I. Solution and hydrolysis of variscite and strengite. J. Soil Sci. 14: 113-123.

Barrow, N.J. and Shaw, T.C. (1975). The slow reactions between soils and anions. V. Effect of period of prior contact on the desorption of phosphate from soils. Soil Sci. 119: 311-320.

Barshad, I. (1965). Thermal analysis techniques for mineral identification and mineralogical composition. In Black, C.A., Evans, D.D., Ensminger, L.E., White, J.L. and Clark, F.E. (eds.) Methods of Soil Analysis. pp. 699-741. American Society of Agronomy, Madison Wisc.

Beckwith, R.S. (1965). Sorbed phosphate at standard supernatant concentrations as an estimate of the phosphate needs of soils. Austr. J. Exp. Agric. Anim. Husb. 5: 52-58

Bhat, L. and Bouyer, S. (1968). Influence de la matiere organique sur le phosphore isotopiquement diluable dans quelques types de soils tropicaux. In Isotopes and Radiation in Soil Organic Matter Studies. IAEA-Vienna. (quoted by Kalpage, F.S.C.I. Tropical Soils. pp. 110-124 (1974). Macmillan Press, London).

Bikerman, J.J. (1958). Surface Chemistry Theory and Applications. p. 199. Academic Press Inc., New York.

Bray, R.H. Kurtz, L.T. (1945). Determination of total organic and available phosphorus in soils. Soil Sci. 59: 39-45.

Bremner, J.M. (1965). Total Nitrogen. In Black, C.A., Evans, D.D., Ensminger, L.E., White, J.L. and Clark, F.E. (eds). Methods of Soil Analysis. pp. 1149-1178. American Society of Agronomy. Madison, Wisc.

Brown, H.G. and Loewenstein, H. (1978). Relationship of soil properties to P fixing capacity of soils in Northern Idaho. Comm. Soil Sci. and Plant Analysis.

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

Chapman, H.D. (1965). Cation-Exchange Capacity. In Black, C.A., Evans, D.D., Ensminger, L.E., White, J.L. and Clark, F.E. (eds.) Methods of Soil Analysis. pp. 891 - 901. American Society of Agronomy, Madison, Wisc.

Chapman, H.D. and Pratt, P.F. (1961) Methods of Analysis for Soils Plants and Waters. pp. 161-174. University of California, Riverside.

Chee, T.K., Furgeson, J.E., Campell, A.S. and Richmond, T.R. (1978). Phosphate sorption properties of some Fijian soils. N.Z.J. Sci. 21: 157-164.

Chen, T.T. and Wang, L.C. (1974). Phosphorus adsorption and available phosphorus indexes of some Taiwan soils. J.Chinese Agric. Soc.12: 78-80. (Abstract in Soils Fert. (1978) 41:12 (23).

Dalton, J.D. Russell, G.C. and Sieling, D.H. (1952). Effect of organic matter on phosphate availability. Soil Sci. 73: 173-181.

Fox, R.L. and Kamprath, E.J. (1970) Phosphate sorption isotherms for evaluating the phosphate requirements of soils. Soil Sci. Soc. Am. Proc. 34: 902-907.

Fox, R.L., Plucknett, D.L. and Whitney, A.S. (1968) Phosphate requirements of Hawaiian Latosols and residual effects of fertilizer phosphorus. Int. Cong. Soil Sci. Trans. 9th, Adelaide, Aust. 2: 301-310.

Fox, R.L., Hassan, S.M. and Jones, R.C. (1971). Phosphate and sulphate sorption by Latosols. Proc. Int. Symp. on Soil Fert. Evaln., New Delhi. 1: 857-864.

Fox, R.L., Nishimoto, R.K., Thompson, J.R. and De la Pena, R.S. (1974). Comparative external phosphorus requirements of plants growing in tropical soils. Int. Cong. Soil Sci. Trans. 10th, Moscow, Russia. 4: 232-239.

Gebhardt, H. and Coleman, N.T. (1974). Anion adsorption by allophanic tropical soils. III. Phosphate adsorption. Soil Sci. Soc. Am. Proc. 38: 263-266.

Griffin, R.A. and Jurinak, J.J. (1973). The interaction of phosphate with calcite. Soil Sci. Soc. Am. Proc. 37: 847-850.

Harter, R.D. (1969). Phosphorus adsorption sites in soils. Soil Sci. Soc. Am. Proc. 33 : 630-632.

Hingston, F.J., Atkinson, R.J., Posner, A.M. and Quirk, J.P. (1968). Specific adsorption of anions on goethite. Int. Cong. Soil Sci. Trans. 9th, Adelaide, Aust. 1: 669-678.

Jackson, M.L. (1958). Soil Chemical Analysis pp. 134-182. Prentice Hall Inc. Englewood Cliffs, New Jersey.

Jackson, M.L. (1967). Soil Chemical Analysis Advanced Course. Published by the author. University of Wisconsin, Madison, Wisc.

Kafkafi, U., Posner, A.M. and Quirk, J.P. (1967). Desorption of phosphate from kaolinite. Soil Sci. Soc. Am. Proc. 31: 348-353.

Kilmer, V.J. (1965). Silicon. In Black, C.A., Evans, D.D., Ensminger, L.E., White, J.L. and Clark, F.E. (eds.) Methods of Soil Analysis. pp. 959-962. American Society of Agronomy, Madison, Wisc.

Kuo, S. and Lotse, E.G. (1972). Kinetics of phosphate adsorption by calcium carbonate and Ca-kaolinite. Soil Sci. Soc. Am. Proc. 36: 725-729.

Low, P.A. and Black, C.A. (1950). Reactions of phosphate with kaolinite. Soil Sci. 70: 273-290.

Lopez-Hernandez, D.I. and Burnham, C.P. (1974). The effect of pH on phosphate adsorption in soils. J. Soil Sci. 25: 207-216.

Swenson, J.M., Warren, C.F. and Langston, R. (1959). Effect of iron, aluminum and humic acid on phosphorus fixation by organic soils. Soil Sci. Soc. Am. Proc. 23: 438-440.

Jackson, M.O. (1965). Aluminium. In Black, C.A., Evans, D.D., Ensminger, L.E., White, J.L. and Clark, F.E. (eds.) Methods of Soil Analysis. pp. 978-998. American Society of Agronomy, Madison, Wisc.

Mattson, S., Alvsaker, E., Kountler-Anderson, E., Berkoff, E., and Vahtras, K. (1950). Phosphate relations to soil and plant. Ann.Roy. Agric. Coll. Sweden. 17: 141-160

Muljadi, D., Posner, A.M. and Quirk, J.P. (1966). The mechanism of phosphate adsorption by kaolinite, gibbsite and pseudoboehmite. I. The isotherms and the effect of pH on adsorption. J. Soil Sci. 17: 212-229.

Mrema, J.P. (1973). The response of cowpea (Vigna unguiculata) to different levels of 0.5 M-NaHCO$_3$ soil soluble phosphorus and soil soil solution phosphorus. M. Agric. Sc. Thesis - University of Reading.

Munns, D.N. and Fox, R.L. (1976). The slow reaction that continues after phosphate adsorption: Kinetics and equilibrium in some tropical soils. Soil Sci. Soc. Am. J. 40: 46-51.

Nishimoto, R.K., Fox, R.L. and Parvin, P.J. (1975). External and internal phosphorus requirements of field grown Chrysanthemums. Hort. Sci. 10: 279-280.

Olsen, S.R. Watanabe, F.S. and Danielson, R.E. (19). phosphorus absorption by corn roots as affected by moisture and phosphorus concentration. Soil Sci. Soc. Am. Proc. 25: 289-294.

Olsen, S.R. and Watanabe, F.S. (1957). A method to determine a phosphorus adsorption maximum of soil as measured by the Langmuir isotherm. Soil Sci. Soc. Am. Proc. 21: 144-149.

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

Parfitt, R.L. and Atkinson, R.J. (1976). Phosphate adsorption on goethite. Nature Lond. 264: 740-742.

Parfitt, R.L. and Mavo, B. (1975). Phosphate fixation in some Papua New Guinea soils. Science in New Guinea 3: 179-190.

Parmar, K.M. (1978). Adsorption of nitrate and chloride in some Tanzanian soils dominant in allophanic and kaolinitic clays. M.Sc. Thesis - University of Dar es Salaam.

Peech, M. Cowan, R.L. and Baker, J.H. (1962). A critical study of the $BaCl_2$- triethanolamine and the ammonium acetate methods for determining the exchange hydrogen content of soils. Soil Sci. Soc. Am. Proc. 26: 37-40.

Rajan, S.S.S. (1973). Phosphorus adsorption characteristics of Hawaiian soils and their relationships to equilibrium phosphorus concentrations required for maximum growth of millet. Plant and Soil. 39: 519-532.

Rajan, S.S.S. (1975). Phosphate adsorption and the displacement of structural silicon in an allophane clay. J.Soil Sci. 26: 520-256.

Rajan, S.S.S. and Fox, R.L. (1972). Phosphate adsorption by soils. Influence of time and ionic environment on phosphate adsorption. Comm. in Soil Sci. and Plant Analysis. 3: 493-504.

Rajan, S.S.S. and Fox, R.L. (1975). Phosphate adsorption by soils. 11. Reactions in tropical acid soils. Soil Sci. Soc. Am. Proc. 39: 846-851.

Rajan, S.S.S. and Perrott, K.W. (1975). Phosphate adsorption by synthetic amorphous aluminosilicates. J. Soil Sci. 26: 257-266.

Rajan, S.S.S. Perrott, K.W. and Saunders, W.M.H. (1974). Identification of phosphate-reactive sites of hydrous alumina from proton consumption during phosphate adsorption at constant pH values. J. Soil Sci. 25: 438-447.

Rengasamy, P., Sarma, V.A.K. and Krishna Murti, G.S.R.(1975). Quantitative mineralogical analysis of soil clays containing amorphous materials: A modification of the Alexiades and Jackson procedure. Clays and Clay Minerals. 25: 78-80

Rengasamy, P., Sarma, V.A.K. and Krishna Murti, G.S.R. (1978). Mineralogy genesis and classification of ferruginous soils of the eastern Mysore plateau, India, J. Soil Sci. 29: 431-445.

Nicles, E.R. (1975). Phosphate sorption isotherms for some Sierra Leone soils. J. Sci. Fd. Agric. 26: 895-902

Ryden, J.C. and Syers, J.K. (1977). Desorption and isotopic exchange relationships of phosphate sorbed by soils and hydrous ferric oxides . J. Soil Sci. 28: 596-609.

Ryden, J.C., McLaughlin, J.R. and Syers, J. . (1977a). Mechanisms of phosphate sorption by soils and hydrous ferric oxide gel. J. Soil Sci. 28: 72-92.

Ryden, J.R. McLaughlin, J.R. and Syers, J.K. (1977b). Time dependent sorption of phosphate by soils and hydrous ferric oxides. J. Soil Sci. 28: 585-595.

Silva, J.A. and Fox, R.L. (1974). Assessing P. fertilizer requirements of soils with phosphorus sorption ... isotherms. Planning and Org. Meeting Fertilizer Input Project Oct. 2-25-Honolulu: 100-105.

Singh, B.B. and Jones, J.P. (1976). Phosphorus sorption and desorption by organic residues. Soil Sci. Soc. Am. J. 40:389-394.

Soil Survey Staff, (1975). Soil Taxonomy: A basic system of soil classification for making and interpreting soil surveys. Agric. Handbook 436 U.S. Dept. Agric. Washington, D.C.

Stout, P.R. (1939). Alterations in the clay structure of clay minerals as a result of phosphate fixation. Soil Sci. Soc. Am. Proc. 4: 177-184.

Taylor, R.J. and Ellis, B.G. (1978). A mechanism of phosphate adsorption on soil and anion exchange resin surfaces. Soil Sci. Soc. Am. J. 42: 432-436

Udo, E.J. and Uzu, F.O. (1972). Characteristics of phosphorus adsorption by some Nigerian soils. Soil Sci. Soc. Am. Proc. 36: 879-883.

Uriyo, A.P. and Kesseba, A. (1972). An evaluation of NH_4F as a selective extractant for Al-P in two soils of the tropics. Geoderma 8: 207-220.

Uriyo, A.P. and Kesseba, A. (1973). Phosphate fractions in some Tanzanian soils. Geoderm. 10: 191-192.

Uriyo, A.P. and Kesseba, A. (1975). Amounts and distribution of organic phosphorus in some profiles in Tanzania. Soil Sci. 119: 119-126.

Van Raij, B. and Peech, M. (1972). Electrochemical properties of some Oxisols and Alfisols of the tropics. Soil Sci. Soc. Am. Proc. 36: 587-593.

Williams, E.G., Stout, P.M. and McDonald, M.J. (1958). Soil properties and phosphate sorption. J. Sci. Fd. Agric. 9: 551-559.

White, R.E. and Taylor, A.W. (1977). Effect of pH on phosphate adsorption and isotopic exchange in acid soils at low and high additions of soluble phosphate. J. Soil Sci. 28: 48-61

Woodruff, J.R. and Kamprath, E.J. (1965). Phosphorus adsorption maximum as measured by the Langmuir isotherm and its relationship to phosphorus availability. Soil Sci. Soc. Am. Proc. 29: 148-150.

Appendix 1.

Soil Profile Characteristics

A. Nzumbe Soil

(i) External Features

Location: Nzumbe Secondary School, Morogoro.

Map Coordinates: 36° 56' E 37° 55'.

Date of Description and Sampling: 25th July, 1977.

Elevation: Approximately 520m.

Climate: Rainfall: Mean Annual: 670mm.

Classification: Ustic.

Soil Temperature: Iso-hyperthermic

Geology: Metasediments of the Usagaran System.

Petrography: Micaceous gneiss.

Mode of Formation: Formed in place.

Land Form: General: Flat to undulating.

Specific at site: Slope gradient: 3-4%

Slope direction: Northwestwards.

Slope Form: Linear

Position on slope: Upper middle.

Vegetation: Natural: Woodland.

Present Land Use: Maize farming

Drainage: Moderate to rapid.

Rock outcrops: None.

Stoniness: None.

Erosion: Nil

Specific remarks: Soil samples collected at depth of 0-15cm.

(ii) Internal features

A_I. 0-19 cm Dark reddish brown (2.5 YR 3/4 dry), dark reddish brown (5YR 3/3 wet); clay loam; moderate fine porous crumb structure; slightly sticky and slightly plastic when wet, many fine to medium discontinuous random inped pores; abundant fine and few medium roots; artifacts absent; presence of insect nests; clear and smooth boundary towards B_{21}

B_{21}. 19-49 cm Dark red (2.5 YR 3/6 dry), dark red (2.5YR 3/6 wet); clay loam; weak to moderate porous sub-angular blocky structure; sticky and plastic when wet, friable, soft; no cutans; many fine discontinuous random inped and few medium exped pores; many fine and few medium roots; arbitrary boundary towards B_{22}.

B_{22}. 49-120cm. Dark red (10R 4/6 dry), dark red (10R 3/6 wet); clay loam; moderate fine porous sub-angular blocky structure; slightly sticky and stightly

plastic when wet; friable, soft; no cutans; abundant fine discontinuous random inped pores; few fine and coarse roots. The lower boundary of B_2 was not reached.

B. Olmotonyi Soil

(i) External Features

Location: Olmotonyi Forest Reserve, Arusha.

Map Coordinates: E35° 39' N 3°16'.

Date of Description and Sampling: 15th July, 1977.

Elevation: Approximately 1,600m.

Climate: Rainfall: Mean annual 950mm.

Classification: Udic.

Soil Temperature: Isothermic.

Geology: Neogene - Volcanic formation.

Petrography: Basic volcanic ash.

Mode of Formation: Formed in place.

Land Form: General: Hilly

Specific at Site: Slope gradient - 10%

Slope form: Convex.

Slope direction: Northeastwards.

Position on slope: middle.

Vegetation: Natural: Forest

Present Land Use: Forest reserve. Pinus patula-dominant.

Drainage: Well drained.

Rock outcrops: None

Stoniness: None

Erosion: Nil

Specific remarks: Soil samples collected at depth of 0-15cm.

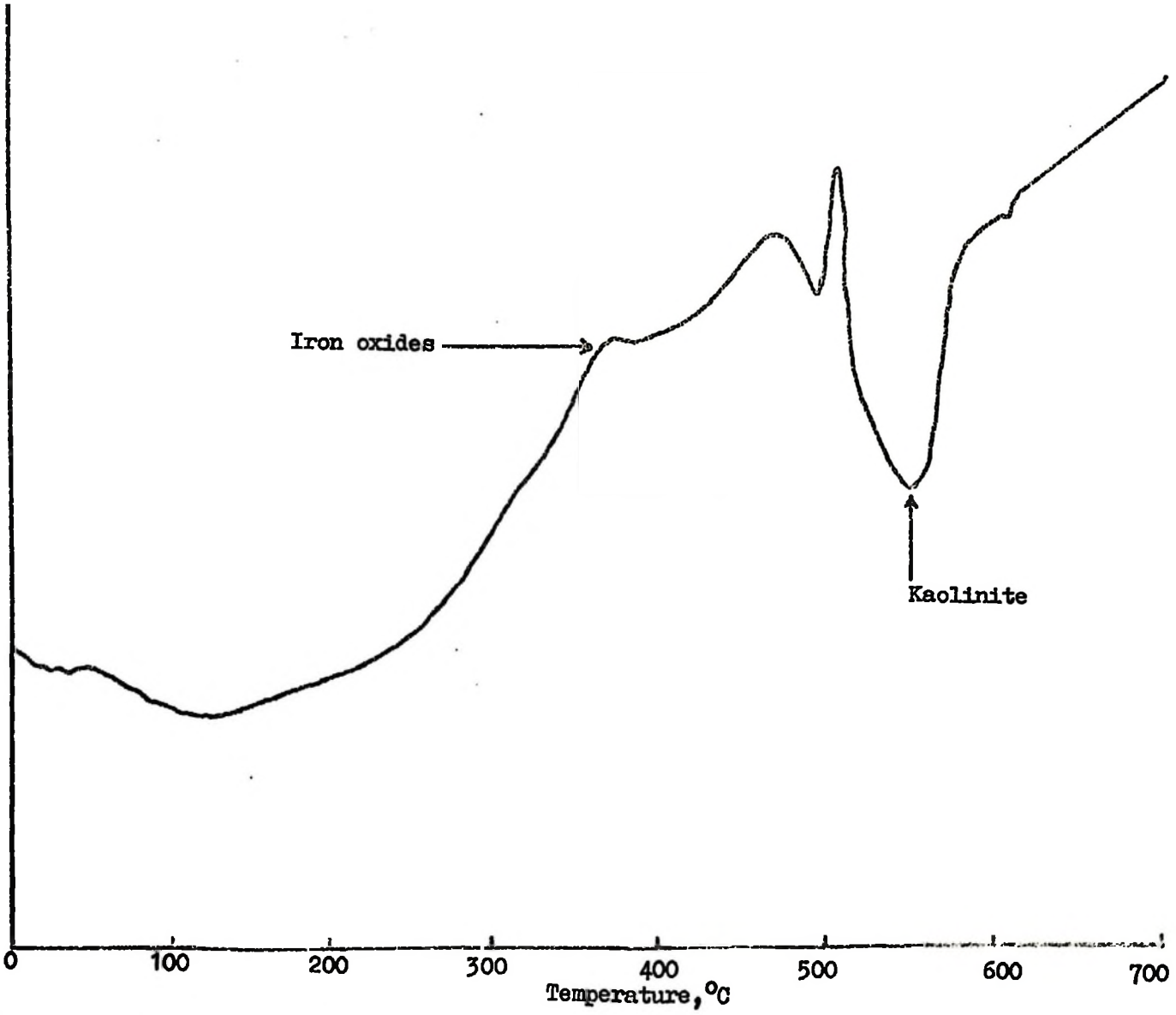
(ii) Internal Features

A. 0-20cm Very dark greyish brown (10YR 3/2 dry), very dark brown (10YR 3/2 wet); silt loam; weak very fine porous crumb structure; slightly sticky, non-plastic when wet, friable, soft; many fine discontinuous random in ped pores; abundant fine roots; artifacts absent; presence of insect nests and worm casts; clear smooth boundary towards an albic horizon.

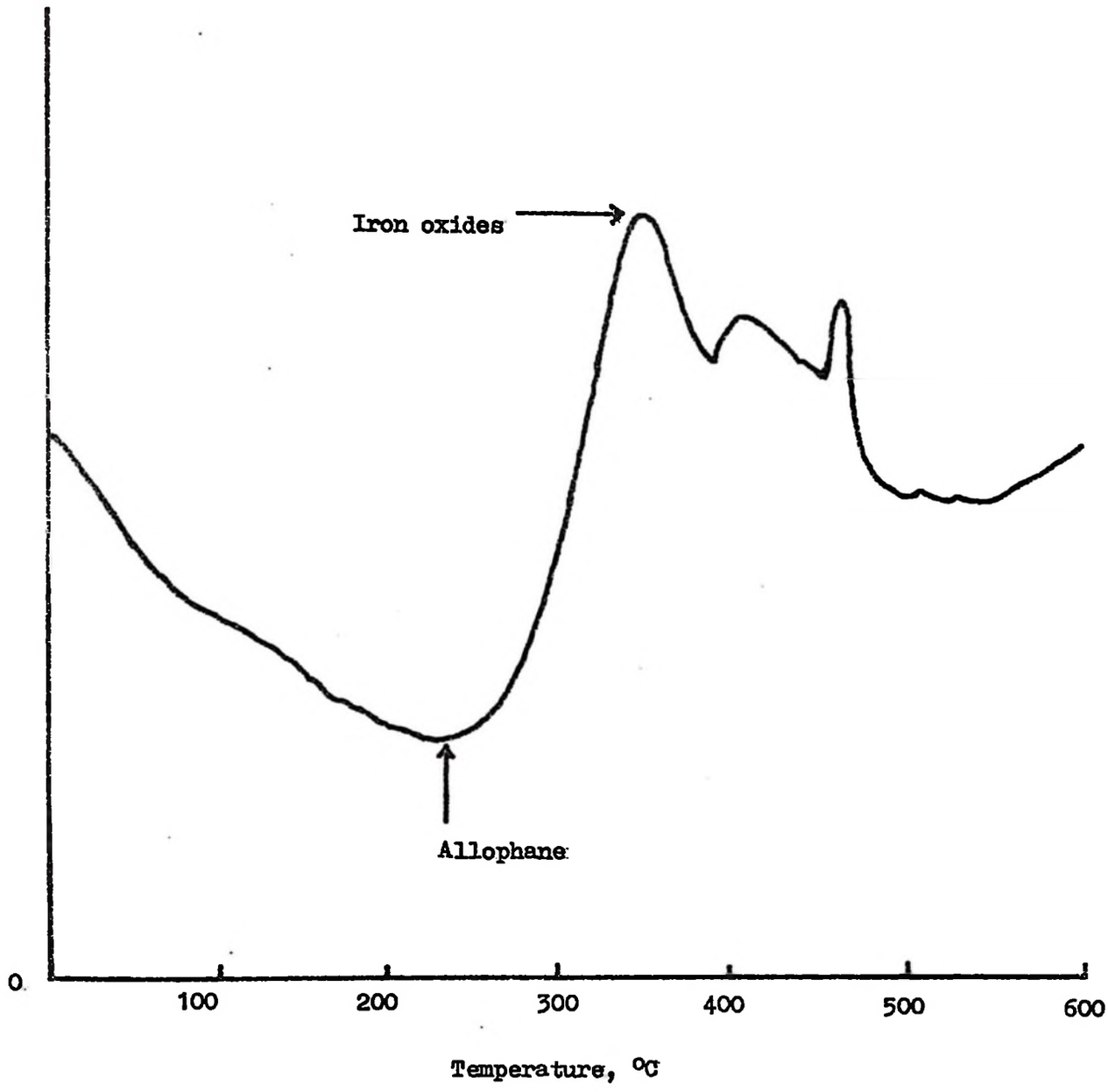
20-30cm (albic horizon)

Grey (10YR 6/1 dry), very dark greyish brown (2.5YR 3/2 wet); silt loam; weak to moderate fine porous sub-angular blocky structure; non-stiky and non-plastic, friable, slightly hard; absence of cutans; many fine discontinuous random inped pores; many medium roots; artifacts absent; abrupt smooth boundary towards II.

II. 35-150+cm Dark brown (10YR 3/3 dry), black (7.5YR 2/0 wet); silt loam; moderate fine sub-angular blocky structure; slightly sticky and slightly plastic when wet, friable, soft; absence of cutans; common discontinuous irped micro-pores; absence of artifacts. Lower boundary of II was not reached.



Appendix 2. Differential thermal analysis for the Haplustox soil



Appendix 3. Differential thermal analysis for the Vitrandept soil