PHOSPHORUS ADSORPTION MAXIMA OF SELECTED GHANAIAN SOILS AND THEIR RELATIONSHIP TO PHOSPHORUS AVAILABILITY

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INTRODUCTION

An adequate knowledge of the chemical reactions which occur when fertilizer is placed in soils is a pre-requisite to the development of sound fertilizer practices. Without such a knowledge, there is the possibility of applying either too much or too little fertilizer than is necessary with its consequent crop failure. Phosphorus is one of the major nutrient elements required by plants for growth. The role of phosphorus in plant nutrition includes its effect on cell division, flowering, fruiting and seed formation, crop maturation, root development, especially of lateral and fibrous rootlets, strength of straw in cereals, and crop quality of vegetables.

The problem of phosphorus deficiency in Ghanaian soils and its attendant low crop yields has long been recognized by many research workers. Between 5.0 ppm and 14.5 ppm phosphorus has been found in the topsoil (0" - 6") of many forest profiles in Ghana (Hardy and Amoroso-Centeno 1938; DeEndredy and Montgomery 1954; Nye 1952). Using Bray's rapid extraction procedure with 0.1N HCl and 0.03N NH_4F Nye (1952) obtained 4 ppm phosphorus in the topsoil (0" - 6") of sixty-three soils from savanna sites in Ghana. In spite of these very low value of available phosphorus in Ghanaian

soils, Nye (1952) reports that response to phosphorus application has not been always conclusive. This lack of response has often been attributed to the high fixation capacity of tropical soils, especially the strong acid ones with high content of iron and aluminium rendering small dressings of phosphate ineffective.

Several observations made by agronomists the world-over on crop response to applied phosphate give credence to those made in Ghana. These indicate that fertilizer phosphate after it has been applied is not recovered wholly in the crop that is immediately planted. Hemwall (1957) in a review, reports that crops recover only 10 to 30% of applied phosphorus. Sauchelli (1965) also reports that plants on phosphorus-fertilized soils generally recover just 20 to 30% of the added phosphate. The general consensus among soil chemists is that chemical precipitation and colloidal adsorption are chiefly responsible for the loss.

As indicated earlier on, most Ghanaian soils are deficient in phosphorus and yet would not give any response to applied phosphorus fertilizer. Investigation by many research workers have also proved the methods of assessing the availability of phosphorus quite inadequate. We therefore propose to tackle the problem of phosphorus availability studies from another angle.

In our view before any economic yield can be realized from any phosphorus fertilizer application it is necessary to understand the phenomenon of phosphorus adsorption in soils and how the phosphorus is made available to plants. The purpose of the present study, therefore, is to investigate the phosphorus adsorption phenomenon in some selected Ghanaian soils with a view to greater understanding of the ways of avoiding problems associated with phosphate fertilizer application to these soils and also with a view to maximizing the efficient use of such fertilizer applications. The research programme was designed to:-

(i) determine the phosphorus adsorption maxima of selected Ghanaian soils using the Langmuir isotherm as modified by Olsen and Watanable (1957),

(ii) relate these maxima to phosphorus availability,

(iii) relate the adsorption maxima to some soil properties and,

(iv) estimate the rates of P application necessary to obtain optimum yield on the soil series used.

CHAPTER I
LITERATURE REVIEW

1.1. Definition of the terms Adsorption and Availability.

Adsorption may be defined broadly as the attraction of ions or compounds to the surface of a solid. Silicate clay minerals have on their broken or exposed edges hydrous oxides of aluminium and iron. These complex hydrous oxides of aluminium and iron when in contact with soil solution become hydrolyzed as follows:-

$$R\text{-}OH + HOH = R\text{-}OH_2^+OH^- \quad .. \quad .. \quad .. \quad .. \quad (1)$$

The hydroxyl ions of the complex aluminium or iron hydrous oxides thus formed can exchange positions with the phosphate ions in solution supplied from a native or fertilizer phosphorus source as shown in equation (2).

$$R\text{-}OH_2^+OH^- + H_2PO_4^- = R\text{-}OH_2^+H_2PO_4^- + OH^- \quad .. \quad .. \quad (2)$$

$$R\text{-}OH_2^+OH^- + H^+Cl^- = R\text{-}OH_2^+Cl^- + H^+OH^- \quad .. \quad .. \quad (3)$$

$$R\text{-}OH_2^+Cl^- + H_2PO_4^- = R\text{-}OH_2^+H_2PO_4^- + Cl^- \quad .. \quad .. \quad (4)$$

Alternatively the hydroxyl ions can exchange places with Cl^-, $SO_4^{-\ -}$ or NO_3^- ions in solution which in turn can be exchanged with phosphate ions in solution (refer to equations (3) and (4) above). Also calcium attached to clay minerals may attract to themselves hydroxyl ions or other anions.

These attached ions may, in the presence of phosphate ions, exchange places. Furthermore, phosphate ions in solution may be attracted directly to the calcium attached to clay minerals. In either of these latter reactions involving calcium attached to clay minerals a clay-Ca-phosphate linkage is formed. The phosphate ions so attracted are said to be adsorbed phosphate ions and the mechanism involved is correspondingly termed adsorption or, more specifically, phosphate adsorption.

Evidence in support of the above theory of phosphorus adsorption is provided by Fried and Dean (1955). They determined the phosphate-fixing characteristics of iron- and aluminium-saturated cation exchange resins. They found that these materials are capable of fixing phosphorus and concluded that a similar phenomenon could occur in the soil via the clay minerals. They also presented experimental data which show that 75% of the phosphorus retained by the ferrated exchange resins was readily exchangeable with radioactive phosphorus. They stated that this is an "improbably high exchangeability for a precipitate" and, hence, must be an adsorption.

The term "available", as applied to nutrients, refers to their existence in the soil in a chemical condition

in which they may be absorbed by plant roots or may be readily converted into such a condition. Nutrients adsorbed on colloidal fraction in an easily replaceable state would be considered available in this context. Phosphate which is soluble and capable of entering the soil solution and of being absorbed by plants would, therefore, be considered as available phosphorus.

The availability of inorganic phosphorus is largely determined by the following factors: soil pH; soluble iron, aluminium, and manganese; presence of iron-, aluminium-, and manganese - containing minerals; available calcium and calcium minerals; amount and extent of decomposition of organic matter and the activities of microorganisms.

Phosphorus availability can be assessed in diverse ways. Different research workers adopt different methods which best suit their particular objective to establish phosphorus availability. In this particular research work the straight chemical extraction procedure whereby the available inorganic phosphorus is extracted with dilute acids and bases was adopted for assessement of the availability index of the native phosphorus in the soils used for the study. Availability of applied phosphorus was also assessed by plant uptake and subsequent chemical analysis of the plant

for the inorganic phosphorus concentration.

1.2. The Phosphorus Adsorption Phenomenon.

Phosphorus fixation was first recognized in Europe around 1850. At that time, reports Hemwall (1957), various workers in the field just reported that soil had the ability to "retain" phosphorus. Similar reports were known to have appeared in the United States shortly after 1900. Yet the greatest strides which helped to throw light on the basic chemistry of this phenomenon and how to control it began only in the 1930's.

G. Barbier and associates in France (quoted by Sauchelli (1965) pp. 163) concluded from an experiment conducted over a period of ten years that almost all of the soluble phosphate added to the soil remained after ten years in forms which are either extractable by dilute acids or are capable of returning spontaneously to the first form under natural conditions. The first form comprises a linkage of phosphoric ions with exchangeable cations notably calcium located on the surfaces of the clay. The resultant combination represents a sort of adsorption phenomenon. This exchangeable phosphate, they believed, can pass back and forth in solution in the presence of dilute acids. The second form is believed to comprise a linkage of phosphate ions with exchangeable cations,

notably iron, whose hydroxides strongly hold on to phosphate ions in an acid medium but are easily released in an alkaline medium.

Report from an Illinois Bulletin (also quoted by Sauchelli (1965) pp. 166) stated that soluble phosphate fertilizers are either adsorbed on surfaces of clay minerals as "adsorbed phosphorus" or are changed to forms of calcium phosphate which are designated as "easily acid-soluble" phosphorus. The added phosphorus fertilizers are not reverted to unavailable forms on contact with the soil as had been reported earlier by some workers. Infact the adsorbed and easily acid-soluble forms of phosphorus are believed to be of primary importance in plant feeding.

E.G. Williams of the Macauley Institute for Soil Research, Aberdeen, is quoted by Sauchelli (1965, pp. 165) to have likened the adsorption of phosphate to the taking up of water by sponge. When only a small amount of water is added to a dry sponge it is held tightly, but as more water is added it becomes more easily squeezed out. In an analogous manner according to Williams, the reserve of phosphate in the soil must be built up to a certain extent before the phosphate becomes available to plants.

A research work carried out by Sell and Olsen (1946) gives credence to Williams' postulate referred to above. Sell and Olsen (1946) found that the higher the amount of phosphorus applied the greater the amount of phosphorus available to the plant that grows on the soil. It is indicative from the results that a soil has a certain capacity to fix phosphorus, and after that capacity has been filled, phosphorus may then become available.

A pertinent question to pose at this juncture, however, is what are the fixation capacities of various soils of agricultural importance? This question had plagued the minds of many of the earlier researchers. In their bid to find solutions they conducted experiments designed to study phosphorus adsorption. Davis (1935), Kurtz et al. (1946), and Russell and Low (1954) pointed out from their respective studies that the reaction of added phosphorus with soils at low concentrations can be described by means of the classical Freundlich equation. This equation expresses the relation between adsorption and concentration and may be stated as $X/m=KC^{P}$, where X is the amount of solute adsorbed by m grams of soil, C is the equilibrium concentration of the solution and K and p are constants.

Burd and Murphy (1939) proposed that a knowledge of the degree of the adsorption constituents of a soil should help provide a useful index of phosphate availability. This degree of saturation of the adsorption constituents of a soil can be calculated if the amount of adsorbed phosphate actually present in the soil is known, together with the amount of phosphate which the adsorbing minerals could hold at saturation. This latter quantity is the adsorption capacity or adsorption maximum of the soil for phosphorus.

Olsen and Watanabe (1957), Thompson (1958), Rennie and McKercher (1959), Weir and Soper (1962), Gunary (1970), Udo and Uzu (1972) and Syers et al. (1973) have made use of Langmuir (1918) isotherm to calculate phosphorus adsorption maxima in soils. The adsorption equation of Langmuir (1918) is based on a theoretical consideration of the process of adsorption. It may be expressed as:-

$$x/m = \frac{Kbc}{1 + Kc}$$

in which x is the amount of solute adsorbed by the mass m of soil, c is the equilibrium P concentration, b is the adsorption maximum and K is a constant related to the bonding energy of the absorbent for the absorbate.

In linear form: $c/(x/m) = \frac{1}{Kb} + \frac{c}{b}$

For cases in which the equation represents the data c/(x/m) may be plotted as a linear function of c with slope 1/b and intercept 1/Kb.

The Langmuir euqation is preferred by most workers to the Freundlich equation in that the former has a sound theoretical derivation, is specific for smaller amount of adsorbed phosphorus and more dilute equilibrium phosphorus concentration (more likely to be encountered in normal phosphorus fertilizer application). Moreover with the Langmuir equation an adsorption maximum can be calculated whereas in the more empirical equation of Freundlich calculation of adsorption maximum is impossible.

The Langmuir adsorption equation,like most other good things, has its drawbacks too. One disadvantage of the equation is that at higher equilibrium concentrations the plot of c/(x/m) against c fails to give a linear relationship. Olsen and Watanable (1957) and Thompson (1958) for instance, found that in more concentrated solutions the Langmuir plots were no longer linear. Weir and Soper (1962) in adsorption and exchange studies of phosphorus observed that the phosphorus adsorption followed the Langmuir isotherm only when the phosphorus solution concentrations were less than 25 to 30 micrograms

phosphorus per millilitre of solution.

Hsu and Rennie (1962) in a study which included, among other things, an investigation of the Langmuir adsorption isotherm as an indicator of adsorption found that a straight line relationship of the plot of c/(x/m) against c suggests that the main reaction removing phosphate from solution is possibly adsorption. They found also that where precipitation of phosphate occurs the plot fails to give the straight line relationship. However, they believed that when phosphate precipitated is much less than that adsorbed on the soil surface a straight line relationship is evident.

Larsen (1967) also argued that "it is doubtful that their (Olsen and Watanabe's 1957) observation even at lower concentrations are generally applicable." Larsen based his argument on the fact that at Levington Research Station, phosphorus adsorption isotherms were determined for 120 soils and the relationship between c/(x/m) and c was curvilinear in the majority of the soils even when they were equilibrated with very dilute solutions giving equilibrium concentration values of phosphorus less than 6×10^{-4}M.

Gunary (1970) in a study designed to find out adsorption isotherm for phosphate in soils observed that on a range of soils he worked with phosphate sorption does not

obey the Langmuir equation. He further questioned the reliability of phosphate adsorption maximum values calculated from the Langmuir equation. Gunary based his criticism on the fact that for 24 soils used in the above study the plot of c/(x/m) against *c* appeared to be slightly but consistently convex to the *c* axis. He therefore suggested alternative equations of which the one given below was observed to give the best fit:

$$1/y = B + A/C + D/C$$

where *y* is the adsorbed phosphate, *c* is the equilibrium concentration of phosphate in solution and *B*, *A*, and *D* are all constants.

Syers *et al.* (1973) also found out from their study that two linear relationships are obtained when phosphate sorption data are plotted according to the conventional Langmuir equation. They proceeded further to rearrange the Langmuir equation as follows:-

$$x/m = K_2 - (x/m)/K_1C$$

in which x/m is the amount of P adsorbed per unit weight of soil, K_1 is a constant related to the bonding energy, K_2 is the adsorption maximum and *C* is the equilibrium P concentration. The rearranged form of the Langmuir equation according to Syers *et al.* (1973) should be preferred

to the conventional Langmuir equation, since it is more useful for evaluating phosphate sorption at low equilibrium phosphorus concentrations.

In view of the fact that the percentage saturation of adsorption maximum may serve as a measure of the capacity of the soil to supply phosphorus to the soil solution and hence to plant roots in contact with this solution, Woodruff and Kamprath (1965) studied the relationship between the growth of millet and the degree of saturation of phosphorus adsorption maximum. They found that soils with large P adsorption maximum did not require as high a P saturation as those with a low P adsorption maximum. They therefore concluded that P adsorption are important parameters in the study of soil phosphorus levels needed for optimum growth.

1.3. Factors Affecting Phosphorus Adsorption in Soils.

Even though the work of Olsen and Watanabe (1957) provided the basis for determination of phosphorus adsorption maximum of soils, it did not provide information concerning the mechanism by which phosphorus is retained. Several workers however, have attempted to relate phosphorus adsorption to soil properties. Compound of iron and aluminium, soluble calcium and clay minerals have

been investigated to determine their role in phosphorus fixation. The iron and aluminium oxides and hydroxides have been recognized by many workers as playing significant role in phosphorus fixation. Several arguments in support of this view are presented in reviews by Dean (1949), Wild (1950), and Hemwall (1957). The most direct argument is based on the observation that phosphate sorption is reduced markedly when oxides of aluminium and iron are removed by chemical extraction. Toth (1937) and (1939), and Kelley and Midgley (1943) used the hydrogen sulphide method of Drosdoff and Truog (1935) to show that the removal of iron and aluminium-oxides from soil colloids reduced phosphate sorption. A similar result has been reported by a number of workers (Black, 1942; Chandler, 1941; Coleman, 1942 and 1944 (a); Metzger, 1934) after iron and aluminium had been removed by slightly modified hydrogen sulphide method after Truog *et al.* (1936).

Many other early workers (Davis, 1935; Kelley and Midgley, 1943; Perkins and King, 1944; Kurtz *et al.*, 1946 Ensminger, 1948; Swenson *et al.*,1949; Struthers and Sieling, 1950; Bradley and Sieling, 1953) also have postulated and demonstrated that oxides of iron and aluminium play an important role in phosphorus fixation.

Several recent reports presented by Williams et al., (1958), Coleman et al., (1960) and Bromfield (1965), however, indicated that aluminium plays a more dominant role in phosphorus retention than iron. The work of Weir and Soper (1963) also indicated and confirmed previous observation that organometallic complexes may also be important in phosphate sorption. Saini and MacLean (1965) in their investigation with some New Brunswick soils also found that aluminium exerted more influence on phosphorus retention capacity than iron. They also found a significant correlation between organic matter and retention capacity but clay per se was adjudged to be a less important criterion of phosphorus retention.

Correlations have been established between phosphate sorption and the amounts of iron and aluminium in soils and also the ratio of SiO_2 to Fe_2O_3 plus Al_2O_3. Several investigators, namely Mattson (1931), Scarseth and Tidmore (1934), and Toth (1937) have shown that phosphate sorption varies inversely as the $SiO_2/(Fe_2O_3 + Al_2O_3)$ ratio of soil colloids decreased. Metzger (1941) also using forty-two soil samples found a significant correlation between total Al_2O_3, $(Al_2O_3 + Fe_2O_3)$, and phosphate sorption in soils.

Thompson (1957) reported that the amount of free iron and aluminium (that which is not combined in the clay crystal) greatly affects the solubility of phosphorus.

He claimed that as the ratio of iron plus aluminium to silica increases consequent upon the weathering of silica there is a corresponding increase in active iron and aluminium combined with phosphate to form insoluble compounds. Thompson (1957) therefore subscribed to the opinion of many research workers that a high efficiency from the use of soluble phosphate can best be associated with soils low in free iron and aluminium. Soils high in free iron and aluminium have a high fixing capacity for phosphate.

Sauchelli (1965) also observed that the solubility of phosphate in the soil is influenced greatly by the kind of chemical compounds present. Sauchelli therefore listed, among other things, a high silica to sesquioxide ratio as a factor favouring the solubility of phosphate in soil solutions.

Coleman (1944(a) and (b) was, infact, the first soil scientist clearly to postulate that phosphate fixation by clay minerals is due to the aluminium content of the clays and has nothing to do with the intact clay minerals. He showed that the amount of phosphorus fixed by clays is proportional to the amount of free aluminium oxides on the clays.

Williams et al. (1958) found that aluminium extracted by the Tamm acid-oxalate method gives highly significant correlations with phosphate sorption in all groups of soils they worked with. It is, in their opinion, the best single criterion of phosphate sorption.

Bromfield (1965) from studies on relative importance of iron and aluminium in phosphate sorption concluded tentatively that for most soils phosphate sorption was due to acid soluble aluminium. The contribution of reducible iron in the original soils, according to Bromfield, remains in doubt, but he claimed it could be but a minor one as well.

Pissarides et al. (1968) however, found that the values obtained for the phosphorus adsorption maxima of soils they worked with were a function of both the type of clay and the saturating cations.

Rajagopal and Idnani (1963) working with some of the laterite and acid soils of South India found that free oxides of iron and aluminium were more reactive than the combined oxides in respect of P fixation.

Ahenkorah (1968) in Ghana also concluded that organic carbon, iron and their interactions with pH are the dominant factors active in phosphorus retention by Ghana cocoa growing soils.

Syers et al. (1971) in their investigation on phosphate sorption parameters found that for most soils components such as crystalline iron oxides and associated alumina which are not extracted by oxalate are apparently involved in the sorption of added phosphate. These findings however, contradict those obtained from a range of Scottish soils by Williams et al.(1958) referred to in a previous paragraph. In this latter study, treatment of soils with oxalate lowered the phosphorus adsorption capacity by between 80 and 95 percent. For a large number of Australian soils (Bromfield, 1965) the phosphorus adsorption capacity after oxalate treatment was reduced by between 6 and 67 percent.

Shukla et al. (1971) also found in their study that oxalate-extractable iron is the most important contributor to the sorption of added phosphorus by non-calcareous and calcareous lake sediments.

Biddappa and Venkat Rao (1973) working on coffee soils of South India reported that free iron oxides were seen to show high correlation with phosphorus fixing capacity indicating that free iron oxides are more active in trapping the phosphorus in the soils thus rendering it unavailable.

Phosphorus fixation in alkaline and calcareous soils is usually attributed to the formation of phosphate

compounds of calcium. In addition, however, iron and aluminium are also responsible for some fixation in soils of higher pH. Burd (1948) working with calcareous soils pointed out that the very general occurrence of potentially soluble calcium-compounds in soils and the relatively low solubility of the calcium-phosphates would lead to the formation of some form of calcium-phosphate upon the addition of phosphatic fertilizers. He showed that the concentration of calcium in the soil solution is the dominant factor in determining phosphate concentration in the liquid phase of the soil, thus confirming the role of calcium in phosphate fixation.

1.4. Methods of Determination of Available Phosphorus.

Generally, the determination of soil nutrient supply can be made in the laboratory in two ways:

a.) by chemical methods, and

b.) by biological methods.

Chemical methods involve techniques of extracting the nutrient in question with different chemical extracting reagents. Biological methods include those techniques in which the nutrient is extracted from the soil by agents such as bacteria, fungi, algae, seedlings, and even entire plants.

1.4.1. Chemical Methods of Determination of Available Phosphorus.

Of the procedures for assessing available phosphorus in soils chemical extraction methods have been found most convenient. This is because chemical determinations can be made rapidly. Present-day instrumentation is such that chemical methods, when used in modern laboratories, can be accurate and rapid. The main problem, however, is to select a chemical method which will give as good a correlation as possible with crop response for the soils in a given region. The chemical extraction methods so far developed for testing phosphorus in soils may be divided into:

i. methods employing water and carbon dioxide saturated water,

ii. acids, bases, salts and buffered solutions,

iii. isotopic dilution with P^{32} tagged orthophosphate,

iv. electrodialysis and ion exchangers.

A critical review of the literature reveals that though acids, bases, salts, and buffered solutions etc. have been frequently used, water and carbon dioxide saturated water have been regarded with some reservations, even though this method is one of the oldest used methods and has proved reliable in many cases.

Hibbard (1931), Blenkinsop (1938), Burd and Murphy (1939), McGeorge (1939), Bray and Dickman (1942), Forsee (1945), and Bingham (1949) were among the early research workers who employed this technique with some success. The criticism levelled against the use of water as an extractant has been that water dissolves far too little phosphorus as compared to the amounts taken up by plants. Consequently the quantities of phosphorus found in water extracts do not provide a very good index of phosphorus availability to plants. Another major objection to the use of water as an extractant of soil available phosphorus determination is the frequent failure to obtain a clear extract.

However, present-day instrumentation is such that the problems outlined above cease to be a serious impediment to the determination of soil available phosphorus using the water extraction method. Infact several of the contemporary workers in the field (for example Arnon, 1953; Fried and Shapiro, 1956; Larsen et al., 1959; Thompson et al. 1960; and Daughtrey et al., 1973) have evaluated this method and found it to be still useful.

Fried and Shapiro (1956) and later Daughtrey et al., (1973) employed the water extraction method in studies on the phosphate supply pattern of some soils.

A successive extraction with distilled water was used to study the intensity and the capacity of the soil to supply the soil solution with phosphorus. The capacity factor is regarded as a measure of the phosphate reserve in the soil and is related to the amount and forms of solid-phase phosphorus. The intensity factor, on the other hand, is the amount of phosphate in the soil solution at any given time. The reasoning behind the adoption of the successive water extraction was that the phosphate taken up by the plant roots from solution is continually replenished by the release of phosphate from the solid-phase. From a plot of P extracted against the extraction number they observed two different patterns of phosphorus release. In one case there was an increase in P removed with each successive extraction. In the other case there was a reduction in P removal with successive extractions. They suggested that both the intensity of soil phosphate supply and the capacity of the soil to replenish this supply must be carefully evaluated to be able to describe precisely plant available phosphorus in the soil.

Oteng (1969) also concluded from studies on availability of phosphorus in Ghana soils that of the ten conventional methods employed only the water, Bray No.2, Morgan and

Olsen's method are significantly correlated with phosphorus uptake by millet. The water extractable phosphorus however, provided the highest correlation coefficient with phosphorus uptake.

The acid extraction methods commonly employed in studies on soil available phosphorus can be divided into organic acid and inorganic acid methods. The organic acid extractions which have been proposed and still widely used are:

i. the citric acid methods proposed by Dyer (1894),

ii. the lactic acid method of Egner (1941), and

iii. the acetic acid method of Hibbard (1931).

The mineral acids used include the 0.7N HCl by Olsen (1946), and 0.05N HCl plus 0.025N H_2SO_4 by Mehlich (unpublished). The mixture of 0.05N HCl and 0.025N H_2SO_4, according to Nelson *et al*. (1953) is very effective in extracting a larger proportion of the difficultly available phosphorus.

Other research workers have used buffered solutions of acids. Truog (1930) used 0.002N H_2SO_4 buffered at pH 3.0 with $(NH_4)_2SO_4$. Morgan (1937) proposed acetic acid buffered near pH 4.8 with sodium acetate. Peech and English (1944) used acetic acid buffered at pH 4.8 with

ammonium acetate. Bray (1948) used hydrochloric acid buffered with NH_4F. Ghani (1943) also used acetic acid in the presence of 8 hydroxyquinoline and Cooke (1951) employed 0.5N acetic acid at pH 2.5 mixed with various complexing agents.

Alkali extractions have also been used primary on red soils. These include 0.5M $NaHCO_3$ used by Olsen et al., (1954), 0.5N NaOH recommended by Jones (1949). Others are the 1% potassium carbonate proposed by Das (1930).

The numerous acid extraction methods that have been reported for assessing the available-phosphate status of soils have been adopted in the tropics. But Birch (1952) and Birch and Friend (1960) reported that crop responses were not significantly related to the amounts of acid ammonium fluoride soluble (0.01N HCl, Bray and Kurtz, 1945) phosphate.

Nye (1952) concludes that the conventional methods such as dilute acid extraction method using 0.03N NH_4F solution and 0.025N HCl for soil chemical analysis for available phosphorus have been generally disappointing on tropical soils.

Piggot (1953) found that Truog (1945) and Purdue quick-test methods yielded no correlation with responses to superphosphate on a large number of trials on swamp rice in Sierra-Leone.

In his recent studies, Stephens (1968) has also stated that the determination of available phosphorus by the Truog (1945) method was of no use in assessing the effects of superphosphate on crop yield in Uganda.

Birch (1953) working in East Africa, has found that for certain soils and crops the lower the pH of the soil or the lower the percentage saturation of the exchange complex with bases, the greater the probability of a response to phosphate. On these soils he found there were no correlation between response and the amount of phosphate extracted by the usual solvents, which was usually quite high.

Even in the temperate countries where the acid extraction methods have been known to give satisfactory results there have still been some reports of failure. Larsen et al., (1959) for instance, found that most of the acid extractants remove more phosphorus from mineral soil and sod muck than from virgin or deeply ploughed muck.

It is evident from the work of Moser et al, (1959)

and Thompson *et al.* (1960) that the phosphorus concentration in 0.01M $CaCl_2$ gives a more reliable indication of the phosphorus uptake by crops, especially in the greenhouse, than the amount of phosphorus removed by the conventional extractants, eg., NH_4F - HCl, citric, and lactic acid.

1.4.2. Biological Methods of Determination of Available Phosphorus.

Biological methods for evaluation of soil phosphorus availability comprise the use of both higher plants and microplants. Biological methods involving growing plants in small quantities of soil in the greenhouse help to bridge the gap between soil analysis and field experiments. In this method, the comparative yields and/or uptake of plant nutrients from treated and untreated portions of soil are usually taken as a measure of plant nutrient status. The quantities of fertilizers or other materials to be added are usually calculated on the basis of pounds of soil in the jar. It is customary also to use a moisture content near the field capacity of the soil unless soil-moisture content is one of the problems involved in the study. In consequence then, in extreme cases the jars are weighed

and made up to weight everyday. A more common practice, wrote Millar (1965), is to weigh the cultures about once a week and calculate the daily loss of water. This amount of water is added each day.

The extraction of mineral nutrients from soil by growing crops is a unique type of soil chemical analysis. Plant tissue analysis aids in the characterization of soil chemical properties in terms of soil fertility and mineral nutrition of plants. In many respects, the plant should be a good indicator of the soil environment as it tends to integrate all factors. It is an indisputable fact, however, that time and method of sampling, plant species, and weather will all affect plant composition, yet from all indications the method should be preferred or help to correlate data for effective fertilizer recommendations or prediction of fertility of soils.

The analysis of plants as a means of ascertaining the nutrient content of crops was undertaken early in the history of agricultural chemistry. According to Millar (1965), the method has been in use for almost 200 years now. Plant analysis was employed by early workers to establish many of the principles of plant nutrition.

It also received considerable attention as a method of approach to the practical problem of determining the availability of soil nutrients. De Saussure was reported by Ulrich (1943) to have adopted the biological method, in as far back as 1804, to analyze the ash of plants and observed that its composition varied with the soil, with the part of the plant, and with the age of the plant. Hall (1905) also analyzed the soil by means of the plant that can grow on it and concluded that " the proportion of phosphoric acid and of potash in the ash of any given plant varies with the amount of these substances available in the soil as measured by the response of the crops to phosphoric and potassium manures respectively ". Salter and Ames (1928) however, after due consideration of the problem of plant analysis as a diagnostic procedure concluded that so many factors influence the nutrient composition of the plant that use of plant analysis as a guide for evaluating fertilizer requirements of crops is precluded.

In greenhouse experiments aimed at determining nutrient element availability by biological methods excess soluble salts may become a serious problem when large quantities of fertilizer are applied. This is because greenhouse soils are not exposed to natural leaching by rainwater.

Chlorides, sulphates, and nitrates are the major anions that are likely to contribute to excess soluble salt accumulation. Minor element shortages, as well as, excesses are also possible in greenhouse experiments.

Phosphorus interaction resulting from heavy dressings of phosphatic fertilizers have been investigated to varying extents in many parts of the world, and particularly at Riverside, California, since 1953. Evidences in support of the above observations have been given by Bingham et al. (1956 and 1958) who reported that $Ca(H_2PO_4)_2$ when applied to a variety of soils found in southern California usually reduced the availability of Cu, B, and Zn, and increased the availability of Mg and Mn. Chapman (1951) is also quoted by Bingham and Martin (1956) to have suggested that excessive applications of phosphorus, besides the effect on minor element, reduce the efficiency of nitrogen fertilization.

Other interactions among various nutrient elements resulting in deficiency of one nutrient element or the other have been reported. For instance, high rates of nitrogen fertilization has been reported by Reuther and Labanauskas (1966) to cause copper deficiency. Excessive phosphate and sulphate may also induce molybdenum deficiency on account of

enhanced growth resulting in high demand for molybdenum (Johnson, 1966).

The crucial factor that influences the optimal development of the plant, according to Arnon and Hoagland (1940) is " the availability and accessibility at each stage of growth of sufficient quantity of each essential element within suitable total concentration ranges and fairly broad limits of ionic proportions. " It is pertinent from evidence accumulating, that in all greenhouse experiments basal dressings of nutrient solution be added to bring the soils or growth medium to suitable total concentrations of the essential nutrient elements. Moreover, basal nutrient dressings will help remedy the adverse conditions of shortages or excesses induced by higher dressings of nutrient elements under investigations in the soils.

The idea of the use of nutrient solutions to culture plants was initiated and perfected in the years before 1860 by Sachs and Knop. Sachs' nutrient solution consisted of KNO_3, $Ca_3(PO_4)_2$, Mg SO_4.7 H_2O, $CaSO_4$, NaCl and Fe SO_4. Knop's solution, on the other hand, was made up of $Ca(NO_3)_2.4H_2O$, KNO_3, KH_2PO_4, Mg $SO_4.7H_2O$, and $FePO_4$.

Following Sachs and Knop's initiative other workers in the field attempted to develop simpler nutrient solutions which would produce optimal growth. It is reported that American plant physiologists became particularly interested in plant nutrition in the years following 1900. Bonner and Galston (1952), and Salisbury and Ross (1969) have reported that much work was performed by John Shive, W.R. Robbins, D.R. Hoagland, Daniel Arnon, A.L. Somner, Perry Stout, and Tottingham. These American workers and others, such as E.J. Hewitt, in England, improved the nutrient formulae given by Sachs and Knop.

At present there are nutrient solutions of varied composition such as those of Pfeffer, Crones, Shive, Knudson, and Hoagland. Recent introductions, such as those of Arnon and Hoagland (1940), Hoagland and Arnon (1950), and Hewitt (1963) are very popular and are used for various greenhouse experiment. In addition to the foregoing Salisbury and Ross (1969) have also reported that the concentration in ppm of micronutrients in nutrient solutions which could be regarded suitable for many aqueous solution culture lie, depending upon the plant species, within the following ranges:

Fe (0.5 to 5.0) Mn (0.1 to 0.5), B(0.1 to 1.0), Zn(0.02 to 0.2),

Cu(0.01 to 0.05) and Mo (0.01 to 0.05). Higher concentrations than these they claim, are often toxic to many plants.

The aqueous solution culture technique initiated by Sachs and Knop was later modified to involve soil samples. This pot culture technique, using plant samples to extract nutrient elements from soils and also to study the availability of nutrient elements to plants, was proposed as far back as 1909 by Mitscherlich and, later by Neubauer in 1923. In Mitscherlich's (1909) procedure reported by Vandecaveye (1948) nutrient solution, containing N as NH_4NO_3, K_2O as K_2SO_4, P_2O_5 as super-phosphate, and NaCl and $MgSO_4$ was added to soil samples in pots in a case where a " complete fertilizer" treatment was required. In later work by other investigators such as Schuster and Stephenson (1940), Stephenson and Schuster (1941), Colwell (1943), and Jenny et al. (1950), just to mention only a few, nutrient solutions to supply Ca, Mg, S, Cu, Zn, B, Mn, Mo, in addition to the major nutrient elements N,P,K, were added to the soil samples in varied composition to suit the specific work envisaged. For instance, in a work by Stephenson and Schuster (1941) a nutrient solution to supply the following K, 350 ppm; P, 217 ppm; Mg, 168 ppm; S, 224 ppm; N, 200 ppm

was added to the soil samples.

In greenhouse experiments using sand, gravel, soil, or sand-soil mixture culture, nutrient solution is applied in one of three ways:

i. slop culture technique,

ii. drip culture technique, and

iii. subirrigation technique.

In slop culture nutrient solution is periodically supplied to the surface of the culture and allowed to seep through, where as in drip culture nutrient solution is continuously dripped onto the culture. In subirrigation the nutrient solution is pumped from a bottom reservoir up through the culture or is added through a tube inserted in the culture until the solution reaches the surface. The slop culture technique, writes Bonner and Galston (1952) is the simplest way to grow plants under conditions of controlled nutrition.

Salisbury and Ross (1969) report that most greenhouse experiments can be safely conducted in borosilicate glass containers, polyethylene beakers or buckets, and in pyrex galss containers. These authors, however, suggest that borosilicate glass containers provide small amounts of boron whilst polyethylene containers supply sufficient zinc for plant growth.

Pyrex glass containers, Salisbury and Ross (1969) profess, are usually very suitable.

Salisbury and Ross (1969) write that certain seeds provide sufficient amounts of nutrient elements, especially the micronutrients Cu, Mo, and Zn, for the entire growth and reproductive period of greenhouse plants. They are therefore of the opinion that plants having large seeds are able to supply elements in sufficient quantities to developing seedlings than those having small seeds and hence recommended small seeds for greenhouse experiments.

After sampling, plant material is usually subjected to four different preparative steps before the actual chemical analysis is carried out:

i. cleaning the material to remove surface contamination,

ii. drying to stop enzymatic reactions and prepare the material for grinding,

iii. mechanical grinding to reduce the material to a fineness suitable for analysis, and

iv. final drying to constant weight to obtain a standardized value on which to base the analytical figures.

Plant parts selected for sampling are always covered with a thin film of dust which is very difficult to remove

by mechanical wiping or brushing. Anyway failure to remove dust normally affects only Fe unless the dust cover is thick or of specific composition (Jones and Steyn, 1973). Steyn (1959) showed that a satisfactory way of removing contamination is by washing the tissue in 0.1 to 0.3% detergents solution followed by rinsing in pure water.

After washing, plant tissue samples should be dried as rapidly as possible so as to minimize chemical and biological changes. If drying is unduly delayed, considerable loss in dry weight may occur due to respiration (Lockman, 1970), while proteins are broken down to simpler nitrogenous compounds. Also too high drying temperature can affect the dry weight (Grant and MacNaughlain, 1968). According to Tauber (1949) enzyme action is reduced or stopped if plant material is heated to above 60°C. Jones and Steyn (1973) however, recommended heating in a forced - draft oven set at 65°C.

Customarily, dried plant material are ground before analysis, partly for greater ease in manipulation, partly to ensure greater uniformity in composition. Because of the laborious nature of hand grinding, particularly when samples are large, mechanical grinding in mills is

favoured by most workers. Jones and Steyn (1973) have recommended storage of the tissue powder in a clean, dry bottle. Further drying for an additional 24 hours at 65°C in order to remove the moisture picked up during grinding is also recommended before sub- samples may be weighed out for analysis.

1.5. Assessment of P Requirements of Soils from P Sorption.

Many researchers the world-over have adopted numerous techniques designed to estimate the P requirements of soils for optimum crop yields. These invariably include field trials and laboratory determinations. The field trials are slow, laborious and the results are useful only for local applicability. Amongst the laboratory estimations the methods of Bray and Kurtz (1945), Olsen et al. (1954), and Bingham (1962) are noteworthy. The above laboratory methods give some measure of both the amount of phosphate already present in the soil and its degree of availability. However, they fail to satisfactorily indicate the amount of phosphate that will be required to give optimum crop yields in different soils

Since the amount of phosphate needed to be applied to soils to give an optimum production is of more concern

than the existing supply, a more direct method of assessing plant P needs was desired. In response to this world-wide desire for a method of assessing plant P needs in soils, Ozanne and Shaw (1967) tried a method for the direct assessment of plant P needs through phosphate sorption by soils. In the study of Ozanne and Shaw (1967) the amount of phosphate sorbed at equilibrium concentration of 0.3 ppm P was measured in a preliminary investigation. They subsequently examined the extent to which the above measurement would allow the estimation of the optimum amount of phosphate that need be applied to obtain near-maximum yields. From the data accumulated from their investigation they concluded that the measurement of phosphate sorption may be adequate to predict the phosphate requirements of plants.

Following Ozanne and Shaw's (1967) initiative Singh et al., (1971) adopted a similar technique to determine phosphate requirement of soil for cereal crops. Singh et al.,(1971) also observed that in any programme of P application for getting optimum crop responses and yields, due consideration should be given to the capacity of soil for sorption of P rather than the initial P status.

CHAPTER 2

MATERIALS AND METHODS

2.1. Description of Soils.

Soil samples used in the present study were taken from the 0cm to 23 cm. layer of twelve soil series of Ghana. Table 1 provides a description of the soils as follows: series name, great soil group classification, type of parent material, textural classification and vegetation associated with the soils.

Table 1. Description of Soils Used.

Identification No. of Soil	Soil Series Name	Great Soil Group	Parent Material	Textural Classification	Vegetation
1	Abenia	Forest Oxysol	Biotite Granite Schist	Sandy Clay	Forest
2	Ankasa	Forest Oxysol	Biotite Granite	Sandy Clay Loam	Forest
3	Boi	Forest Oxysol	Phyllite	Sandy Clay Loam	Forest
4	Tikobo	Forest Oxysol	Tertiary Sand	Loamy Sand	Forest Re-growth
5	K'dua	Forest Oxysol Rubrisol Intergrade	Biotite Granodiorite	Sandy Clay Loam	Forest
6	Wacri	Forest Ochrosol Rubrisol Intergrade	Hornblende Granodiorite	Sandy Clay Loam	Forest
7	Mamfe	Forest Ochrosol	Quartzite Granite	Sandy Loam	Forest
8	Oyarifa	Savanna Ochrosol	Sandstone	Sandy Loam	Thicket
9	Toje	Savanna Ochrosol	Tertiary Sand	Sand	Tall Grass Savanna
10	Akuse	Tropical Black Clay	Hornblende Gneiss	Clay Loam	Savanna
11	Prampram	Tropical Black Earth	Basic Gneiss	Sandy Clay Loam	Tall Grass Savanna
12	Agawtaw	Tropical Grey Clay	Acid Gneiss and Schist	Loamy Sand	Savanna

Table 2 presents further information on the soil as determined in the laboratory during the present study. The information includes values for pH, organic carbon, clay content, silica content, "free" aluminium oxide (Al_2O_3) and iron oxide (Fe_2O_3) of the soil.

Table 2. Some Properties of Soils Used.

Identification No. of Soil	Soil Series Name	pH (in 0.01M $CaCl_2$)	% Org. Carbon	Clay Content %	Silica Content %	"Free" Al_2O_3 %	"Free" Fe_2O_3 %
1	Abenia	4.00	1.51	35.92	20.30	0.74	0.35
2	Ankasa	4.00	1.20	23.20	24.44	0.48	0.30
3	Boi	4.15	0.99	32.87	33.86	1.95	0.27
4	Tikobo	4.00	0.77	12.44	39.72	0.74	0.25
5	Koforidua	6.95	1.41	22.53	23.42	7.04	0.20
6	Wacri	6.35	1.18	25.39	30.08	6.58	0.20
7	Mamfe	4.60	1.85	14.30	41.54	0.34	0.22
8	Oyarifa	6.40	0.85	19.86	42.78	0.29	0.15
9	Toje	5.35	0.20	6.39	54.26	0.25	0.11
10	Akuse	6.60	0.79	32.53	33.46	11.26	0.18
11	Prampram	7.12	0.79	34.48	32.78	13.20	0.31
12	Agawtaw	5.90	0.34	8.00	55.50	3.44	0.09

The selected soils have pH values ranging from 4.00 to 7.12. The pH values for the soil series Abenia, Ankasa, Boi and Tikobo are in the range 4.00 to 4.15. These are soils from high rainfall (70" or more/1780 mm or more) areas where normally there is pronounced through leaching of cations Ca^{2+},Mg^{2+},K^{+}, and Na^{+} from the topsoil deep down into the profile thus resulting in acid reaction. Consequently the low pH values (well in the acid range) obtained for these soils were as expected. Mamfe series, a soil from a forest area with moderate rainfall 50" to 60" or 1270 mm to 1520 mm also has pH of 4.60 which is very acid. This particular soil series is believed to have developed over Quartzite Granite (Table I) and therefore not much soluble bases are released to the soil consequent upon weathering. Hence the pH value cannot be expected to fall in the slightly acid or near neutral range as might be the case of many soils from regions with moderate rainfall. Toje and Agawtaw series which are soils from savanna region have moderately acid reaction. These soils are underlain by inert rock materials mainly. Infact Toje is believed to have developed over Tertiary Sand whilst Agawtaw is formed over Acid Gneiss and Schist, all of which release only minute quantities of bases to the soil when weathered.

The soil series Koforidua and Wacri, which are from forest areas with moderate rainfall (50" to 60" or 1270 mm to 1520 mm per annum) have pH value which are slightly acid (pH 6.35 to 6.95). These soils are subjected to only sporadic leaching of their soluble bases and are therefore expected to show only slightly acidic reaction. Akuse and Prampram soil series have also pH of 6.60 and 7.12 respectively. These soils are formed over basic parent material, therefore, the pH of near neutral and neutral is as expected since more basic materials are released when the underlying rocks do weather.

As expected, Abenia, Ankasa, Boi, Koforidua, Wacri, and Mamfe, which are soils from forest region, have relatively high organic carbon content. Tikobo, however, has a comparatively low organic carbon content of only 0.77%. This particular soil series has a sandy loam texture and there is the possibility of eluviation of organic matter from the topsoil into the subsoil. In contrast, the savanna soils, namely, Oyarifa, Toje, Akuse, Prampram, and Agawtaw have relatively low organic carbon content ranging from 0.2% in Toje to 0.85% in Oyarifa. This reflects on the vegetative cover and periodic burning of grasses in the savanna areas in Ghana.

The clay content appears to be fairly high in the soil series Abenia (35.92% clay) and Prampram (34.48% clay). These soils have been derived from parent materials rich in basic minerals and which are less resistant to weathering and as such weather easily to give clay particles to these soils. On the other hand, those soils derived mainly from sand, quartzite granite and acid gneiss such as Tikobo, Mamfe, Oyarifa, Toje, and Agawtaw have comparatively low clay content.

The silica content ranges from 20.30% in Abenia to 55.50% in Agawtaw. Abenia, Ankasa, Boi, Koforidua, Wacri, Akuse, and Prampram soils with high clay content also have comparatively low silica. On the contrary, Tikobo, Mamfe, Oyarifa, Toje and Agawtaw which show low clay content have, in turn, high silica content.

The "free" aluminium oxide content of the soils used is in the range 0.25% to 13.20%. Infact the "free" aluminium oxide content follows no particular trend. Akuse and Prampram soils have high "free" aluminium oxide of 11.26% and 13.20% respectively. The normal range of Al_2O_3 content of soils generally is 2 - 15%. Koforidua and Wacri also have moderately high "free" aluminium oxide content of 7.04% and 6.58% respectively. Abenia, Ankasa, Boi, Tikobo, Mamfe, Oyarifa, Toje, and Agawtaw soils, on

the other hand, have low "free" aluminium oxide content ranging from 0.25% to 3.44%. The "free" iron oxide content as Fe_2O_3 of the soils used in the investigation is low ranging from 0.09% in Agawtaw to 0.35% in Abenia as compared to the normal range of Fe_2O_3 content of soils which generally is 0.1 to 8.0%.

2.2. Preparation and Storage of Soil Samples.

The soil samples which were taken from uncultivated sites were air-dried, ground with a wooden pestle and mortar and sieved through a 2 mm. sieve with square holes to get only the "fine earth" samples. The sieved soil samples were stored in polythene bags.

2.3. Determination of the Adsorption Maximum.

The method of Olsen and Watanabe (1957) was used to obtain data for plotting the Langmuir isotherm. Subsamples of the fine earth fractions were sieved with a 72 mesh (0.211 mm) screen. The rationale behind the resieving was to obtain subsamples which contain largely clay and silt fractions. This was deemed necessary since adsorbed phosphorus can be found on the clay and silt fractions and hardly on the sand fraction. The subsamples thus obtained were then stored in wax-coated paper containers for the analytical tests.

Five grams samples of the 72-mesh soil samples were weighed into 125-ml. polypropylene extraction bottles and shaken in 100 ml. of KH_2PO_4 solutions for 24 hours. Seven different equilibrations were made with KH_2PO_4 solutions of the following concentrations: $1X10^{-4}$M, $2X10^{-4}$M, $3X10^{-4}$M, $7X10^{-4}$M, $9X10^{-4}$M and $12X10^{-4}$M. All KH_2PO_4 solutions were adjusted to pH 7.0 initially. Forty millilitres aliquots of the soil suspension were centrifuged in "Sorval" superspeed angle centrifuge at 7,000 rpm. for twenty minutes, and the supernatant solutions were decanted into separate tubes. Ten millilitres aliquots of the supernatant solutions were pipetted into 100 ml. volumetric flasks and then made up to volume with distilled water. The phosphorus concentration was determined by a modified Truog and Meyer (1929) method. Suitable aliquots of the diluted clear extracts were pipetted into matched test tubes calibrated at 45-ml. volume and 2 ml. acid ammonium molybdate solution were added. The mixtures were then made up to mark with distilled water and were thoroughly shaken. Three drops of stannous chloride reductant solution were added, the mixtures were shaken again and the phosphorus content was measured with a Bausch and Lomb "Spectronic-20" spectrophotometer at 660 millimicron wavelength in exactly ten minutes.

The difference between the amount of phosphorus in solution after shaking and the amount initially present was taken as the amount of phosphorus adsorbed by the soil from the KH_2PO_4 solution. The adsorption maxima of the soils were calculated from the reciprocal of the slope of the straight-line obtained from a plot of the equilibrium phosphate concentration expressed as $\underline{C} \times 10^4$ moles litre $^{-1}$ against the equilibrium phosphate concentration $\underline{C} \times 10^4$ in moles litre $^{-1}$ divided by the milligrams of phosphate adsorbed per 100 g of soil, $(C/(x/m))$ in moles litre $^{-1}$.

2.4. Determination of "Free" Fe and Al Oxides.

An estimate of the "free" iron and aluminium oxides in the soils was obtained using a modified ammonium oxalate extraction technique based on the method of Tamm (1922).

One gram of soil sample, previously screened through a 2 mm. sieve, was weighed and transferred quantitatively into an extraction bottle. One gram of sodium dithionite was added followed by 40 ml. Tamm solution (a mixture of oxalic acid and ammonium oxalate). The extraction bottle was heated to a temperature of 85^{o}C in an oven for twenty minutes, swirling the bottle after five minutes.

The suspension was centrifuged and the supernatant solution was decanted through a filter paper into a 200-ml. volumetric flask. The above extraction was repeated twice. The residue was then washed twice with 25 ml saturated sodium chloride solution. The extract was diluted to the 200-ml. mark and mixed thoroughly.

Five millilitres aliquots of the extracts were pipetted into 50-ml. Kjeldahl flasks and 2.5 ml. aqua regia were added. The mixture was heated on a Kjeldahl microdigestion rack until nitrous oxide vapour ceased to escape. The flask and its contents were cooled. Five millilitres aqua regia were added to the contents of the flask and heated again to dryness. This latter treatment was repeated. Twenty millilitres of water and 1.0 ml. of 4N hydrochloric acid were then added to the contents of the flask and heated gently for ten minutes. The flask and its contents were cooled and transferred quantitatively into a 50-ml. volumetric flask and the volume adjusted with water. Suitable aliquots of the extract were pipetted for the colorimetric determination of iron and aluminium.

The iron content of the extract was determined colorimetrically by Olsen, R.V. method outlined in Black et. al. ed. "Methods of Soil Analysis", Agronomy No.9, Part 2, Chemical and Microbiological Properties, 1965.

A suitable aliquot, generally 1.0 ml., of the test solution was pipetted into a 50-ml. volumetric flask and then 2ml. of 5N ammonium acetate and 1.0 ml. of 10% hydroxylamine hydrochloride were added. The solution was mixed and 1.0 ml of orthophenanthroline reagent and 0.5 ml of 6N hydrochloric acid were added. The solution was diluted to volume and mixed thoroughly. The coloured test solutions were transferred to photometer tubes and placed in a Bausch and Lomb "Spectronic-20" spectrophotometer using a wave-length setting of 510 millimicron. The galvanometer was set to 100% light transmission with the blank solution.

The aluminium concentration of the above extract was also measured colorimetrically using pyrocatechol violet indicator. A suitable aliquot, generally 10 ml., of the extract was pipetted into a 50-ml. volumetric flask. One millilitre of hydroxylamine hydrochloride and 1.0 ml. of O-phenanthroline solution were added one after the other to the contents of the flask. Next 1.0 ml of pyrocatechol solution was also added. Twenty-five millilitres of a buffer solution, made up of aqueous ammonium acetate solution adjusted to pH 6.2 with acetic acid, were added followed by a drop of ammonia solution. The mixture was then diluted to the 50-ml. mark and set aside for two hours.

The percentage of light transmittance was measured on a Bausch and Lomb "Spectronic-20" spectrophotometer at 580 millimicron wavelength using blank solution to adjust the galvanometer to 100% transmission.

2.5. Determination of Silica Content of Soils.

The silica content of the soils was determined by a modified method of Corey and Jackson (1953), and Shapiro and Brannock (1956) outlined in Black et al. ed. "Methods of Soil Analysis", Agronomy No.9, Part 2, Chemical and Microbiological Properties, 1965. Ten millilitres of 15% sodium hydroxide solution measured with a plastic graduated cylinder were transferred into a platinum crucible, and evaporated the solution to dryness on a hot plate. A sample of 0.05 g. of 100-mesh soil sample was placed into the crucible. The crucible was covered and heated to dull redness for about five minutes in a muffle furnace. The melt was allowed to cool, and approximately 15 ml. of water were added and then allowed to stand overnight. The content of the crucible was transferred to a 600-ml. beaker containing about 400 ml. of water and 20 ml. of 6N hydrochloric acid. The crucible was scrubbed well with a rubber policeman and the remaining residue washed into the beaker. The solution was finally transferred to a one-litre volumetric flask and adjusted with distilled water to volume.

Ten millilitres of the test solution were pipetted and transferred to a 100-ml. volumetric flask. One millilitre of ammonium molybdate reagent was added, swirling the contents of the flask to mix the solution well. One millilitre of reducing solution made up of sodium sulphite, 1-amino-2-naphthol-sulphonic acid and sodium bisulphite, was added and the solution was diluted to the 100-ml. mark, mixed well and allowed to stand for about thirty minutes. The coloured test solutions were transferred to photometer tubes and placed in a Bausch and Lomb "Spectronic-20" spectrophotometer using a wavelength of 650 millimicron. The galvanometer was earlier on set to 100% light transmission with the blank solution.

2.6. Estimation of Organic-C, pH and Clay content of Soils.

The percent organic carbon content of the soils was estimated by the wet oxidation method of Walkley and Black (1934). A suitable amount of soil samples previously passed through a 0.5 mm sieve, generally 2 g samples, was weighed into a 500-ml. Erlenmeyer flask and to which was added 10 ml. of potassium dichromate solution from a burette. Twenty millilitres of concentrated sulphuric acid were added. The flask was swirled and allowed to stand for thirty minutes. 200 ml. of distilled water were then added followed by 10 ml. of orthophosphoric acid. Three drops of diphenylamine indicator were added and

titrated against ferrous ammonium sulphate solution to a green end-point. A blank was run in the same way as described above. The percent organic carbon was calculated from the titration readings.

The pH of the soils was measured in 0.01M calcium chloride solution with a WG-Pye glass electode pH-meter on a 1:2 soil to solution ratio. Twenty grams of the 2 mm. soil samples were weighed into a 50-ml beaker and added 40 ml. of 0.01M calcium chloride solution. The suspension was stirred several times during a period of thirty minutes and then allowed to stand for another thirty minutes. The electrode was immersed and the pH was measured.

Mechanical analysis to estimate the per cent clay of the soil samples was done by the pipette method. Approximately 10 g of the 2 mm soil samples were weighed into tared 250-ml. beaker and reweighed to the nearest 0.01 g. The samples were dried overnight at 105^{o}C, cooled in a desiccator, and reweighed. About 30 ml. of water were added followed by a few millilitres of 30% hydrogen peroxide, then covered the beaker with a watch glass and stirred the contents by swirling the beaker. When the reaction had subsided additional amounts of hydrogen peroxide were added and then completed the digestion by heating the beaker for one hour on a hot-plate.

Other beakers containing the soil suspension of each soil sample was placed in an oven at 105°C for about 24 hours, cooled in a desiccator, and weighed the beaker and its contents to get the weight of the organic matter-free soil samples.

Twenty-five millilitres of calgon were added to the organic matter-free soil suspension and transferred into a 250-ml shaker bottle. Some water was added to the suspension to bring it to about 150-ml. volume, the bottle was stoppered and shaken for 4 hours in a reciprocating shaker. A wide-mouth funnel was put in a 500-ml. graduated cylinder and a 60 micron sieve was placed on the funnel. The partly settled suspension was poured into the sieve. The remaining soil practicles in the cylinder were washed into the funnel with a jet of water and finally washed the sand particles on the sieve with a jet of water. The sand particles were transferred into a beaker, oven-dried, and weighed.

The suspension was made up to the 500-ml. mark with water and transferred the cylinder to the sedimentation cabinet. A plunger was inserted in the suspension and moved it up and down to mix the contents thoroughly. The cylinder was moved into position in the pipette stand, then clamped the clean, dry, 10-ml. pipette in its holder

and attached the tubing. Three samplings of the suspension were made at 4 minutes, 45 minutes and 6 hours 45 minutes time at the 10 cm. depth. The samples of the clay and silt suspension were poured into tared aluminium boxes, oven-dried, and weighed. The per cent clay in the soil samples were calculated from the readings recorded.

2.7. Determination of Available Phosphorus in the Soils.

The initial phosphorus status of the soils used in the investigation was estimated by the Bray and Kurtz (1945) method.

A 2.85 grams sample of crushed, sieved soil was weighed out into a 125-millilitres polypropylene extraction bottle. Twenty millilitres of extraction solution (0.03N NH_4F in 0.025N HCl) were added from a pipette and the bottle was shaken for five minutes. The suspension was centrifuged and filtered through Whatman No. 42 filter paper. A two millilitres aliquot of the clear filtrate was pipetted into colorimeter tubes. Then five millilitres of distilled water and two millilitres of ammonium molybdate reagent were added in succession. The solution was thoroughly mixed on a rotary mixer. One millilitre of freshly diluted stannous chloride reagent was added and the intensity of the blue colour

was measured after five to six minutes and before fifteen to twenty minutes on a Bausch and Lomb "Spectronic-20" colorimeter at 660 millimicron wavelength. The P standards were made in the range of 0.1 to 1.0 ppm of P through the same steps as in the above procedure. Two millilitres of extraction solution were added to each aliquot of diluted standard P solution and the final solution was of ten millilitres volume. A reagent blank was prepared and was employed for the 100 per cent transmission setting.

2.8. Greenhouse Experiment.

In a greenhouse experiment phosphorus was added to ten of the twelve soil series used in the adsorption maximum studies as KH_2PO_4 and K_2HPO_4 at various rates of zero, $\frac{1}{8}$, $\frac{1}{4}$, $\frac{1}{2}$, 1 and 2 times the P adsorption maximum. The soil series used were 2, Ankasa; 3, Boi; 4, Tikobo; 5, Koforidua; 6, Wacri; 7, Mamfe; 8, Oyarifa; 9, Toje; 10, Akuse; 12, Agawtaw.

2.8.1. Amounts of KH_2PO_4 and K_2HPO_4 Applied to Soils.

The following is a sample calculation, using the Ankasa series, adopted to estimate the quantity of phosphorus needed to be applied to the soil samples in the pot experiment. The P adsorption maximum for the Ankasa series is 35.714 milligrams P per 100 grams of soil or 0.0357 grams per 100 grams of soil.

But 454 grams of soil sample was used in the pot experiment.

If 100 grams of soil sample required 0.0357g. P

454 grams of soil sample will require $\frac{(0.0357)(454)\ g.P}{100}$

$= (0.0357)(4.54)g.P$

$= 0.1620$ grams P.

Thus the amount of P needed to be applied to 454 grams soil sample of Ankasa series to attain the P adsorption maximum is 0.1620 grams P. To obtain the amount of P to be applied at $\frac{1}{8}$, $\frac{1}{4}$, $\frac{1}{2}$ and 2 times the P adsorption maximum the value 0.1620 grams was multiplied by $\frac{1}{8}$, $\frac{1}{4}$, $\frac{1}{2}$ and 2, respectively.

The table below presents the amount of P applied to the soil samples at the varied rates of $\frac{1}{8}$, $\frac{1}{4}$, $\frac{1}{2}$, 1 and 2 times the P adsorption maximum of the various soil series used in the investigation.

The following is a sample calculation, using the Ankasa series, adopted to estimate the amount of KH_2PO_4 required to be added to the soil samples. To attain the adsorption maximum 0.1620 grams P was required. In the KH_2PO_4 salt there is an atom of P.

Table 3. Amounts of P Applied to the Soils.

Soil Series Name	P Adsorption Maximum mg/100g Soil	Phosphorus Application Rates									
		1/8	1/4	1/2	1	2	1/8	1/4	1/2	1	2
		g.P per pot (454g. soil)					kg. P per hectare				
Ankasa	35.714	0.0203	0.0405	0.0810	0.1620	0.3240	100	200	400	800	1600
Boi	31.250	0.0178	0.0355	0.0709	0.1418	0.2836	88	175	350	700	1400
Tikobo	27.027	0.0154	0.0307	0.0614	0.1227	0.2454	76	152	303	606	1212
Koforidua	27.778	0.0158	0.0315	0.0630	0.1260	0.2520	78	156	311	622	1244
Wacri	25.641	0.0146	0.0291	0.0582	0.1164	0.2328	72	144	287	575	1150
Mamfe	30.303	0.0175	0.0344	0.0688	0.1376	0.2752	85	170	340	680	1359
Oyarifa	23.256	0.0132	0.0264	0.0528	0.1056	0.2112	65	130	261	521	1043
Toje	25.641	0.0146	0.0291	0.0582	0.1164	0.2328	72	144	287	575	1150
Akuse	31.250	0.0178	0.0355	0.0709	0.1418	0.2836	88	175	350	700	1400
Agawtaw	26.316	0.0149	0.0299	0.0598	0.1195	0.2390	74	148	295	590	1180

The atomic weight of P is 30.98 grams and the molecular weight of KH_2PO_4 is 136.09 grams.

If 30.98 g. P are supplied by 136.09g. KH_2PO_4

0.1620g. P will be supplied by $\frac{(136.09)(0.1620)}{30.98}$g. KH_2PO_4

$= 0.7116$g. KH_2PO_4

The amount of KH_2PO_4 needed to be applied to 454 grams soil sample of Ankasa series to attain the adsorption maximum is 0.7116 grams. To obtain the amount of KH_2PO_4 salt needed to be added to attain $\frac{1}{8}$, $\frac{1}{4}$, $\frac{1}{2}$ and 2 times adsorption maximum the value 0.7116 grams was multiplied by $\frac{1}{8}$, $\frac{1}{4}$, $\frac{1}{2}$ and 2, respectively.

Table 4 presents the amounts of KH_2PO_4 salt added to the soil samples to get the respective amounts of P at $\frac{1}{8}$, $\frac{1}{4}$, $\frac{1}{2}$, 1 and 2 times the P adsorption maximum.

The following is yet another sample calculation, using Ankasa series, adopted to estimate the amount of K_2HPO_4 needed to be added to the soil samples. The amount of P required to be applied to attain P adsorption maximum on Ankasa series is 0.1620 grams P per pot of 454 grams soil. In the K_2HPO_4 salt there is an atom of P. Atomic weight of P is 30.98 grams and the molecular weight of K_2HPO_4 is 174.18 grams.

Table 4. Amounts of KH_2PO_4 Salt Added to Soils.

Soil Series Name	Amounts of KH_2PO_4 Added					Equiv. Amounts of K Supplied				
	$\frac{1}{8}$	$\frac{1}{4}$	$\frac{1}{2}$	1	2	$\frac{1}{8}$	$\frac{1}{4}$	$\frac{1}{2}$	1	2
	grams per					pot (454g. soil)				
Ankasa	0.0890	0.1779	0.3558	0.7116	1.4232	0.0256	0.0512	0.1023	0.2045	0.4090
Boi	0.0779	0.1557	0.3115	0.6229	1.2458	0.0224	0.0448	0.0895	0.1790	0.3580
Tikobo	0.0674	0.1348	0.2695	0.5390	1.0780	0.0194	0.0388	0.0775	0.1549	0.3098
Koforidua	0.0692	0.1384	0.2768	0.5535	1.1070	0.0199	0.0398	0.0795	0.1590	0.3180
Wacri	0.0639	0.1278	0.2557	0.5113	1.0226	0.0184	0.0368	0.0735	0.1469	0.2938
Mamfe	0.0756	0.1511	0.3023	0.6045	1.2090	0.0218	0.0435	0.0869	0.1737	0.3474
Oyarifa	0.0580	0.1160	0.2320	0.4639	0.9278	0.0167	0.0334	0.0667	0.1333	0.2666
Toje	0.0639	0.1278	0.2557	0.5113	1.0226	0.0184	0.0368	0.0735	0.1469	0.2938
Akuse	0.0779	0.1557	0.3115	0.6229	1.2458	0.0224	0.0448	0.0895	0.1790	0.3580
Agawtaw	0.0656	0.1312	0.2625	0.5249	1.0498	0.0189	0.0377	0.0754	0.1508	0.3016

If 30.98g. P are supplied by 174.18g. K_2HPO_4

0.1620g. P will be supplied by $\frac{(174.18)(0.1620)}{30.98}$ g. K_2HPO_4

= 0.9108 grams K_2HPO_4.

The amount of K_2HPO_4 salt needed to be applied to 454 grams soil sample of Ankasa series to attain the adsorption maximum is 0.9108 grams. To obtain the amount of K_2HPO_4 needed to be added to attain $\frac{1}{8}$, $\frac{1}{4}$, $\frac{1}{2}$ and 2 times adsorption maximum the value 0.9108 grams was multiplied by $\frac{1}{8}$, $\frac{1}{4}$, $\frac{1}{2}$ and 2 respectively.

Table 5 presents the amounts of K_2HPO_4 salt added to the soil samples to obtain the respective amounts of P at $\frac{1}{8}$, $\frac{1}{4}$, $\frac{1}{2}$, 1 and 2 times P adsorption maximum.

Examination of the last five columns of Tables 4 and 5, headed "equivalent amounts of K supplied" reveals that the KH_2PO_4 and K_2HPO_4 salts added to attain 2 times adsorption maximum on the Ankasa series supplied the highest amounts of K^+ ion. The K^+ ion supplied are equal to 0.4090 grams for KH_2PO_4 and 0.8180 grams for K_2HPO_4 per pot of 454 grams soil. Since P was supposed to be the only nutrient element whose amount in the soil samples was to be varied, it was deemed necessary to add another salt which would supply the additional K^+ ion. Potassium carbonate (K_2CO_3) salt was accordingly added in various amounts to the soil samples to bring the added K to a level of 0.4090 grams for KH_2PO_4- treated soils and 0.8180

Table 5. Amounts of K_2HPO_4 Salt Added to Soils.

Soil Series Name	Amounts of K_2HPO_4 Added					Equiv. Amounts of K Supplied				
	1/8	1/4	1/2	1	2	1/8	1/4	1/2	1	2
	grams per					pot (454g. Soil)				
Ankasa	0.1139	0.2277	0.4554	0.9108	1.8216	0.0511	0.1022	0.2045	0.4090	0.8180
Boi	0.0997	0.1993	0.3986	0.7972	1.5944	0.0448	0.0895	0.1790	0.3580	0.7160
Tikobo	0.0862	0.1725	0.3450	0.6899	1.3798	0.0388	0.0775	0.1549	0.3098	0.6196
Koforidua	0.0886	0.1771	0.3542	0.7084	1.4168	0.0398	0.0795	0.1590	0.3181	0.6362
Wacri	0.0818	0.1636	0.3272	0.6544	1.3088	0.0368	0.0735	0.1470	0.2939	0.5878
Mamfe	0.0967	0.1934	0.3868	0.7736	1.5472	0.0435	0.0869	0.1737	0.3474	0.6948
Oyarifa	0.0742	0.1484	0.2969	0.5937	1.1874	0.0334	0.0667	0.1333	0.2666	0.5332
Toje	0.0818	0.1636	0.3272	0.6544	1.3088	0.0368	0.0735	0.1470	0.2939	0.5878
Akuse	0.0997	0.1993	0.3986	0.7972	1.5944	0.0448	0.0895	0.1790	0.3580	0.7160
Agawtaw	0.0840	0.1680	0.3360	0.6719	1.3438	0.0379	0.0757	0.1514	0.3028	0.6056

grams for K_2HPO_4- treated soils per pot of 454 grams soil. The only exception was the soil samples of the Ankasa series which received the highest P treatment of 2 times P adsorption maximum. The various amounts of K_2CO_3 salt added to the KH_2PO_4- treated soils are presented in Table 6 whilst those added to the K_2HPO_4- treated soils are presented in Table 7.

2.8.2. Incubation Technique.

Weighed quantities (454 grams) of the soil series under investigation were mixed with KH_2PO_4 or K_2HPO_4 salts, as the case may be, and K_2CO_3 salt in amounts as given in Tables 4, 5, 6 and 7. Each treatment was replicated twice. The soil samples and the inorganic salts were thoroughly mixed using a "Kenwood" domestic mixer. The soil samples with the added salts were then watered daily with distilled water for two weeks.

2.8.3. Seeding of Soil Samples with Test-Crop.

After the two weeks incubation period the dried soil samples were pulverised and thoroughly mixed with a "Kenwood" domestic mixer. Each 454-grams soil sample was mixed with 227 grams of acid- treated beach sand (ratio of soil to sand was 2:1). About 150 grams of thoroughly washed quartz gravel were weighed into empty plastic pot of 1340 millilitres capacity. A plastic tube measuring 11.5 centimetres long and 1.10 centimetres in diameter was placed on the quartz gravel at an

Table 6. Amounts of K_2CO_3 Salt Added to KH_2PO_4-Treated Soils.

Soil Series Name	P Saturation of Adsorption Maximum					
	0	$\frac{1}{8}$	$\frac{1}{4}$	$\frac{1}{2}$	1	2
	grams K_2CO_3 Salt Added					
Ankasa	0.7226	0.6774	0.6322	0.5419	0.3612	Nil
Boi	0.7226	0.6831	0.6435	0.5645	0.4063	0.0901
Tikobo	0.7226	0.6884	0.6558	0.5857	0.4489	0.1753
Koforidua	0.7226	0.6875	0.6523	0.5821	0.4416	0.1606
Wacri	0.7226	0.6901	0.6576	0.5928	0.4630	0.2034
Mamfe	0.7226	0.6841	0.6458	0.5691	0.4157	0.1089
Oyarifa	0.7226	0.6931	0.6636	0.6048	0.4871	0.2515
Toje	0.7226	0.6901	0.6576	0.5928	0.4630	0.2034
Akuse	0.7226	0.6831	0.6435	0.5645	0.4063	0.0901
Agawtaw	0.7226	0.6892	0.6560	0.5894	0.4561	0.1896

Table 7. Amounts of K_2CO_3 Salt Added to K_2HPO_4- Treated Soils.

Soil Series Name	P Saturation of Adsorption Maximum					
	0	$\frac{1}{8}$	$\frac{1}{4}$	$\frac{1}{2}$	1	2
	grams K_2CO_3 Salt Added					
Ankasa	1.4455	1.3552	1.2649	1.0841	0.7226	Nil
Boi	1.4455	1.3663	1.2873	1.1291	0.8128	0.1803
Tikobo	1.4455	1.3769	1.3085	1.1717	0.8980	0.3506
Koforidua	1.4455	1.3751	1.3050	1.1645	0.8833	0.3213
Wacri	1.4455	1.3804	1.3156	1.1857	0.9261	0.4068
Mamfe	1.4455	1.3686	1.2919	1.1385	0.8315	0.2177
Oyarifa	1.4455	1.3864	1.3276	1.2099	0.9743	0.5033
Toje	1.4455	1.3804	1.3156	1.1857	0.9261	0.4068
Akuse	1.4455	1.3663	1.2873	1.1291	0.8128	0.1803
Agawtaw	1.4455	1.3803	1.3117	1.1779	0.9103	0.3705

inclined position to the wall of the plastic pot. Each plastic pot was then filled with the soil-sand mixture. A solution to supply the following nutrient elements was applied to each pot: 170mg. Ca as $Ca(NO_3)_2$; 100 mg. N as NH_4NO_3 and $Ca(NO_3)_2$; 20 mg. Mg as $MgSO_4.7H_2O$; 2 mg. Fe as $FeSO_4.7H_2O$; 0.175 mg. Mn as $MnCl_2.4H_2O$; 0.08mg Cu as $CuSO_4.5H_2O$; 0.25 mg. Zn as $ZnSO_4.7H_2O$; 0.8 mg. B as H_3BO_3; 10 microgram Mo as $(NH_4)_6\ MO_7O_{24}.4H_2O$. Twelve millet (Pennisetum typhoides) seeds were sown in each pot. The resulting seedlings were eventually thinned after emergence to eight seedlings per pot. The soil samples were moistened daily throughout the growing period with distilled water.

After the third week of growth the plants started showing symptoms of certain nutrient disorder. The symptoms were characterised by a breakdown and subsequent drying of the tips of the newly emerged leaves. The symptoms were initially only visible on plants growing on soil samples of the soil series Boi, Koforidua, Wacri, Mamfe and Agawtaw with P application rates of 1 and 2 times the P adsorption maximum. By the fourth week of growth the symptomos had become visible on almost all the plants but, as at the start, more pronounced on plants growing in the soil samples with the P application rates

of 1 and 2 times the P adsorption maximum. For Koforidua and Wacri series, however, those soil samples with P application rates of only ½ times P adsorption maximum showed the symptoms also by the fourth week of growth. Due to the nature of the symptoms, and since only plants on soil samples with high P application rates showed the symptoms, P-induced micronutrient element deficiencies were suspected. Further addition of nutrient solution containing mainly calcium, magnesium and micronutrient elements was applied on the twenty-third day of growth. The total concentrations of nutrient elements after the second application were as follows: 220 mg. Ca; 100 mg.N; 40mg Mg; 20 mg. Fe; 2.175mg. Mn; 0.28mg. Cu; 0.45mg. Zn; 3.0 mg. B; 10 micrograms Mo. Following further application of nutrient elements the new leaves which emerged during the fifth week and thereafter did not show the characteristic breakdown of the tissues which was evident at the initial stages of growth.

The plants were harvested when they were forty-two days old. The above ground portions of the millet plants were cut. The cut plants were thoroughly washed in distilled water. The washed plant parts were placed in clean brown paper bags and placed in a forced-draft oven set at 65°C.

After drying for forty-eight hours at this temperature the oven-dried samples were weighed and the weights were recorded.

2.9. Laboratory Analysis of Plant Material for P, Ca, Mg, Fe and Mn.

The oven-dried plant materials were ground using a Willey mill. After grinding the ground plant material was stored in clean, dry bottles. Further drying for an additional twenty-four hours at 65°C was carried out just before subsamples were weighed out for digestion and eventual analysis.

2.9.1. Degestion of Plant Material.

The ground plant material was digested by a procedure outlined by Black (1957). Generally one-gram sample of the ground plant material was weighed out into 150-millilitres conical flask. Fifteen millilitres of concentrated nitric acid were added to the ground plant material. Another fifteen millilitres portion of the concentrated nitric acid were added to another conical flask containing no plant material and carried that flask through a similar procedure to provide a blank. The conical flasks and their contents were heated gently at first and then more strongly until the contents of the flasks were almost dry. The flasks were cooled and then 10 millilitres of 8 N nitric acid and

10 millilitres of 70% perchloric acid were added to the contents of each conical flask. The resulting solutions were evaporated to dryness on a hot plate at a relatively low temperature. Fifteen millilitres of 2 N hydrochloric acid were added to the contents of the flasks which were heated for ten minutes to dissolve the salts. The digests were filtered through Whatman No.41 filter papers into 100-millilitres volumetric flasks and the contents of the volumetric flasks were diluted to volume with distilled water and the solutions were thoroughly mixed.

2.9.2. Colorimetric Determination of P in Plant Material.

Analysis of the digest for phosphorus was done by a modified phospho-molybdate-vanadate colorimetric technique outlined by Black (1957). Ten millilitres aliquot of the diluted digest of the plant material and blank were pipetted into separate 150-millilitres conical flasks. Five millilitres of 2 N nitric acid were added and the solution was evaporated to dryness on a hot plate. Finally five millilitres of 0.1 N nitric acid and twenty-five millilitres of distilled water were added to the dry residue in the flask by means of a pipette. The solutions were swirled, then set aside for about ten minutes and then swirled again several times. A suitable aliquot, generally five millilitres of

the solution were pipetted into 50-millilitres test-tube and twenty-five millilitres molybdate-vanadate reagent were added from a pipette. The resulting solutions were mixed thoroughly and the transmittancy of the solutions were measured on a Bausch and Lomb "Spectronic-20" colorimeter at 420 millimicron wavelength within one to twenty-four hours. The galvanometer had been previously set at 100% transmission using a solution prepared from five millilitres of distilled water and twenty-five millilitres of molybdate-vanadate reagent.

2.9.3. Colorimetric Determination of Fe in Plant Material.

The concentration of iron in the plant digest was determined colorimetrically by a procedure outlined by Black (1957). Generally five millilitres aliquot of diluted digests of plant material and of the blank digest were pipetted into separate 50-millilitres volumetric flasks. Five millilitres of sodium acetate-acetic acid and one millilitre of hydroxylamine hydrochloride solutions were added. The resulting solutions were mixed thoroughly, allowed to stand for one minute, and then five millilitres of orthophenanthroline indicator solutions were added. The contents of the volumetric flasks were made up to the mark with distilled water and the solutions were thoroughly mixed again. The percentage transmittancy of the solutions were measured on a Bausch and Lomb "Spectronic-20" colorimeter at 520 millimicron wavelength.

Earlier the galvanometer had been set at 100% transmission using reagent blank made up of distilled water, 0.75 millilitres of 2 N hydrochloric acid and all the other reagents enumerated above.

2.9.4. Colorimetric Determination of Mn in Plant Material.

Colorimetric determination of manganese in the plant digests was carried out by a procedure outlined by Black (1957). Fifteen millilitres aliquot of diluted digests of plant samples and the blank were pipetted into separate 150-millilitres conical falsks. Ten millilitres of concentrated nitric acid were added and the solutions were evaporated to dryness on a hot plate. Twenty-five millilitres of distilled water, 2.5 millilitres of concentrated sulphuric acid and then 0.1 gram of solid potassium periodate were added to the contents of the flasks. The resulting solutions were then boiled for five minutes to develop the colour and the solutions were allowed to cool. The solutions were transferred to 50-millilitres volumetric flasks and were diluted to a volume of fifty millilitres with distilled water that previously had been boiled for ten minutes with 0.5 gram of potassium periodate per litre of water and cooled. The solutions were thoroughly mixed and then the percentage transmittancy was measured on a Bausch and Lomb "Spectronic-20"

colorimeter at 420 millimicron wavelength within one to twenty-four hours. The galvanometer had been previously set at 100% transmission with reagent blanks.

2.9.5. Determination of Ca and Mg in Plant Material.

The calcium and magnesium concentrations of the plant digests were estimated by the EDTA titration method outlined in Black et. al., (1965). The digests for the determination were obtained from the nitric, perchloric and hydrochloric acid digestion outlined in a previous paragraph.

CHAPTER 3

RESULTS

3.1. Phosphorus Adsorption Maximum of Soils Used.

Table 8 represents the data obtained in the adsorption maximum studies. The equilibrium P concentration is expressed as 10^4 X C moles per litre, and x/m represents the milligrams of P adsorbed per 100 grams of soil. A linear relationship was obtained for almost all the soils at least within the range of concentrations of 1 x 10^{-4}M to 7 x 10^{-4}M. However, beyond an initial concentration of KH_2PO_4 solution of 7 x 10^{-4}M, slight deviations of the isotherm from a straight line were observed for some of the soils.

Figure 1 shows the Langmuir plot of the adsorption maximum data presented in Table 8 for three selected soils. Soil 5, Koforidua, represents the soils (6, Wacri; 8, Oyarifa; 10, Akuse) which closely follow the adsorption equation. Soil 3, Boi (representing soils 1, Abenia; 2, Ankasa; 4, Tikobo; 11, Prampram) shows a slight deviation of the isotherm from a straight line relationship. Infact with these soils there is a drop in the curve beyond the initial concentration of KH_2PO_4 solution of 9 x 10^{-4}M. Soil 9, Toje (also representing soils 7, Mamfe, and 12, Agawtaw)

shows the poorest fit. Here also the last two points corresponding to initial concentration of KH_2PO_4 solution of 9×10^{-4}M, fell farther off above the curve.

The textural classification of the soils used in the investigation falls under clay loam, sandy clay, sandy clay loam, loamy sand, sandy loam and sand (Table 1). Abenia series, a sandy clay soil with the highest clay content (35.92%) has the highest adsorption maximum of 50.000 milligrams P per 100 grams of soil. Prampram, a sandy clay loam, with the second highest clay content (34.48%) also has the second highest adsorption maximum of 40.000 milligrams P per 100 grams of soil. Oyarifa series has the lowest adsorption maximum of 23.256 milligrams P per 100 grams of soil. Toje series also has a comparatively low adsorption maximum of 25.641 milligrams P per 100 grams of soil. The adsorption maximum values obtained for all the soil samples used in the investigation are just as expected. Those soils from the high rain forest areas with high clay content and less silica have high adsorption maximum values. Also some of the savanna soils with high clay content and also contain less silica have high adsorption maximum values.

In contrast, the other high rain forest and savanna soils formed over acid parent materials with less clay content but high silica content have low adsorption maximum values.

A constant K, related to the bonding energy of the absorbent for the absorbate was also calculated from the slope and intercept values presented in Table 8. From the linear form of the Langmuir equation expressed as $c/(x/m) = 1/Kb + c/b$, $c/(x/m)$ may be plotted as a linear function of c with slope $1/b$ and intercept $1/Kb$. If therefore, the value for the slope of the linear curve is divided by the value for the intercept another value, representing the constant, K, is obtained. This constant, K, ranges, in this investigation, from 1.185 to 12.333.

The bonding energy appears to increase as adsorption maximum increases. However, there is no significant relationship between adsorption maximum and bonding energy. The correlation coefficient is only r = + 0.408.

3.2. Relation of Adsorption Maximum and Bonding Energy to Some Soil Properties.

Table 9 presents the relation between adsorption maximum, bonding energy, and some soil properties. Simple correlation coefficients obtained for the relationship between the adsorption maximum and some soil properties

Table 8. Adsorption Maximum Data.

Identification No. of Soil	Soil Series Name	Equilibrium P Concentration, $Cx10^{-4}$ moles/litre	x/m mg.P/100g Soil	c/(x/m)	Slope	Intercept	Adsorption maximum mg.P/100g Soil	Constant related to bonding energy K
1	Abenia	0.015	6.098	0.003	0.020	0.002	50.000	10.000
		0.025	12.232	0.002				
		0.043	18.324	0.002				
		0.328	28.948	0.011				
		0.313	41.432	0.008				
		1.282	47.824	0.027				
		2.620	58.118	0.045				
2	Ankasa	0.021	6.066	0.003	0.028	0.003	35.714	9.333
		0.054	12.056	0.005				
		0.110	17.908	0.006				
		0.550	27.570	0.020				
		0.901	37.790	0.024				
		3.397	34.716	0.098				
		5.008	43.322	0.116				
3	Boi	0.028	6.022	0.005	0.032	0.004	31.250	8.000
		0.078	11.908	0.007				
		0.201	17.344	0.012				
		0.930	25.216	0.037				
		1.684	32.936	0.051				
		4.208	29.692	0.142				
		6.095	36.586	0.167				
4	Tikobo	0.026	6.038	0.004	0.037	0.003	27.027	12.333
		0.102	11.762	0.009				
		0.249	17.046	0.015				
		1.096	24.192	0.045				
		1.956	31.252	0.063				
		4.768	26.224	0.182				
		7.129	30.180	0.236				

Table 8. Contd.

Identification No. of Soil	Soil Series Name	Equilibrium P Concentration, Cx10^{-4} moles/litre	x/m mg.P/100g Soil	c/(x/m)	Slope	Intercept	Adsorption maximum mg.P/100g Soil	Constant related to bonding energy K
5	Koforidua	0.101	5.568	0.018	0.036	0.010	27.778	3.600
		0.226	10.994	0.020				
		0.393	16.154	0.024				
		1.308	22.878	0.057				
		5.284	23.232	0.230				
		7.503	27.862	0.269				
6	Wacri	0.065	5.794	0.011	0.039	0.006	25.641	6.500
		0.164	11.374	0.014				
		0.335	16.512	0.020				
		1.253	23.214	0.054				
		2.259	29.376	0.077				
		5.445	22.028	0.247				
		7.808	25.972	0.300				
7	Mamfe	0.120	5.454	0.022	0.033	0.018	30.303	1.833
		0.278	10.668	0.026				
		0.503	15.470	0.033				
		1.695	20.480	0.083				
		2.754	26.310	0.105				
		6.586	14.960	0.440				
		8.769	20.020	0.438				
8	Oyarifa	0.102	5.562	0.018	0.043	0.009	23.256	4.778
		0.247	10.862	0.023				
		0.432	15.912	0.027				
		1.414	22.220	0.064				
		2.375	28.658	0.083				
		6.090	18.030	0.338				
		7.755	26.302	0.295				

Table 8. Contd.

Identification No. of Soil	Soil Series Name	Equilibrium P Concentration $Cx10^{4}$ moles/litre	x/m mg.P/100g Soil	c/(x/m)	Slope	Intercept	Adsorption maximum mg.P/100g Soil	Constant related to bonding energy K
9	Toje	0.119	5.460	0.022	0.039	0.017	25.641	2.294
		0.303	10.512	0.029				
		0.547	15.200	0.036				
		1.695	20.480	0.083				
		2.651	22.083	0.120				
		6.981	12.508	0.558				
		8.769	20.020	0.438				
10	Akuse	0.052	5.874	0.089	0.032	0.027	31.250	1.185
		0.154	11.440	0.013				
		0.291	16.786	0.017				
		1.183	23.650	0.050				
		2.058	30.618	0.067				
		5.124	24.016	0.213				
		7.327	28.954	0.253				
11	Prampram	0.035	5.982	0.006	0.025	0.004	40.00	6.250
		0.042	12.132	0.004				
		0.091	18.026	0.005				
		0.421	28.374	0.015				
		1.103	36.536	0.030				
		2.954	37.456	0.079				
		4.780	44.734	0.107				
12	Agawtaw	0.130	5.392	0.024	0.038	0.017	26.316	2.235
		0.274	10.690	0.026				
		0.508	15.442	0.033				
		1.658	20.702	0.080				
		2.750	22.083	0.120				
		6.675	14.408	0.463				
		8.913	19.126	0.466				

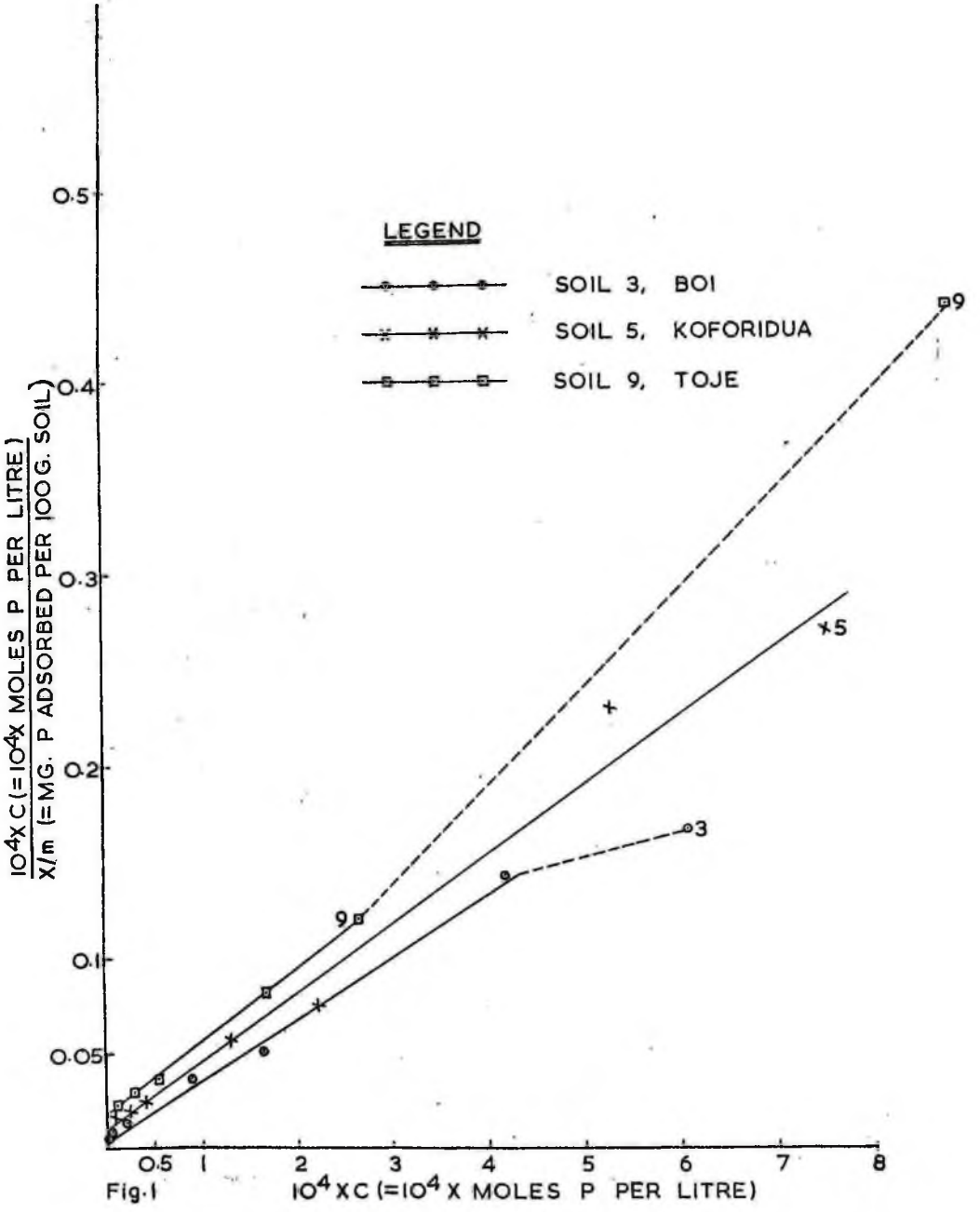

Fig. 1 PHOSPHORUS ADSORPTION DATA PLOTTED ACCORDING TO THE LANGMUIR ISOTHERM

indicate that adsorption maximum is significantly related to only clay, free iron oxide, and negatively to silica. A constant, K, related to the bonding energy of the absorbent for the absorbate is also significantly related to pH, free iron oxide, and silica.

All the correlation coefficients between adsorption maximum and soil properties which are significant are in the range $r = 0.617$ to 0.815. The best relationship between adsorption maximum and soil properties, however, is given by the free iron oxide with coefficient of correlation $r = 0.815$ (positive) which is significant at the 0.1% level. Per cent clay is also highly correlated to adsorption maximum with a coefficient of correlation $r = 0.667$ (positive). This correlation coefficient is significant at the 2% level. The relation between adsorption maximum and silica is also quite good and significant, but negative. The specific correlation coefficient is $r = 0.617$ (negative), and is significant at the 5% level. These simple correlation coefficients between adsorption maximum and soil properties indicate that free iron oxide is mainly responsible for the magnitude of phosphorus adsorption in the soils used.

Table 9 . Phosphorus Adsorption Maximum and Bonding Energy in Relation to Some Soil Properties

Soil Series	Adsorption Maximum mg.P/100g. Soil	Bonding Energy K	Free Fe_2O_3	% Clay	% Silica	pH	Organic Carbon %	Free Al_2O_3
Abenia	50.000	10.000	0.35	35.92	20.30	4.00	1.51	0.75
Prampram	40.000	6.250	0.31	34.48	32.78	7.12	0.79	13.20
Ankasa	35.714	9.333	0.30	23.20	24.44	4.00	1.20	0.48
Akuse	31.250	1.185	0.18	32.53	33.46	6.60	0.79	11.26
Boi	31.250	8.000	0.27	32.87	33.86	4.15	0.99	1.95
Mamfe	30.303	1.833	0.22	14.30	41.54	4.60	1.85	0.34
Koforidua	27.778	3.600	0.20	22.53	23.42	6.95	1.41	7.04
Tikobo	27.027	12.333	0.25	12.44	39.72	4.00	0.77	0.74
Agawtaw	26.316	2.235	0.09	8.00	55.50	5.90	0.34	3.44
Wacri	25.641	6.500	0.20	25.39	30.08	6.35	1.18	6.58
Toje	25.641	2.294	0.11	6.39	54.26	5.35	0.20	0.25
Oyarifa	23.256	4.778	0.15	19.86	42.78	6.40	0.85	0.29

Clay also contributes but its effect relative to free iron oxide may not be as great. Increase in silica content of soils, however, appears to reduce considerably phosphorus adsorption maximum.

No significant relationship was observed between adsorption maximum and organic carbon (r = + 0.388), and also between adsorption maximum and free aluminium oxide (r = + 0.129). The pH is also poorly related to adsorption maximum. The correlation coefficient is only 0.306 (negative). Organic matter, pH, and free aluminium oxide appear to have very little or no influence on phosphorus adsorption maximum.

The correlation coefficients between the constant, K, related to bonding energy and soil properties which are significant fall within the range r = 0.473 to 0.717. A very close relationship was found between the bonding energy and free iron oxide (r = + 0.717). This very close relationship is significant at the 1% level. The pH is also fairly correlated to bonding energy (r = - 0.594) and is significant at 5% level whilst the correlation coefficient between bonding energy and silica is r = - 0.473 and is also significant at 10% level. The negative correlation between bonding energy, and pH and silica is an evidence that acid soils will generally retain phosphorus with greater bonding

energy than alkaline soils whilst soils high in silica content will retain phosphorus with much less bonding energy.

There is no significant relationship between the bonding energy and organic carbon, clay, and free aluminium oxide. The correlation coefficient between the bonding energy and organic carbon is r = 0.177 (positive). The correlation coefficient between bonding energy and free aluminium oxide is r = 0.287 (negative), whilst that between bonding energy and clay is r = 0.289 (positive).

3.3. Dry Matter Yield as Related to the Adsorption Maximum.

Data showing the effect of P application on dry matter yield are presented in Table 10. Columns five and six of that table give data on dry matter yield in grams per pot of 454 grams soil. The maximum dry matter yield on Ankasa, Koforidua, Wacri, and Akuse soils occurred at ½ the P adsorption maximum. Dry matter yield on Tikobo, Mamfe and Oyarifa soils with KH_2PO_4 treatment appears to increase with increasing addition of phosphorus. But on Mamfe and Oyarifa soils with K_2HPO_4 treatment maximum dry matter yield occurred at ½ the P adsorption maximum and the P adsorption maximum, respectively. The maximum yield on Boi, Toje, and Agawtaw soils, however, was obtained at the P adsorption maximum.

Examination of the absolute dry matter values reveals that for Koforidua, Wacri, and Akuse soils with high initial P status (10ppm and more) dry matter yield is high initially but the range of increase is narrow. The absolute range values for the KH_2PO_4 treatment, for instance, are 5.10 to 6.92, 2.64 to 5.60, and 2.75 to 9.68 grams per pot, respectively. For Ankasa, Boi, Tikobo, Mamfe, Oyarifa, Toje, and Agawtaw soils with low initial P status (less than 10ppm) although the initial dry matter yield is low the range is wider. The range in values for the KH_2PO_4 treatment are 0.22 to 5.20, 0.24 to 6.15, 0.25 to 6.53, 0.36 to 6.95, 0.40 to 7.73, 0.28 to 6.65, and 0.35 to 7.49 grams per pot, respectively.

Those soils with P adsorption maximum of 27 milligrams per 100 grams soil and above (Ankasa, Akuse, Boi, Koforidua, Mamfe, Tikobo) produced maximum dry matter yield at $\frac{1}{2}$ the P adsorption maximum. The exceptions are Boi and Tikobo soils. On the other hand, those soils with P adsorption maximum of less than 27 milligrams per 100 grams soil (Agawtaw, Oyarifa, Toje, Wacri) produced maximum dry matter yield at the P adsorption maximum. An exception to this latter rule is the Wacri soil.

Table 10. Effect of P Application on Dry Matter Yield.

Soil Series Name	Initial P Status of Soil (ppm) Bray & Kurtz Method	P Saturation of Adsorption Maximum	Doses of P Applied Kg/ha	Dry Matter Yield in grams per pot		Relative Dry Matter Yield at Zero	
				KH_2PO_4	K_2HPO_4	KH_2PO_4	K_2HPO_4
Ankasa	4.50	zero	zero	0.22	0.22		
		1/8	100	0.48	0.43	2.2	2.0
		1/4	200	2.25	1.01	10.2	4.6
		1/2	400	5.20	4.10	23.6	18.6
		1	800	4.65	4.18	21.1	19.0
		2	1600	4.77	4.48	21.7	20.4
Boi	2.78	zero	zero	0.24	0.24		
		1/8	88	0.83	0.41	3.5	1.7
		1/4	175	2.50	0.99	10.4	4.1
		1/2	350	4.90	4.87	20.4	20.3
		1	700	6.15	6.08	25.6	25.3
		2	1400	6.13	6.05	25.5	25.2
Tikobo	3.70	zero	zero	0.25	0.25		
		1/8	76	0.29	0.22	1.2	0.9
		1/4	152	1.99	0.21	8.0	0.8
		1/2	303	2.51	0.73	10.0	2.9
		1	606	4.04	3.20	16.2	12.8
		2	1212	6.53	5.70	26.1	22.8
Koforidua	31.60	zero	zero	5.10	5.10		
		1/8	78	5.50	5.70	1.1	1.1
		1/4	156	5.48	6.56	1.1	1.1
		1/2	311	6.92	6.76	1.4	1.3
		1	622	6.50	7.42	1.3	1.4
		2	1244	6.91	7.06	1.4	1.4

Table 10. Contd.

Soil Series Name	Initial P Status of Soil (ppm). Bray & Kurtz Method	P Saturation of Adsorption Maximum	Doses of P Applied Kg/ha	Dry Matter Yield in grams per pot		Relative Dry Matter at zero	
				KH_2PO_4	K_2HPO_4	KH_2PO_4	K_2HPO_4
Wacri	15.35	zero	zero	2.64	2.64		
		1/8	72	4.30	2.95	1.6	1.1
		1/4	144	4.52	3.62	1.7	1.4
		1/2	287	5.60	4.39	2.1	1.7
		1	575	5.31	4.05	2.0	1.5
		2	1150	4.90	4.89	1.9	1.8
Mamfe	4.04	zero	zero	0.36	0.36		
		1/8	85	2.20	3.19	6.1	8.9
		1/4	170	2.85	4.94	7.9	13.7
		1/2	340	5.40	6.82	15.0	18.9
		1	680	5.88	6.21	16.3	17.2
		2	1359	6.95	6.59	19.3	18.3
Oyarifa	4.12	zero	zero	0.40	0.40		
		1/8	65	1.87	1.56	4.7	3.9
		1/4	130	2.90	3.43	7.2	8.6
		1/2	260	6.85	5.65	17.1	14.1
		1	521	7.00	6.36	17.5	15.9
		2	1042	7.73	6.37	19.3	15.9
Toje	1.78	zero	zero	0.28	0.28		
		1/8	72	2.06	0.80	7.4	2.9
		1/4	144	4.69	1.60	16.8	5.7
		1/2	287	5.75	3.34	20.5	11.9
		1	575	6.50	3.85	23.2	13.8
		2	1150	6.65	4.32	23.8	15.4

Table 10.Contd.

Soil Series Name	Initial P Status of Soil (ppm). Bray & Kurtz Method	P Saturation of Adsorption Maximum
Akuse	10.40	zero 1/8 1/4 1/2 1 2
Agawtaw	2.03	zero 1/8 1/4 1/2 1 2

Doses of P Applied Kg/ha	Dry Matter Yield in grams per pot		Relative Dry Matter at Zero at Zero	
	KH_2PO_4	K_2HPO_4	KH_2PO_4	K_2HPO_4
zero	2.73	2.73		
88	3.98	3.43	1.5	1.3
175	6.43	4.30	2.4	1.6
350	7.35	6.82	2.7	2.5
700	7.58	6.89	2.8	2.5
1400	9.68	6.75	3.6	2.5
zero	0.35	0.35		
74	2.10	2.05	6.0	5.9
148	4.08	4.03	11.7	11.5
295	6.04	5.30	17.3	15.1
590	6.95	6.20	19.9	17.7
1180	7.49	6.40	21.4	18.3

Boi and Tikobo soils produced maximum yield at the P adsorption maximum and not at ½ the adsorption maximum as would be expected from the above rule. Wacri soil also produced maximum yield at ½ the P adsorption maximum and not at the P adsorption maximum. An explanation to these deviations could be found in the relation of the initial P status to the P saturation of adsorption maximum at which maximum yield occurred. The initial P status of the soils appeared to influence greatly the P saturation of the adsorption maximum at which maximum dry matter yield occurred. Thus Boi and Tikobo soils with high adsorption maximum but very low initial P status of 2.78 and 3.70 ppm, respectively, produced maximum yield at the P adsorption maximum. Wacri soil, however, with its low adsorption maximum but high initial P status of 15.35 ppm produced maximum yield at ½ the P adsorption maximum. It appears that those soils with high initial P status but low P adsorption maximum did not require as high a saturation of the adsorption maximum in order to produce maximum yield as did soils with high adsorption maximum but low initial P status.

Figures 2(a) to (d) present a graphical picture of the relationship between P saturation of adsorption maximum and the relative dry matter yield. For Koforidua, Wacri, and Akuse soils there were rapid increases in relative dry

matter yields up to $\frac{1}{8}$ P saturation of the adsorption maximum. Thereafter, for Koforidua there was a levelling off whilst for Wacri and Akuse soils there were gradual increases up to $\frac{1}{2}$ P saturation of the adsorption maximum before becoming stationary. Ankasa and Mamfe soils both showed similar characteristics in their relationship between P saturation of the adsorption maximum and relative dry matter yield. Both soils produced rapid increases in relative dry matter yields up to $\frac{1}{2}$ P saturation of the adsorption maximum. After that point, for Ankasa with KH_2PO_4 treatment and Mamfe with K_2HPO_4 treatment there was a sharp drop in the curve to the P saturation of adsorption maximum and then levelled off. For Ankasa with K_2HPO_4 treatment and Mamfe with KH_2PO_4 treatment there were tendencies towards increased relative yields after $\frac{1}{2}$ P saturation of the adsorption maximum but the differences were not significant. Agawtaw, Boi, Oyarifa, and Toje soils also showed similar characteristics in their relationship between P saturation of adsorption maximum and relative dry matter yield. Boi and Oyarifa soils produced rapid increases up to $\frac{1}{2}$ P saturation of the adsorption maximum then produced gradual increases up to the P adsorption maximum before levelling off. However for Oyarifa with KH_2PO_4 treatment there was further increase after the P adsorption maximum but again the difference was not significant.

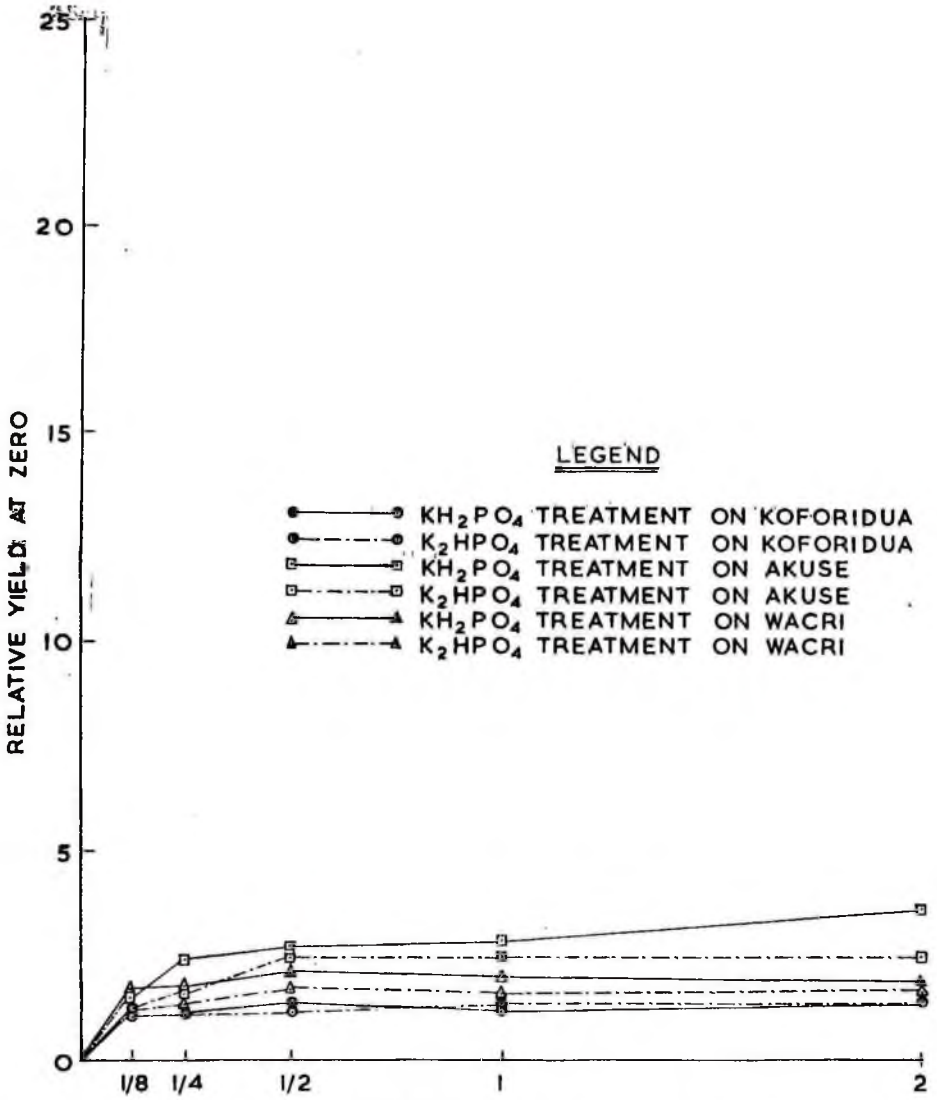

Fig. 2(a) THE RELATIVE YIELD OF MILLET AS RELATED TO THE P SATURATION OF THE ADSORPTION MAXIMUM FOR KOFORIDUA, AKUSE AND WACRI SOILS.

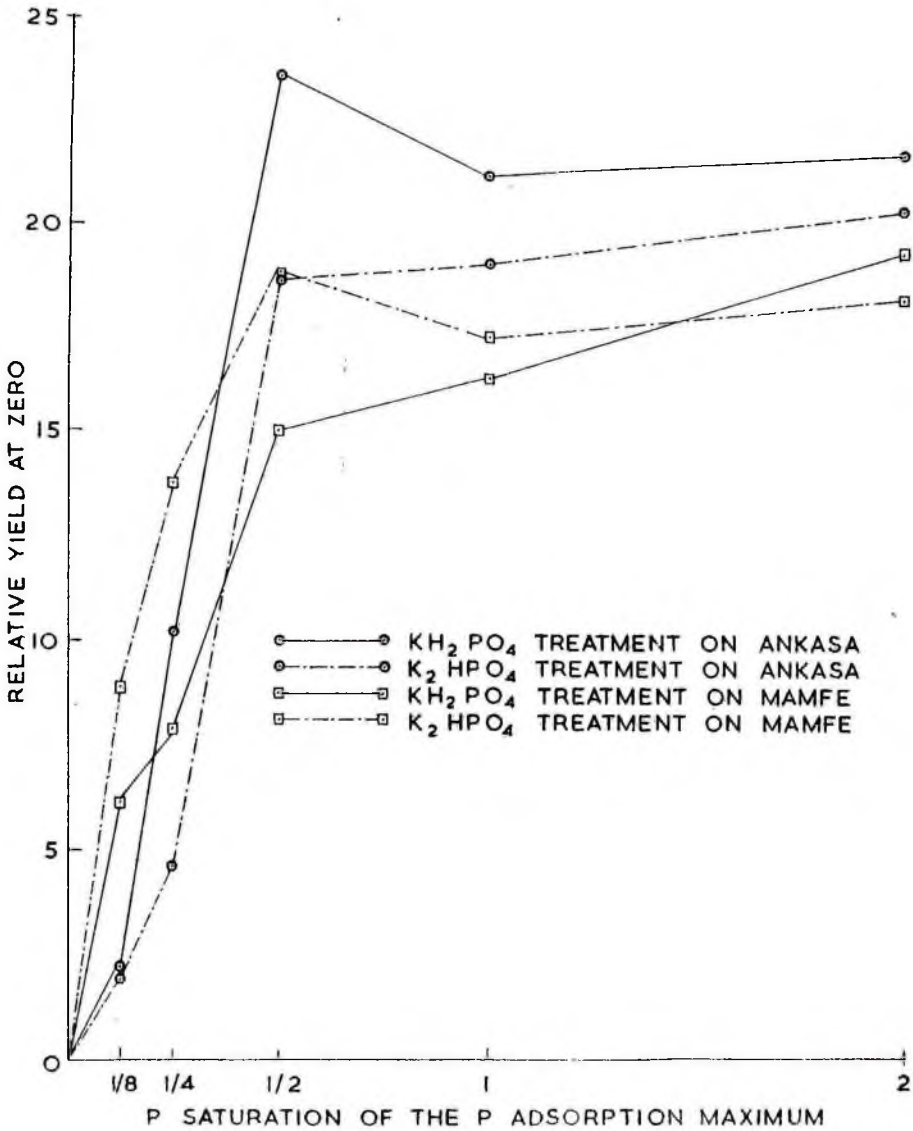

Fig. 2 (b) THE RELATIVE YIELD OF MILLET AS RELATED TO THE THE P SATURATION OF THE ADSORPTION MAXIMUM FOR ANKASA AND MAMFE SOILS.

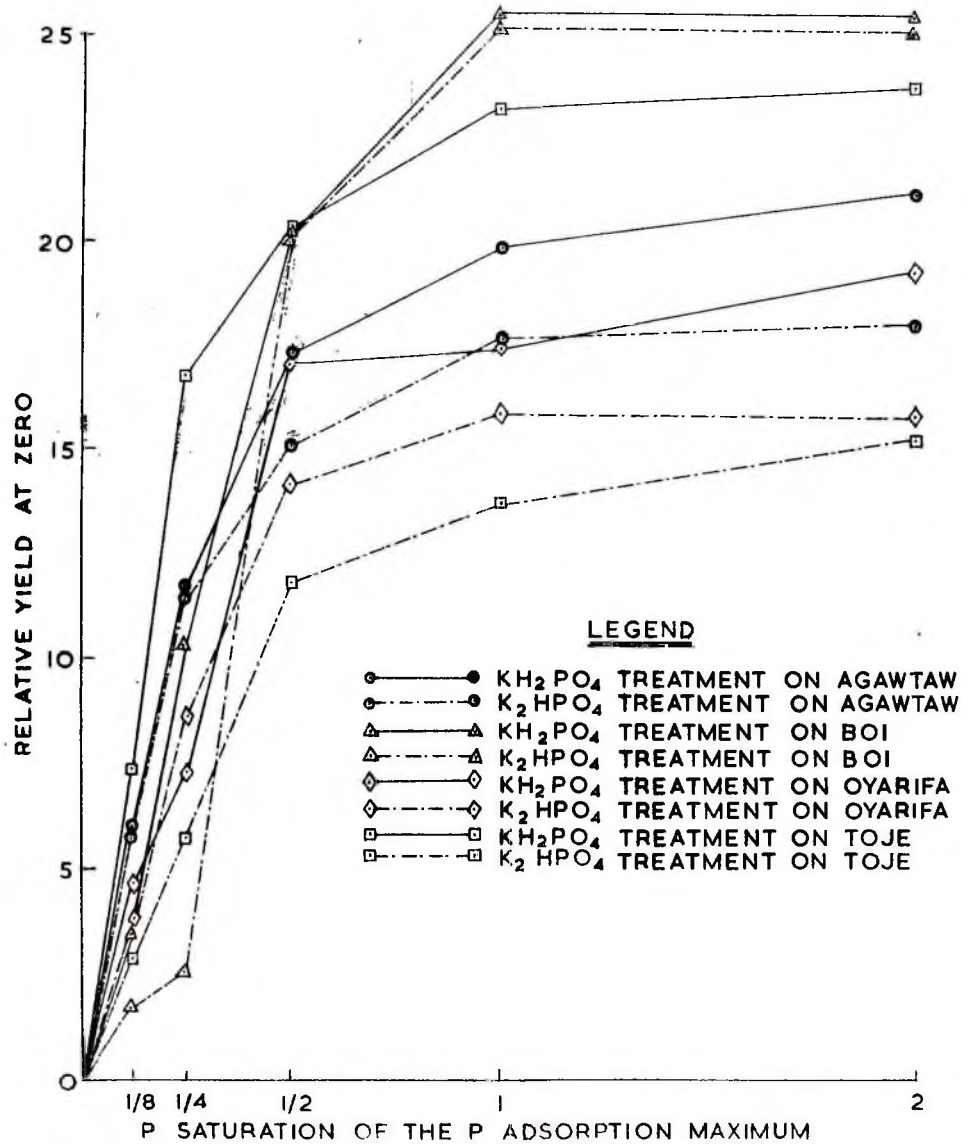

Fig. 2(c)

THE RELATIVE YIELD OF MILLET AS RELATED TO THE P SATURATION OF THE ADSORPTION MAXIMUM FOR AGAWTAW, BOI, OYARIFA AND TOJE SOILS.

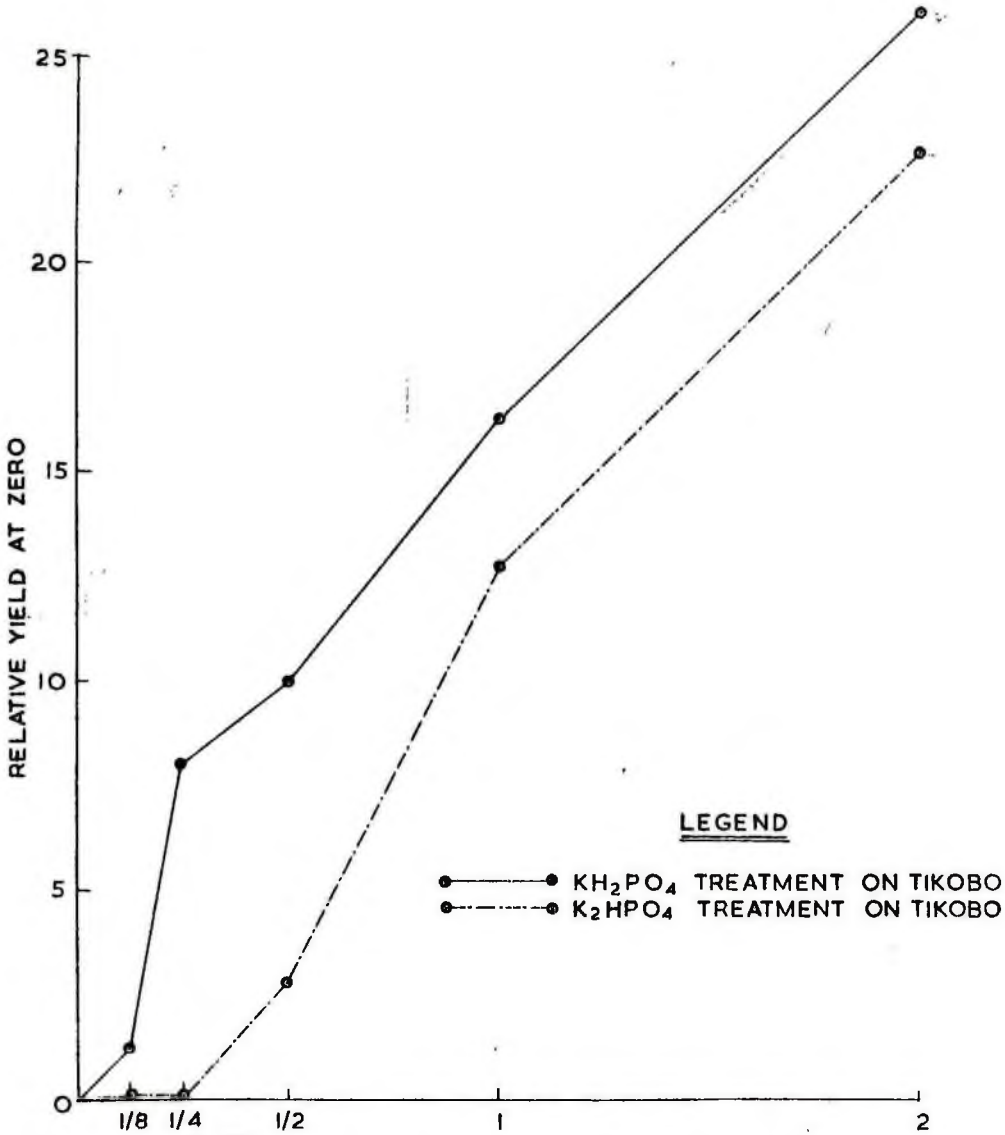

Fig. 2 (d) THE RELATIVE YIELD OF MILLET AS RELATED TO THE P SATURATION OF THE ADSORPTION MAXIMUM FOR TIKOBO SOIL.

For Agawtaw and Toje soils there were rapid increases in relative dry matter yields up to $\frac{1}{4}$ P saturation of the adsorption maximum. Thereafter, there were gradual increases up to the P adsorption maximum before becoming stationary. For Toje with K_2HPO_4 treatment there was rapid increase up to $\frac{1}{2}$ P saturation of adsorption maximum before levelling off slightly. Tikobo soil, on the contrary, behaved differently from all the other soils. It appeared that successive addition of phosphorus produced increased yields in dry matter up to 2 P saturation of adsorption maximum.

Comparison of rates of increase in dry matter with unit addition of P at the various P saturation of adsorption maximum reveals that on most of the soils used optimum dry matter yield could probably be produced at much lower P saturation of the adsorption maximum than the P adsorption maximum. The gradients of the slopes of the curves in Figures 2(a) to (d) calculated at the various P saturation of the adsorption maximum (i.e., $\frac{1}{8}$, $\frac{1}{4}$, $\frac{1}{2}$, 1 and 2) were taken as the rates of increase in dry matter with unit addition of P. For Koforidua, Wacri, Mamfe, Akuse, and Agawtaw soils the rates of increase in dry matter with unit addition of P were greatest at $\frac{1}{8}$ P saturation of the adsorption maximum with both KH_2PO_4 and K_2HPO_4

treatments. On Ankasa, Boi, and Toje soils the rates of increase in dry matter with unit addition of P were greatest at $\frac{1}{4}$ and $\frac{1}{2}$ P saturation of the adsorption maximum with KH_2PO_4 and K_2HPO_4 treatments, respectively. The rate of increase with unit addition of P on Tikobo soil was greatest at $\frac{1}{4}$ P saturation of adsorption maximum with KH_2PO_4 treatment and the P adsorption maximum with K_2HPO_4 treatment. On Oyarifa soil also the rate of increase in dry matter with unit addition of P was greatest at $\frac{1}{2}$ P saturation of adsorption maximum with KH_2PO_4 treatment and $\frac{1}{4}$ P saturation of the adsorption maximum with K_2HPO_4 treatment. It is evident from the foregoing that on all soils used in this investigation optimum dry matter yield could probably be obtained within the range of P fertilizer application rates of $\frac{1}{8}$ the P adsorption maximum and the P adsorption maximum.

3.4. Per cent P Uptake as Related to the Adsorption Maximum.

Data on the effect of P application on the P concentration and uptake of the test-crop for the two P-carrier treatments are presented in Table 11. To obtain the per cent P concentration values the micrograms P per gram plant material values were divided by one million and then multiplied by one hundred.

The per cent P uptake values, on the other hand, were obtained by multiplying the per cent P concentration values by the total dry matter yield in grams per pot. Generally the phosphorus concentration in the plant tissues and the total per cent phosphorus uptake increased as the amount of phosphorus added increased. The relationship between the P saturation of the adsorption maximum and the per cent phosphorus uptake is shown in Figures 3 (a) to (e). Ankasa, Boi, and Mamfe soils showed similar characteristics in their relationship between P saturation of the adsorption maximum and the per cent P uptake. For these soils, although there were slight increases in P uptake from zero-P-treatment, marked increases occurred at $\frac{1}{2}$ the P adsorption maximum. Thereafter there appeared further increases in per cent P uptake. The graphical picture shown by Tikobo soil is slightly different from those for Ankasa, Boi, and Mamfe. There were again slight increases in per cent P uptake from zero-P-treatment but a noticeable increase appeared only at the P adsorption maximum. After that point there were further increases. Agawtaw, Akuse, and Toje soils also showed similar characteristics in their relationship between P saturation of the adsorption maximum and per cent P uptake. Marked increases in per cent P uptake occurred on these soils at $\frac{1}{8}$ the P adsorption maximum.

Table 11. Effect of P Application on P Concentration of Millet

Soil Series Name	Initial P Status of Soil (ppm) Bray & Kurtz Method	P Saturation of Adsorption Maximum	Doses of P Applied Kg/ha	P Content Per cent		Per cent P Uptake	
				KH_2PO_4	K_2HPO_4	KH_2PO_4	K_2HPO_4
Ankasa	4.50	zero	zero	0.09	0.09	0.02	0.02
		1/8	100	0.10	0.07	0.05	0.03
		1/4	200	0.12	0.11	0.27	0.12
		1/2	400	0.25	0.14	1.30	0.62
		1	800	0.32	0.18	1.49	0.75
		2	1600	0.52	0.30	2.48	1.34
Boi	2.78	zero	zero	0.06	0.06	0.02	0.02
		1/8	88	0.06	0.06	0.02	0.02
		1/4	175	0.13	0.12	0.33	0.12
		1/2	350	0.25	0.17	1.23	0.83
		1	700	0.31	0.28	1.91	1.70
		2	1400	0.52	0.55	3.19	3.33
Koforidua	31.60	zero	zero	0.14	0.14	0.71	0.71
		1/8	78	0.20	0.17	1.10	0.97
		1/4	156	0.27	0.23	1.48	1.50
		1/2	311	0.38	0.30	2.63	2.03
		1	622	0.44	0.36	2.86	2.67
		2	1244	0.46	0.58	3.18	4.09
Wacri	15.35	zero	zero	0.12	0.12	0.32	0.32
		1/8	72	0.18	0.16	0.77	0.47
		1/4	144	0.25	0.21	0.99	0.76
		1/2	287	0.33	0.32	1.85	1.40
		1	575	0.44	0.41	2.34	1.66
		2	1150	0.60	0.52	2.94	2.54

Table 11.Contd.

Soil Series Name	Initial P Status of Soil (ppm) Bray & Kurtz Method	P Saturation of Adsorption Maximum	Doses of P Applied Kg/ha	P Content Per cent		Per cent P Uptake	
				KH_2PO_4	K_2HPO_4	KH_2PO_4	K_2HPO_4
Mamfe	4.04	zero	zero	0.06	0.06	0.02	0.02
		1/8	85	0.09	0.09	0.05	0.03
		1/4	170	0.16	0.12	0.27	0.12
		1/2	340	0.25	0.23	1.30	0.62
		1	680	0.40	0.36	1.49	0.75
		2	1359	0.52	0.52	2.48	1.34
Oyarifa	4.12	zero	zero	0.06	0.06	0.02	0.02
		1/8	65	0.07	0.08	0.13	0.12
		1/4	130	0.10	0.09	0.26	0.31
		1/2	260	0.20	0.19	1.30	1.13
		1	520	0.40	0.36	2.80	2.29
		2	1042	0.67	0.35	5.18	2.23
Toje	1.78	zero	zero	0.06	0.06	0.02	0.02
		1/8	72	0.07	0.04	0.14	0.03
		1/4	144	0.10	0.09	0.47	0.14
		1/2	287	0.18	0.12	1.04	0.40
		1	575	0.30	0.25	1.95	0.96
		2	1150	0.66	0.58	4.39	2.51
Akuse	10.40	zero	zero	0.09	0.09	0.25	0.25
		1/8	88	0.13	0.13	0.52	0.45
		1/4	175	0.16	0.20	1.03	0.86
		1/2	350	0.24	0.28	1.76	1.91
		1	700	0.41	0.50	3.11	3.45
		2	1400	0.57	0.59	5.52	3.99

Table 11. Contd.

Soil Series Name	Initial P Status of Soil (ppm) Bray & Kurtz Method	P Saturation of Adsorption Maximum	Doses of P Applied Kg/ha	P Content Per cent		Per cent P Uptake	
				KH_2PO_4	K_2HPO_4	KH_2PO_4	K_2HPO_4
Agawtaw	2.03	zero	zero	0.05	0.05	0.02	0.02
		$\frac{1}{8}$	74	0.10	0.07	0.21	0.14
		$\frac{1}{4}$	148	0.12	0.15	0.49	0.60
		$\frac{1}{2}$	295	0.25	0.22	1.51	1.35
		1	590	0.42	0.38	3.41	2.36
		2	1180	0.63	0.67	4.72	4.29
Tikobo	3.70	zero	zero	0.06	0.06	0.02	0.02
		$\frac{1}{8}$	76	0.08	0.07	0.02	0.02
		$\frac{1}{4}$	152	0.11	0.07	0.22	0.02
		$\frac{1}{2}$	303	0.15	0.12	0.23	0.08
		1	606	0.20	0.17	0.81	0.54
		2	1212	0.45	0.39	2.94	2.22

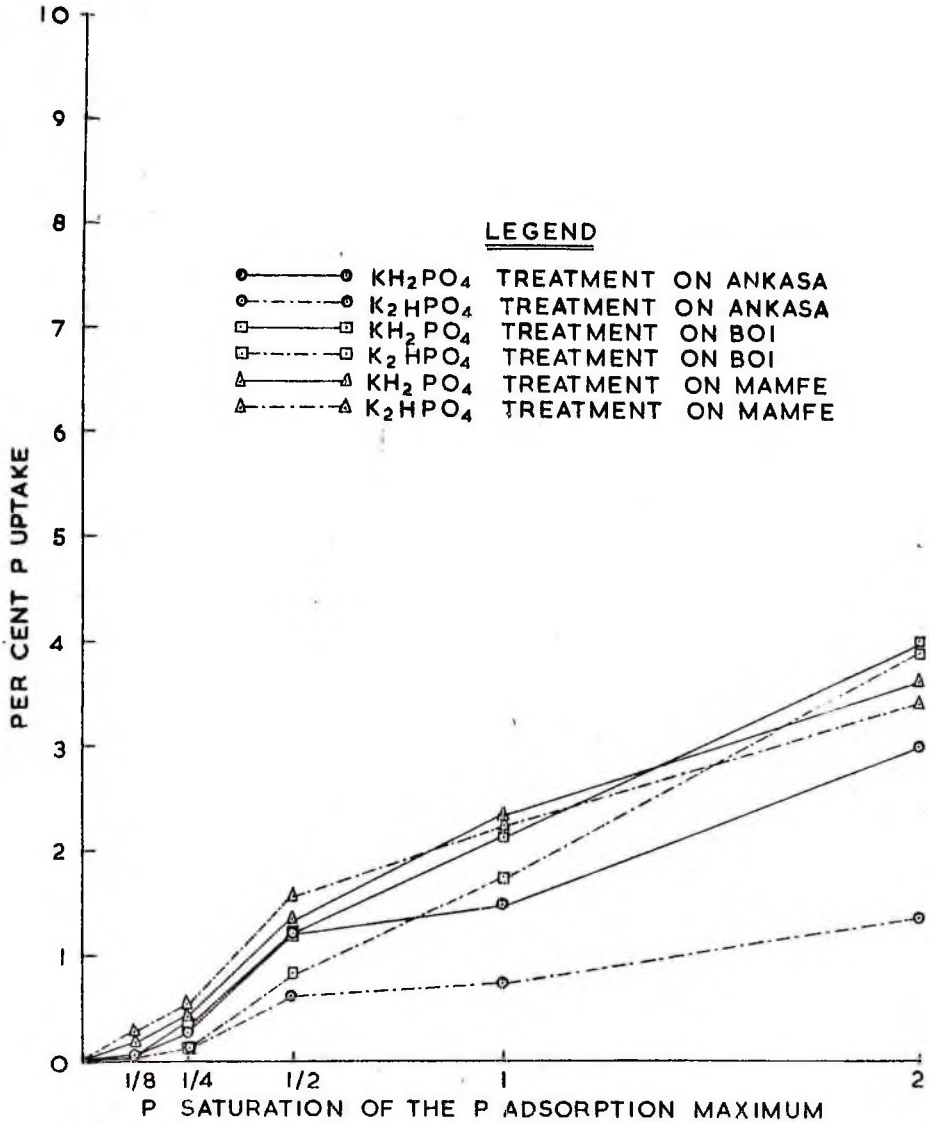

Fig. 3(a)
THE PER CENT P UPTAKE OF MILLET AS RELATED TO THE P SATURATION OF THE P ADSORPTION MAXIMUM FOR THE ANKASA, BOI AND MAMFE SOILS.

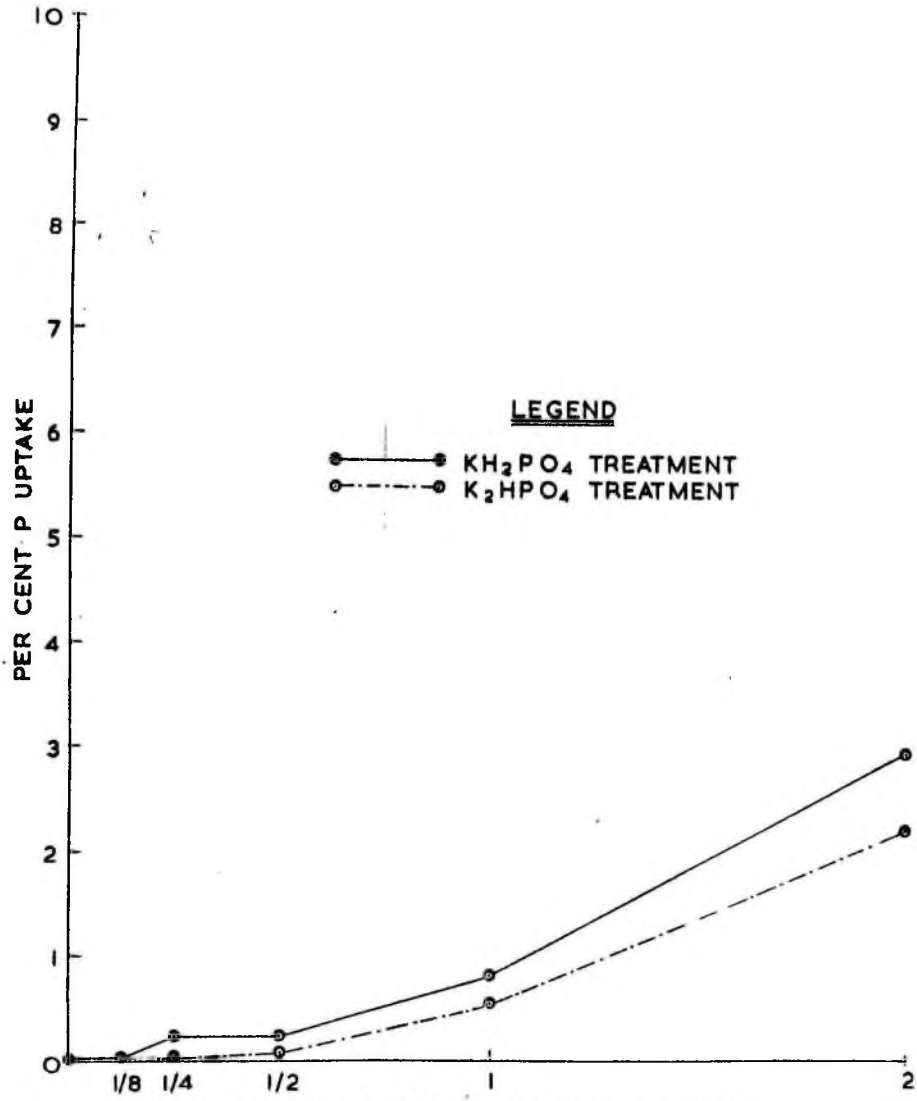

Fig. 3(b)

THE PER CENT P UPTAKE OF MILLET AS RELATED TO THE P SATURATION OF THE P ADSORPTION MAXIMUM FOR THE TIKOBO SOILS.

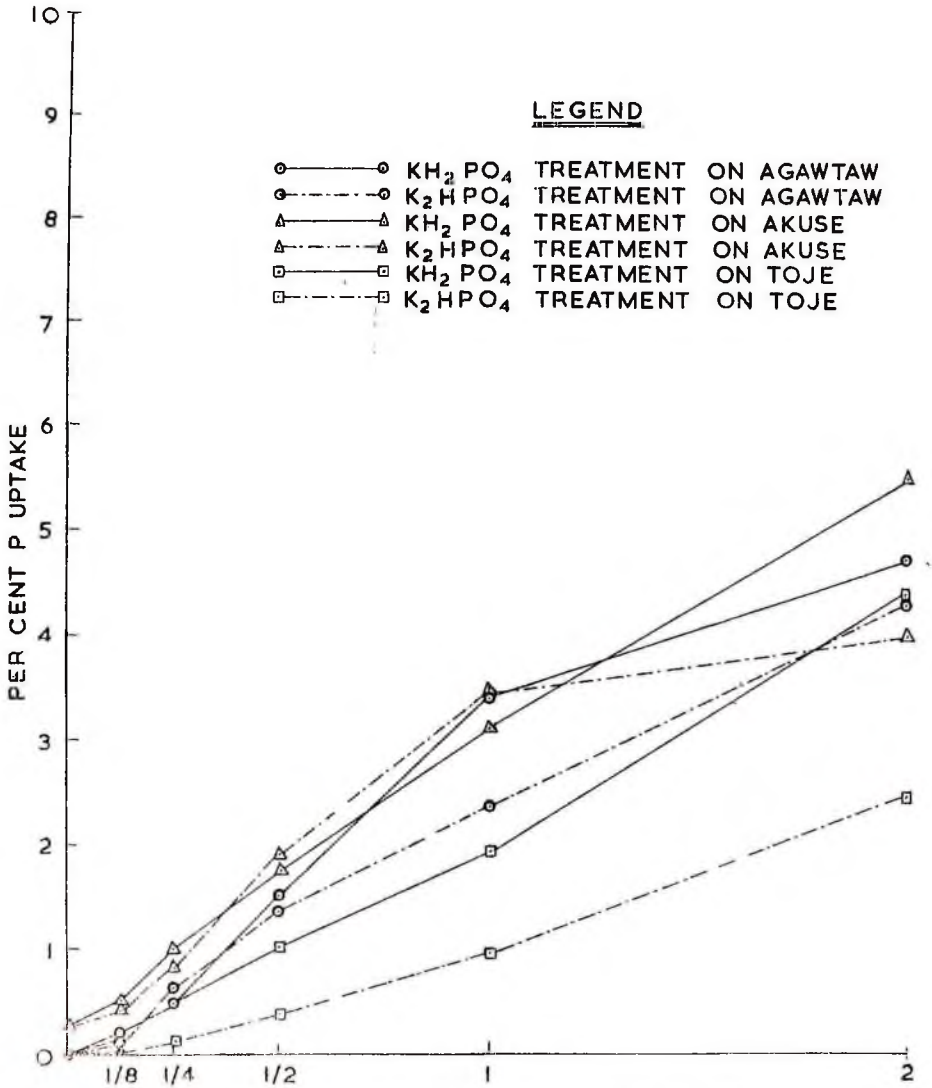

Fig. 3(c)

THE PER CENT P UPTAKE OF MILLET AS RELATED TO THE P SATURATION OF THE P ADSORPTION MAXIMUM FOR THE AGAWTAW, AKUSE AND TOJE SOILS.

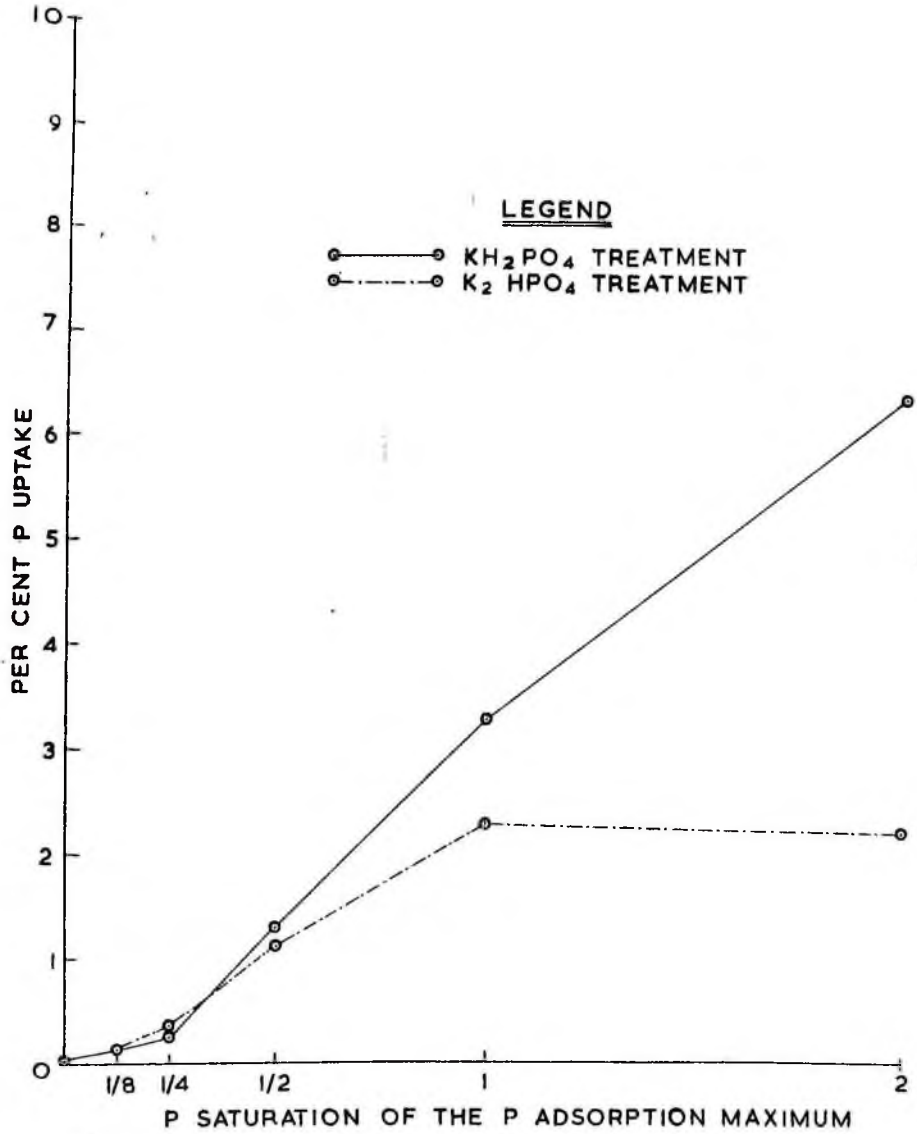

Fig. 3 (d)
THE PER CENT P UPTAKE OF MILLET AS RELATED TO THE P SATURATION OF THE P ADSORPTION MAXIMUM FOR THE OYARIFA SOIL.

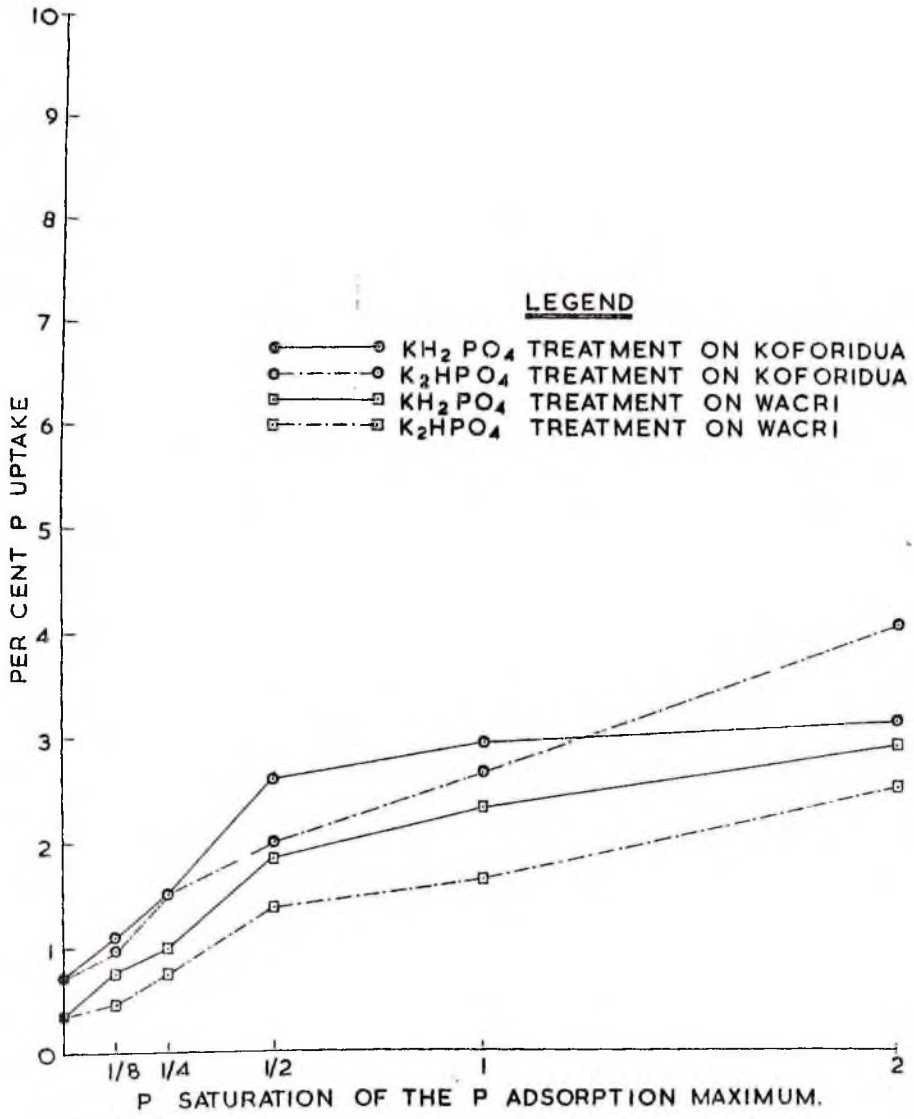

Fig. 3(e) THE PER CENT P UPTAKE OF MILLET AS RELATED TO THE P SATURATION OF THE P ADSORPTION MAXIMUM FOR THE KOFORIDUA AND WACRI SOILS.

Thereafter there appeared further increases except for the K_2HPO_4 treatment on Akuse soil. With this treatment there appeared a drop after the P adsorption maximum. On Oyarifa soil there were also slight increases in per cent P uptake from zero-P-treatment but marked increases occurred only at $\frac{1}{4}$ the P adsorption maximum. Thereafter, for KH_2PO_4 treatment there appeared further increases. However, for K_2HPO_4 treatment there were further increases up to the P adsorption maximum and then levelled off. For Koforidua and Wacri soils there occurred significant increases in per cent P uptake from zero-P-treatment up to $\frac{1}{2}$ the P adsorption maximum. After that point, although there appeared further increases the differences were not significant.

Table 14 summarizes the relationship between P adsorption maximum, bonding energy, and uptake of applied phosphorus. The data on P uptake as per cent of P applied were obtained by dividing the per cent P uptake values by the amount of phosphorus in grams added to the soils (presented in Table 3). On Ankasa, Boi, and Tikobo soils with high adsorption maximum (27 milligrams per 100 grams soil and above) and equally high bonding energy (6.00 and more) uptake of applied P was relatively low. Koforidua soil with high P adsorption maximum gave

high values for uptake of applied P. This soil, however, has a low bonding energy value (less than 6.00). The high uptake of applied P could probably be due to the low bonding energy. Further evidence of the influence of bonding energy on the uptake of applied phosphorus is given by Akuse and Mamfe soils. These soils with relatively high adsorption maximum comparable to that of Boi Soil (30 milligrams per 100 grams soil) gave fairly high uptake of applied P values than the Boi soil. Akuse and Mamfe soils have low bonding energy of 1.833 and 1.185, respectively. The high uptake of applied P could probably be a consequence of the low bonding energy of the soil colloidal particles for added phosphorus. On the other hand, Oyarifa, Toje, and Agawtaw soils with low adsorption maximum and equally low bonding energy gave high values for uptake of applied phosphorus. Wacri soil, however, is an exception. Although it has high bonding energy it still gave high value for uptake of applied phosphorus. In any case its adsorption maximum value is low.

It is obvious from the relationship represented in Table 12 that bonding energy is closely related to P uptake than the adsorption maximum. On those soils with high bonding energy uptake of applied phosphorus was

Table 12. Relation Between Adsorption Maximum, Bonding Energy and Uptake of Applied Phosphorus

Soil Series Name	Initial P Status of Soil (ppm) Bray & Kurtz Method	Phosphorus Adsorption Maximum	Bonding Energy	P Uptake as % of P Applied	
				KH_2PO_4	K_2HPO_4
Ankasa	4.50	35.000	9.333	7	4
Boi	2.78	31.250	8.000	12	9
Tikobo	3.70	27.027	12.333	6	3
Koforidua	31.60	27.778	3.600	39	39
Wacri	15.35	25.641	6.500	30	21
Mamfe	4.04	30.303	1.833	15	17
Oyarifa	4.12	23.256	4.778	21	16
Toje	1.78	25.641	2.294	16	7
Akuse	10.40	31.250	1.185	25	23
Agawtaw	2.03	26.316	2.235	24	18
Range of % Uptake Values	..	..	..	6-39	3-39
Average Values of % Uptake	..	..	..	20	16

comparatively low. The converse, however, is true for those soils with low bonding energy. The correlation coefficients calculated for the relationship between adsorption maximum, bonding energy, and uptake of applied phosphorus support the above assertion. The correlation coefficients show that the bonding energy is a better index of uptake of applied phosphorus than the adsorption maximum. The correlation coefficients between bonding energy and uptake of applied phosphorus are $r = -0.566$ for KH_2PO_4 treatment and $r = -0.562$ for K_2HPO_4 treatment, and are significant at 10% level. The correlation coefficients between adsorption maximum and uptake of applied P are not significant. The specific correlation coefficients are $r = -0.395$ and $r = -0.211$ for KH_2PO_4 and K_2HPO_4, respectively.

3.5. Comparison of Dry Matter Yields and P Uptake Values for KH_2PO_4 and K_2HPO_4 Treatments

A critical examination of the data presented in Table 10 and 11 reveals striking differences between the relative efficiency of the KH_2PO_4 and K_2HPO_4 P-carriers. From the dry matter data it is clear that, except on Koforidua and Mamfe, dry matter yields for KH_2PO_4 treatment were generally higher than K_2HPO_4 treatment.

The per cent P concentration and total P uptake values also support the above observation. The per cent P concentration of the test-crop was generally higher for KH_2PO_4 treatment than K_2HPO_4 treatment. The only exceptions were found on Akuse soil and a few isolated treatments on a few other soils (Boi, Oyarifa, Agawtaw). Similarly, the per cent total P uptake values were, in the majority of treatments, higher for KH_2PO_4 than for K_2HPO_4 treatment. Examination of the P uptake as per cent of applied P values represented in Table 12 further reveals that uptake of applied P was higher for the KH_2PO_4 than for K_2HPO_4 treatment. Koforidua and Mamfe soils are exceptions. On Koforidua soil P uptake as per cent of applied P was equal for both treatments. On Mamfe soil also the P uptake as per cent of applied P was higher for K_2HPO_4 than for KH_2PO_4 treatment. The range of per cent uptake of applied P values for all the soils used are 6 to 39% and 3 to 39% for KH_2PO_4 and K_2HPO_4 treatments, respectively. The differences in per cent uptake of applied P values observed in this investigation for the two P-carrier treatments are true reflection of the relative availability of the $H_2PO_4^-$ and HPO_4^{--} ions. Plants are known to take up their inorganic phosphorus principally as the $H_2PO_4^-$ ion.

Infact plants may take up this inorganic phosphate ion more easily than the HPO_4^{--} ion. Hence the low phosphorus uptake and dry matter yields on KH_2PO_4-treated soil samples were as expected.

3.6. Plant Tissue Composition of Ca, Mg, Fe, Mn.

Data on the effect of phosphorus application rates on the concentration of calcium, magnesium, iron and manganese in the plant tissues are presented in Table 13. On all the soils used in this investigation and for both P-carrier treatments increased phosphorus addition reduced the availability of calcium as judged by the tissue composition of the test-crop. This is evidenced by the very close but negative correlation coefficients obtained for the relationship between the quantity of phosphorus added and the plant tissue concentration of calcium for all the soil treatments put together. The specific correlation coefficients are r = 0.653 (negative) for KH_2PO_4 treatment and r = 0.592 (negative) for K_2HPO_4 treatment. Both correlation coefficients are significant at 0.1% level. In the light of the low calcium content of the plant tissue it is probable that the symptoms observed in the plants as early as the third week of growth on some of the soil samples could be calcium deficiency symptoms.

The symptoms were characterised by a breakdown and subsequent drying of the tips of the newly formed leaves, a nutrient disorder symptom characteristic of calcium shortages.

Availability of magnesium as evidenced by the plant tissue composition, on the other hand, was generally enhanced by increased phosphorus applications. The correlation coefficients calculated for the relationship between the quantity of phosphorus added and magnesium concentration of the plant tissues support the above observation. There are close and positive correlations between the quantity of phosphorus and the plant tissue composition of magnesium for all the soil treatments put together and for both P-carrier treatments. The specific correlation coefficients are $r = 0.385$ (positive) for KH_2PO_4 and $r = 0.313$ (positive) for K_2HPO_4 treatment. The correlation coefficients are significant at 1% level and 5% level for KH_2PO_4 and K_2HPO_4 treatments, respectively.

When the data on the quantity of phosphorus added and the plant tissue concentration of iron and manganese were subjected to statistical analysis no correlation was obtained between the quantity of phosphorus added and the plant content of iron and manganese for all soil treatments put together.

Table 13. Effect of P Application Rates on Concentration of Ca, Mg, Fe, Mn in Millet Tissues.

Soil Series Name	P Saturation of P Ads. Maximum	Doses of P Applied Kg.P/ha	Concentration of Ca, Mg, Fe, Mn in Tissue							
			% Ca Content		% Mg Content		Fe Content (ppm)		Mn Content (ppm)	
			KH_2PO_4	K_2HPO_4	KH_2PO_4	K_2HPO_4	KH_2PO_4	K_2HPO_4	KH_2PO_4	K_2HPO_4
Ankasa	0	zero	4.38	4.38	1.80	1.80	287	287	56	56
	1/8	100	2.61	3.53	1.04	0.71	160	150	92	60
	1/4	200	1.92	2.06	1.06	0.96	156	95	94	89
	1/2	400	0.64	0.88	1.22	0.86	127	119	110	100
	1	800	0.44	0.48	1.70	1.10	128	115	126	94
	2	1600	0.08	0.16	1.73	1.34	106	110	126	94
Boi	0	zero	2.58	2.58	1.31	1.31	219	219	49	49
	1/8	88	2.40	2.16	0.39	0.44	162	176	44	54
	1/4	175	1.60	1.82	0.88	0.96	139	125	52	63
	1/2	350	0.36	1.68	1.77	0.91	137	120	71	86
	1	700	0.16	1.20	1.75	1.15	128	119	86	79
	2	1400	0.08	0.80	1.68	0.86	115	110	79	118
Tikobo	0	zero	4.00	4.00	0.70	0.70	214	214	20	20
	1/8	76	3.84	4.00	0.67	0.59	83	240	51	33
	1/4	152	2.56	3.43	0.96	1.12	191	220	86	49
	1/2	303	1.40	1.90	0.86	0.96	134	153	86	74
	1	606	0.80	0.56	1.44	1.15	153	142	103	86
	2	1212	0.64	0.24	1.56	1.25	141	146	189	103
Koforidua	0	zero	1.24	1.24	1.15	1.15	155	155	122	122
	1/8	78	1.20	0.96	1.18	1.32	165	142	143	126
	1/4	156	1.20	0.84	1.25	1.25	133	133	189	126
	1/2	311	0.72	0.32	1.54	1.34	162	103	160	168
	1	622	0.80	0.48	1.54	1.30	205	215	192	200
	2	1244	0.48	0.32	1.58	1.44	229	211	259	284

Table 13.Contd.

Soil Series Name	P Saturation of P Ads. Maximum	Doses of P Applied Kg.P/ha	Concentration of Ca, Mg, Fe, Mn in Tissue							
			% Ca Content		% Mg Content		Fe Content (ppm)		Mn Content (ppm)	
			K_2PO_4	K_2HPO_4	KH_2PO_4	K_2HPO_4	KH_2PO_4	K_2HPO_4	KH_2PO_4	K_2HPO_4
Wacri	0	zero	1.31	1.31	1.10	1.10	165	165	126	126
	1/8	72	1.25	0.56	1.09	1.15	187	120	69	168
	1/4	144	1.32	0.72	1.34	1.39	171	164	221	192
	1/2	287	1.12	0.76	1.44	1.49	182	133	189	319
	1	575	0.92	0.24	1.49	1.70	220	211	208	319
	2	1150	0.63	0.24	1.63	1.63	229	165	225	259
Mamfe	0	zero	2.60	2.60	1.36	1.36	181	181	56	56
	1/8	85	1.56	0.96	1.10	0.86	146	146	58	71
	1/4	170	1.04	0.72	1.40	0.81	129	120	63	84
	1/2	340	0.48	0.16	1.73	1.44	146	67	47	86
	1	680	0.64	0.48	1.62	1.01	132	80	79	79
	2	1359	0.64	0.32	1.54	1.49	104	106	86	94
Oyarifa	0	zero	2.65	2.65	1.33	1.33	143	143	24	24
	1/8	65	1.72	1.04	0.82	0.99	129	229	39	47
	1/4	130	1.32	1.16	1.37	0.96	102	187	31	39
	1/2	260	1.00	0.60	0.91	1.30	137	115	63	54
	1	520	0.48	0.40	0.96	1.44	127	135	71	63
	2	1042	0.48	0.48	1.44	1.39	120	137	103	94
Toje	0	zero	3.50	3.50	1.45	1.45	279	279	68	68
	1/8	72	2.40	2.38	0.82	1.16	100	220	31	92
	1/4	144	1.20	1.40	1.04	0.76	93	140	110	39
	1/2	287	1.04	0.48	1.06	1.30	120	297	71	94
	1	575	0.54	0.40	1.54	1.54	124	215	110	125
	2	1150	0.36	0.16	1.34	1.73	154	225	110	155

Table 15. Contd.

Soil Series Name	P Saturation of P Ads. Maximum	Doses of P Applied Kg.P/ha	Concentration of Ca, Mg, Fe, Mn in Tissue							
			% Ca Content		% Mg Content		Fe Content (ppm)		Mn Content (ppm)	
			KH_2PO_4	K_2HPO_4	KH_2PO_4	K_2HPO_4	KH_2PO_4	K_2HPO_4	KH_2PO_4	K_2HPO_4
Akuse	0	zero	1.60	1.60	1.54	1.54	102	102	55	55
	1/8	88	1.59	1.28	1.30	1.37	111	146	63	71
	1/4	175	1.52	1.12	1.42	1.42	115	142	71	71
	1/2	350	1.04	0.68	1.85	1.30	146	128	94	110
	1	700	0.32	0.16	2.28	1.70	162	93	110	103
	2	1400	0.64	0.21	1.63	1.44	142	146	120	126
Agawtaw	0	zero	3.27	3.27	1.48	1.48	164	164	37	37
	1/8	74	1.16	1.20	1.03	0.81	119	128	31	55
	1/4	148	1.16	1.04	1.06	0.86	155	174	39	65
	1/2	295	1.20	0.48	1.39	1.25	151	137	45	94
	1	590	0.56	0.16	0.43	1.34	111	142	63	103
	2	1180	0.56	0.08	0.67	1.39	128	137	86	119

However, when the soils were considered separately some correlation was obtained between the quantity of phosphorus added and the plant tissue concentration of iron and manganese for both treatments. The correlation coefficients for the relationship between the quantity of phosphorus added and the iron concentration of the plant tissues are negative. Only the correlation coefficients for Boi (KH_2PO_4 treatment), Koforidua (both KH_2PO_4 and K_2HPO_4 treatments), Mamfe (KH_2PO_4 treatment), Tikobo (K_2HPO_4 treatment), and Wacri (KH_2PO_4 treatment) are significant. The negative correlation suggests a reduction in iron availability whilst the positive correlation suggests an increase in iron availability with increased P addition.

Table 14. Correlation Between Quantity of Phosphorus Added and Plant Tissue Concentration of Iron and Manganese

Soil Series Name	Correlation Coefficients			
	IRON		MANGANESE	
	KH_2PO_4	K_2HPO_4	KH_2PO_4	K_2HPO_4
Ankasa	-0.6545	-0.4798	0.7852*	0.5242
Boi	-0.7142*	-0.6700	0.7910*	0.9451****
Tikobo	-0.1821	-0.7611*	0.9582****	0.9075***
Koforidua	0.9060***	0.7164*	0.9259****	0.9936*****
Wacri	0.9103***	0.3772	0.6217	0.5658
Mamfe	-0.8130**	-0.4932	0.8320**	0.7249*
Oyarifa	-0.2300	-0.4347	0.9609****	0.9612*****
Toje	-0.1316	Failed	0.6068	0.8658**
Akuse	0.6659	0.1518	0.9169****	0.8719**
Agawtaw	-0.4767	-0.3805	0.9865*****	0.8945***

* Significant at 10% level
* * " 5% level
* * * " 2% level
* * * * " 1% level
* * * * * " 0.1% level

The correlation coefficients obtained for the relationship between the quantity of P applied and the manganese concentration of the plant tissues are all positive. This positive correlation suggests that for the individual soils increase in the quantity of phosphorus added increased manganese availability. Except for Ankasa (K_2HPO_4 treatment), Toje (KH_2PO_4 treatment) and Wacri (both KH_2PO_4 and K_2HPO_4 treatments), all correlation coefficients obtained on the individual soils are significant.

3.7. Estimated P Application Rates for the Soils Used.

Phosphorus application rates which will be needed to produce optimum yields are presented in Table 15. Ordinarily, the required P application rates would be estimated from the P saturation of the adsorption maximum which produced maximum dry matter yields. However, the equivalent quantities of phosphorus in kilograms per hectare at the P saturation of adsorption maximum which produced maximum maximum dry matter are too high. Moreover, the rates of increase in dry matter with unit addition of phosphorus at the P saturation of the adsorption maximum which produced maximum dry matter are low. Infact, the greatest rates of increase with unit addition of P were obtained at much lower P saturation of the adsorption maximum.

The specific P saturation of the adsorption maximum with the greatest rates of increase with unit addition of P for the KH_2PO_4 treatment are as follows: $\frac{1}{4}$, $\frac{1}{4}$, $\frac{1}{4}$, $\frac{1}{8}$, $\frac{1}{8}$, $\frac{1}{8}$, $\frac{1}{2}$, $\frac{1}{4}$, $\frac{1}{8}$, $\frac{1}{8}$ times for Ankasa, Boi, Tikobo, Koforidua, Wacri, Mamfe, Oyarifa, Toje, Akuse, and Agawtaw, respectively. For the K_2HPO_4 treatment the P saturation of the adsorption maximum with the greatest increase with unit addition of P are as follows: $\frac{1}{2}$, $\frac{1}{2}$, I, $\frac{1}{8}$, $\frac{1}{8}$, $\frac{1}{8}$, $\frac{1}{4}$, $\frac{1}{2}$, $\frac{1}{8}$, $\frac{1}{8}$ times on Ankasa, Boi, Tikobo, Koforidua, Wacri, Mamfe, Oyarifa, Toje, Akuse, and Agawtaw, respectively. The doses of phosphorus equivalent to the P saturation of adsorption maximum given above for the KH_2PO_4 P-carrier treatment are taken as the phosphorus application rates needed to produce optimum dry matter yields. This is on the grounds that the KH_2PO_4 P-carrier is a more soluble P-carrier than the K_2HPO_4. Hence its availability would be a true reflection of the availability of most common P fertilizers. Moreover, plants are known to take up their inorganic phosphorus principally as the $H_2PO_4^-$ ion. The estimated phosphorus application rates range from 72 kilograms P per hectare on Wacri series to 260 kilograms P per hectare on Oyarifa series.

Table 15. Estimated P Application Rates for Soils Used.

Soil Series Name	Rate of P Application	
	Kilograms per hectare	Pounds per acre
Ankasa	200	178
Boi	175	156
Tikobo	152	136
Koforidua	78	70
Wacri	72	64
Mamfe	85	76
Oyarifa	260	232
Toje	144	128
Akuse	88	79
Agawtaw	74	66

CHAPTER 4

DISCUSSION

A linear relationship of the plot c/(x/m) against c was obtained for all the soils within the range of concentration of 1 x 10^{-4}M. to 7 x 10^{-4}M. Slight deviations of the isotherm from a linear relationship were, however, observed beyond an initial concentration of KH_2PO_4 solution of 7 x 10^{-4}M. This observation that the Langmuir plot of the adsorption maximum data does not follow a linear relationship was not unexpected. Infact Olsen and Watanabe (1957), Thompson (1958), and Weir and Soper (1962) noted some deviations. Moreover, Larsen (1967) at Levington Research Station, England, found that the phosphorus adsorption isotherms were curvilinear for the majority of 120 soils even at very dilute concentrations. Evidence from phosphate adsorption studies on $CaCO_3$ by Cole et al. (1953) has also indicated that in the range of equilibrium concentrations where the Langmuir equation applies, essentially all of the phosphate adsorbed is exchangeable with P^{-32} tagged orthophosphate added in solution. Where the isotherm deviates from a straight line only a portion of the adsorbed phosphate exchanges with P^{32}. A later study by Hsu and Rennie (1962) serves to buttress the observation by Cole et al.

(1953). Hsu and Rennie found that where precipitation of phosphate occurs the Langmuir plots fail to give the straight line relationship. It is therefore probable in this study also that at higher concentrations of KH_2PO_4 some of the soils merely precipitate the added phosphate instead of adsorbing it onto their surfaces.

The soil series with high adsorption maximum values (Abenia, Ankasa, Boi, Mamfe, Akuse and Prampram) except Akuse and Prampram series, are mainly soils of the Forest Oxysol and Forest Ochrosol Great Soil Groups. This finding is in accord with those of De-Datta (1964), Saunders (1965), Younge et al. (1966), and Syers et al. (1971 that most soils from tropical and subtropical regions, which fall in the Great Soil Groups of Latosols and Young Latosols and Red-Yellow Podzolic soils have marked ability to retain applied inorganic phosphates. The soil series Abenia, Ankasa, Boi and Mamfe are soils from areas where the annual rainfall is between 1397mm and 2159mm. Hence there has been pronounced through leaching of soluble cations like Ca^{++}, Mg^{++}, K^{+}, Na^{+} from the surface horizon with the resultant accumulation of Fe and Al. This is evidenced by the analytical values for "free" iron oxide (Fe_2O_3) and aluminium oxide (Al_2O_3) presented in Table 2. The soil series Abenia, Ankasa, Boi, and Mamfe, besides their comparatively fairly high iron and

aluminium oxides content, also abound in clay but contain comparatively less silica. Their high adsorption maximum values could, therefore, be attributed also to the high clay content and less silica. The soil series Tikobo which is also classed under Forest Oxysol Great Soil Group, in contrast, gave comparatively low adsorption maximum. However, this particular soil is believed to be derived from a Tertiary Sand parent material and has a loamy sand texture. Moreover, it has less clay but high silica content. Hence the low adsorption maximum value obtained is consistent since the soil lacks in materials which are believed to contribute positively to phosphorus adsorption in soils.

The soil series Akuse and Prampram are soils which belong to the Tropical Black Clay and Tropical Black Earth Great Soil Groups respectively. These soils have comparatively high aluminium oxide and a fairly appreciable amount of iron oxide. Furthermore, they have high amounts of clay and a not-too-high amount of silica. Akuse and Prampram soil series, especially the Akuse series, are also known to contain appreciable amounts of calcium carbonate hence must have high calcium concentration. The relatively high adsorption maximum of these soils may have been brought about by the high clay content, as well as, the possibly high calcium content.

Koforidua and Wacri soil series are soils of the Forest Oxysol and Forest Ochrosol Rubrisol Intergrade Great Soil Groups respectively. These two soils are very similar in their properties. They have a fair amount of clay, silica, and iron and aluminium oxides. In addition they have very large amounts of organic matter as represented by the organic carbon content. Therefore their comparatively fairly low adsorption maximum values are consistent. Though the fairly high amount of iron and aluminium oxides and clay should have favoured high adsorption maximum the comparatively high silica and organic carbon content tend to mask their effects.

The Oyarifa, Toje and Agawtaw soil series with the lowest adsorption maximum values are soils from a coastal savanna region. They are derived from Sandstone, Tertiary Sand, and Acid Gneiss and Schist parent materials and are of sandy loam, sand, and loamy sand texture respectively. These soils have appreciably low iron and aluminium oxides and clay content. Moreover, they have very high amount of silica, a material which contributes nothing positive to adsorption of phosphorus. The low adsorption maximum values obtained for these latter soils are, therefore, as expected.

On the basis of correlation values clay, silica, and "free" iron oxide showed the greatest association with phosphorus adsorption maximum. The relationship with clay content is in agreement with the findings of Pissarides et al. (1968), Galino et al. (1972), Udo and Uzu (1972), and Schwertmann and Knittel (1973) who found that the values of adsorption maximum obtained in their various investigations were a function of clay. The highly significant correlation between clay and adsorption maximum may point to the fact that clay minerals provide adsorption sites for phosphate ions. The role of clay in phosphorus fixation has been studied by many investigators. There is the hypothesis that phosphorus fixation by clay minerals is due to the aluminium content of the clays (Coleman 1944, Ellis and Truog 1955). It is, however, likely that clay forms part of the complex gel as envisaged by Mattson et al. (1950). This complex gel, consisting of hydrated iron oxide (Fe_2O_3) along with smaller amounts of organic matter, aluminium oxide (Al_2O_3) and associated $Si(OH)_4$ and P, is considered a major site for phosphorus adsorption. There is also the age-long hydroxyl replacement mechanism. It is believed that structural hydroxyl (OH) ions which are less tightly bound readily exchange places with phosphate ions. This latter theory is supported by data on the large amount

of phosphate that can be fixed by kaolinite as compared to montmorillonite reported by Murphy (1939) and Stout (1939). Kelley and Midgley (1943) also found direct relation between the amount of phosphate fixed and the increase in pH obtained when isohydric suspensions of various solid phases and phosphate solutions were mixed.

It was found in this study also that the silica content was highly correlated to phosphorus adsorption maximum but the correlation coefficient was negative. Though there is no published data on the relationship between silica per se and phosphorus adsorption maximum, marked relationship, however, has been found between the silica to sesquioxide ratio and phosphorus adsorption pacacity or phosphorus fixation. Wild (1950), Thompson (1957), and Sauchelli (1965) have all reported independently that many investigators have shown an inverse relationship between the silica to sesquioxide ratio and phosphate sorption or the efficiency of phosphate fertilizers for plant growth. Silica per se is an inert material and, therefore, cannot provide any sites for the adsorption of phosphate ions.

The very close relationship between "free" iron oxide (Fe_2O_3) and adsorption maximum found in this investigation was similarly reported by Rajagopal and Idnani (1963) in India, by Ahenkorah (1968) in Ghana,

by Udo and Uzu (1972) in Nigeria, and again by Bidappa and Venkat Rao (1973) in India. This particular relationship is also in agreement with the findings of Shukla *et al*. (1971) in which phosphorus sorption decreased markedly after the successful removal of oxalate-extractable iron. Williams *et al*. (1958) also reported a similar relationship between iron and phosphorus retention, even though they, like other investigators Bromfield (1964 and 1965), Bromfield and Williams (1963), Saini and MacLean (1965), and Udo and Uzu (1972) found aluminium to be the major factor responsible for phosphorus retention.

In this work no relationship was found between "free" aluminium oxide (Al_2O_3) and phosphorus adsorption maximum. This observation is consistent with that of Ahenkorah (1968) who, in working with some cocoa growing soils of Ghana, found no relationship between aluminium and phosphorus retention. The lack of agreement between the results of this work and those of other investigators quoted in previous paragraph may be due to several differences, among which are the variation in sesquioxides of podzolic and latosolic soils and the dominant parent materials involved. The lack of any relationship between "free" aluminium oxide (Al_2O_3) and phosphorus adsorption maximum may be further explained as being due

to ineffective extraction of the "free" aluminium oxide by the single extraction with the Tamm solution comprising oxalic acid and ammonium oxalate from some of the extremely acidic soils used in this investigation.

Even though Ahenkorah (1968) working with some cocoa growing soils of Ghana and some other investigators have found significant relationship between organic carbon and phosphorus retention, this particular work failed to establish such a relationship. There was some correlation (r = + 0.388) which was not significant. The lack of significance between adsorption maximum and organic carbon is consistent with the findings of Udo and Uzu (1972). Saunders (1965) also did not get any direct evidence to show that phosphorus is retained by soil organic matter. He, however, indicated that organic matter could be part of the complex gel postulated by Mattson et al., (1950). Kardos (1964) has also stated that in reactions involving the adsorption of phosphate ions organic compounds, being dominantly anionic in character, are likely to compete with the phosphate anion in polar adsorption phenomena. Mortensen and Himes (1964) reported that in most agricultural soils which are near a neutral pH, the soil organic matter has a net negative charge. The negatively charged anions and polyanions are apparently linked to clay surfaces through polyvalent

inorganic cations and ionized carboxyl groups (clay-M-OOR). Mortensen and Himes (1964) again reported that positive charges due to exposed lattic-edge aluminium and aluminate surfaces have been shown by several investigators to be adsorption sites for negatively charged, carboxylated polymers. The extent of adsorption, they believe, is governed by, among other factors, the pH. The majority of the soil samples used in this work have pH in the range 4.60 to 7.12- thus the reactions described above may be possible. Hence the lack of singnificance in the correlation between organic carbon and phosphorus adsorption maximum is consistent.

Furthermore, products of organic matter decay, such as organic acids and humus, are thought to be effective in forming complexes with iron and aluminium, compounds. Such complexing of iron and aluminium compounds reduces inorganic phosphate adsorption to a remarkable degree. All the soil samples used in this investigation except Toje (organic - C = 0.20%) and Agawtaw (organic - C = 0.34%) gave appreciable amounts of organic carbon content when analysed. Therefore, it is possible that the complexing of iron and aluminium compounds by organic acids and humus mentioned above is very operative thus rendering the adsorption sites rather ineffective in attracting phosphate ions. A

report by Mortensen and Himes (1964) that mutual coagulation and peptization reactions occur between organic matter and aluminium and iron gives credence to the above observation. Also acids produced in organic matter transformation could decrease the pH thus resulting in enhanced solubilization of iron and aluminium from clay minerals and other iron and aluminium compounds. The dissolved iron and aluminium would then form complexes with other products of organic matter decay or merely precipitate phosphate ions in solution instead of just adsorbing them.

The strong correlation found between the constant K, related to bonding energy and "free" iron oxide suggests that this soil property is mainly responsible for the greater tenacity that some soils have for inorganic phosphate ions. Soils which abound in silica may possibly hold on to inorganic phosphate ions with less tenacity since the correlation found between bonding energy and silica is negative. This observation is in order since sand hardly retains any inorganic phosphate ions on the surfaces of its particles.

The highly significant but negative correlation found between the constant K, related to bonding energy and pH is in agreement with the findings of Olsen and Watanabe (1957). As the value of this constant

increases the bonding energy of the soil for phosphorus increases. Thus the acid soils retain more phosphorus per unit area and also hold the phosphorus with greater bonding energy than the alkaline soils.

Those soils with high adsorption maximum generally produced maximum dry matter yield at ½ the P adsorption maximum whilst those with low adsorption maximum produced maximum dry matter yield at the P adsorption maximum. This finding is in accord with that of Woodruff and Kamprath (1965). However, in this investigation the P saturation of the adsorption maximum at which maximum dry matter yield occurred appear to be markedly influeunced by the initial P status of the soil. Hence for the soil series Koforidua and Wacri with high initial P status maximum dry matter yields were produced at much lower P saturation of adsorption maximum than would be expected. It appears that those soils with low adsorp- maximum but high initial P did not necessarily have to saturate the adsorption maximum in order to produce maximum yield.

It is clear from the relationship between the relative dry matter yield and the P saturation of adsorption maximum that optimum dry matter yields could be obtained at lower (½, ¼, ⅛) P adsorption maximum.

Infact one needs not necessarily saturate the P adsorption maximum in order to obtain optimum dry matter yield. Fertilizer phosphorus application rates must therefore be limited to P saturation of adsorption maximum below the P adsorption maximum. Of course, the initial P status of the soil must always be taken into consideration. There are ample evidence in the data accumulated to show that the initial P status greatly influenced the P saturation of the adsorption maximum at which optimum dry matter yield was produced. The soils with high initial P invariably produced optimum dry matter yield just at $\frac{1}{8}$ the P adsorption maximum.

The high increases in dry matter yields from zero-P-treatment with unit addition of phosphorus up to $\frac{1}{2}$ the P adsorption maximum show that there is moderate response from phosphorus application even at $\frac{1}{8}$ the P adsorption maximum. These modest responses even at very low saturation of the adsorption maximum support the hypothesis of the partially reversible nature of fixed phosphorus. It was found in this investigation that for those soils with low initial P status (Ankasa, Agawtaw, Boi, Mamfe, Oyarifa, Tikobo, Toje) the range of increase in dry matter was wider. On the other hand, for those with high initial P status (Akuse, Koforidua, Wacri) the range of increase in

dry matter was narrower. This finding is in accord with results of F.A.O. fertilizer phosphorus trials reported by Ahn (1968). In one of the trials involving maize and cassava carried out for eight years in the forest zone of Ghana, phosphorus gave large and increasing responses when applied to maize but had little effect on cassava. In the savanna areas it was found out that responses to phosphorus, although erratic, may be small to moderate. The Ankasa, Boi, Tikobo and Mamfe soils are from forest areas whilst Agawtaw, Oyarifa and Toje are from a savanna zone. The finding that these soils gave wider range of increase in dry matter with the addition of phosphorus was consistent.

Data presented on per cent uptake of applied phosphorus reveal that the uptake of applied phosphorus was in the range 6 to 39 per cent for KH_2PO_4 and 3 to 39 per cent for K_2HPO_4 treatment. These ranges of recovery of applied phosphorus by the test-crop, although slightly low as regards their lower limits, are in close agreement with the range value of 10 to 30 per cent reported by Hemwall (1957) and Sauchelli (1965). Fertilizer phosphorus added to soils are believed to be subjected to chemical precipitation and colloidal adsorption. Consequently only a small proportion of the added fertilizer P becomes available to the plants which immediately

grow on the soil. It is evident that on the acidic soils of the Forest Oxysol and Forest Ochrosol Great Soil Groups (Ankasa, Boi, Tikobo Mamfe) uptake of applied phosphorus was generally low. On the contrary on Koforidua and Wacri soils which belong to the Forest Oxysol and Forest Ochrosol Rubrisol Intergrade Great Soil Groups, respectively, uptake of applied phosphorus was very high. Again on the Savanna Ochrosols (Oyarifa and Toje) and the loamy sand Agawtaw soil uptake of applied phosphorus was moderately high. The uptake of applied phosphorus on the Akuse Soil of the Tropical Black Clay was also moderate. If the correlation coefficients between adsorption maximum, bonding energy and uptake of applied phosphorus reflect on the relative importance of these parameters to uptake of applied phosphorus then the constant K, related to bonding energy is a much better index than adsorption maximum.

There were marked increases in per cent P content and per cent P uptake by the test-crop with increased P application. These are evidences that when a certain saturation of the P adsorption maximum is reached availability of adsorbed phosphorus compounds increases considerably. This observation adds support to a similar one made by E.G. Williams of Macauley Institute for Soil Research quoted by Sauchelli (1965) and also that

of Sell and Olson (1946). These workers observed that the phosphate reserve of every soil must be built up to a certain extent before phosphorus becomes available to plants. The observation made in this investigation is also consistent with that of G. Barbier and associates in France quoted by Sauchelli (1965). They found that a greater proportion of soluble phosphate added to soils remained after ten years in forms which are either extractable by dilute acids or are capable of returning spontaneously into the soil solution under natural conditions. This points to the fact that phosphate attached to phosphorus adsorption sites can, with time, be returned into the soil solution. On this note then, the above observation can be explained on the grounds that soils with high adsorption maximum are still capable of returning significant amounts of adsorbed phosphate into the soil solution for plant use, although over some lapse of time. Another report from an Illinois Bulletin, also quoted by Sauchelli (1965) which stated that added phosphorus fertilizer are not reverted to unavailable forms on contact with the soil also serves to buttress the above reasoning.

The significance of the data on dry matter yield and uptake of applied P accumulated is that those soils with high adsorption maximum values but produced maxi-

mum dry matter yield at lower saturation of the adsorption maximum would probably have larger residual effects. This is in view of the fact that although those soils with high adsorption maximum released enough phosphorus to produce maximum yield in dry matter at relatively low P saturation of adsorption maximum, their respective uptake of applied P were very low. This would indicate that still large amounts of phosphate remained attached to the P adsorption sites which would not be dislodged immediately. The attached phosphate would probably come into solution in the long run. These residual effects of adsorbed phosphorus may probably be very important for tree crops like oil palms, rubber and citrus which require considerable amount of phosphate supplied over a long period.

The KH_2PO_4 phosphorus-carrier treatment resulted in comparatively high phosphorus uptake by the test-crop on almost all the soils than the K_2HPO_4 phosphorus-carrier. The former phosphorus-carrier has relatively high solubility in water than the latter. In this particular study the fertilizer phosphorus materials were added to the soils in the solid state. Hence their relative solubilities would greatly influence their uptake by plants. Moreover, plants are believed to take up their phosphorus almost exclusively as

inorganic phosphate and principally as the $H_2PO^-_4$ ion (Hagen and Hopkins, 1955). The relatively high phosphorus uptake from the KH_2PO_4 phosphorus-carrier is therefore consistent.

The estimated P application rates are slightly high especially on the Ankasa, Boi, Tikobo, and Oyarifa soils. The NPK fertilizer application rates recommended for some food crops in Ghana are in the ranges 20 to 200, 20 to 100, and 10 to 100 kilograms per hectare, respectively, (CRI, 1974). For other parts of the tropics and subtropics the recommended P application rates range from 20 to 200 kilograms P per hectare for a variety of crops (de Geus, 1973). The estimated P application rates for the Agawtaw, Akuse, Koforidua, Mamfe and Wacri soils fall within the ranges of P application rates recommended for some crops in Ghana and parts of the tropics and subtropics. In contrast, the estimated rates for Ankasa, Boi, Oyarifa, Tikobo and Toje are just too high in respect of recommended rates for Ghana but are still within the range for the tropics and sub-tropics. Except Oyarifa and Toje soils, the Ankasa, Boi and Tikobo soils are the extremely acidic soils of the high rainfall areas of Ghana. The estimated high application rates may be advantageous in that they will help build up the phosphorus fertility

level to the point where further applications may be just beneficial. The high rates would probably leave a lot of phosphorus in the soils as residual phosphorus. Such a residual phosphorus may be beneficial to tree crops such as oil palm, rubber and citrus which are known to thrive best on those soils.

The findings in this investigation that magnesium and manganese concentrations increased with increased phosphorus applications are in accord with those of Bingham et al. (1958). Although they used citrus as test-crop Bingham et al. (1958) found that actual increases in magnesium and manganese absorption occurred with increased phosphorus applications. They found that iron availability was not very much affected. The only explanation Bingham et al. (1958) could offer for the increased manganese availability consequent upon increased phosphorus additions was a possible formation of very soluble manganese phosphates in the treated soils which are readily absorbed by the plants. Nothing, however, is known of the mechanism bringing about increased magnesium concentration of plant tissues with increased phosphorus additions. The decrease in calcium content following increases in phosphorus applications appear unprecedented since no published work could be found in the literature. Bingham et al. (1958)

did not report of any decrease in calcium content of their indicator plant as a result of increased phosphorus additions. In any case Hahne (1966) found that the application of potash fertilizer markedly decreased the calcium and magnesium content in maize leaf. However, in this study equal amounts of potassium were added to all soil treatments. This therefore, rules out any possible effect of potassium treatment on some soil samples. Infact, phosphorus was the only element whose rates of application were varied. The formation of complex calcium-phosphate compounds with reduced solubility and hence availability to plants is not precluded. Further research, however, would be needed to ascertain the possible mechanism resulting in reduced availability of calcium following increased phosphorus additions found in this investigation. Variable results were noted for the plant tissue content of iron as influenced by increased P additions. However, the finding that on some soils increased P additions caused reduced iron availability is in agreement with the findings of Bingham (1963), and of a research work on soybean by U.S. Department of Agriculture scientists reported by Tisdale and Nelson (1966). Bingham (1963) noted that high P substrate concentrations may restrict the movement of iron in some plants. Tisdale and Nelson (1966) also

reported that high concentrations of phosphorus cause a deposition of iron on the surface or just inside the root of soybeans resulting in decreased iron availability, hence iron chlorosis. No published work was found in the literature to support the finding in this study in which on a few soils increased P additions increased the availability of iron.

The plant tissue concentrations of calcium, magnesium, iron and manganese on soil samples given P treatments equivalent to the estimated P application rates, generally fall within the ranges of sufficiency given by some workers. No published data on nutrient sufficiency ranges for millet could be found in the literature. Nevertheless the sufficiency ranges for grain sorghum estimated by Lockman (1972) and quoted by Jones and Eck (1973) could be taken as standards. Grain sorghum and millet both thrive well on soil types with similar physical and chemical properties, and under the same climatic conditions. It is therefore reasonable to equate them in regard to their nutrient requirements. From Lockman's (1972) data a whole sorghum plant, twenty-three to twenty-nine days old gave phosphorus content of 0.30 to 0.60%. The calcium and magnesium concentrations were in the ranges 0.9 to 1.3% and 0.35 to 0.50%, respectively. The iron

and manganese concentrations were also in the ranges 160 to 250 ppm and 40 to 150 ppm respectively. In the investigation reported herein also the test-crop (millet) was harvested when the seedlings were forty-two days old. The whole seedlings were ground and analysed for the nutrient elements composition. Except for the iron concentration, the calcium, magnesium and manganese content of the plant tissues on soil samples given P treatments equivalent to the estimated P application rates fall within the ranges estimated by Lockman. This is an evidence that with the apparantly high estimated P application rates there would still be a fair amount of secondary and micronutrient elements available to the plants for their proper growth and yield.

CHAPTER 5

SUMMARY AND CONCLUSION

The present study has been concerned with:

(i) the phosphorus adsorption maximum of twelve selected Ghanaian soils using the Langmuir isotherm,

(ii) the relation of adsorption maximum to availability of applied phosphorus to millet,

(iii) the relation of adsorption maximum to some soil properties, and

(iv) estimation of rates of P application necessary to obtain optimum yield on the soil series used in the study.

The soils of the Forest Oxysol, Forest Ochrosol, as well as, the Tropical Black Clay and the Tropical Black Earth Great Soil Groups (Ankasa, Abenia, Boi, Mamfe, Akuse, and Prampram, respectively) have comparatively high phosphorus adsorption maximum. The loamy sand Tikobo series and Koforidua soil have moderately high adsorption maximum. Agawtaw, Wacri, Toje and Oyarifa soils have comparatively low adsorption maximum. Abenia soil has the highest adsorption maximum whilst Oyarifa has the lowest adsorption maximum.

Those soils with high adsorption maximum produced maximum dry matter yield at lower P saturation of the adsorption maximum. In contrast, those soils with low adsorption maximum produced maximum dry matter at higher P saturation of the adsorption maximum. The initial P status of the soils, however, greatly influenced the P saturation of the adsorption maximum at which maximum dry matter yield occurred. Those soils with high phosphorus adsorption maximum apparently are able to supply sufficient phosphorus for growth of crops at a lower saturation of the adsorption maximum than those with low phosphorus adsorption maximum and also low initial P. Evidence accumulating from this investigation indicates that presumably those soils with high adsorption maximum would have larger residual phosphorus effects. The residual phosphorus effects may be essential for tree crops such as oil palms, citrus and rubber.

On those soils with extremely acidic reaction and which also have high phosphorus adsorption maximum, as well as, high bonding energy uptake of applied phosphorus by the test-crop was comparatively low. However, those soils responded quite favourably to phosphorus application as indicated by the high increases in dry matter yields with unit addition of phosphorus. Only Akuse,

Koforidua, and Wacri soils with high initial P did not show any significant response to phosphorus applications. It is clear that the initial phosphorus status of a soil greatly influence its response to phosphorus applications.

From data accumulated it can be concluded also that optimum dry matter yields could be obtained at lower P saturation of the adsorption maximum. Infact it may not be beneficial to saturate a soil beyond the P adsorption maximum. Economic fertilizer P applications should, therefore, always be limited to lower P saturation of the adsorption maximum than the P adsorption maximum.

The soils of the Forest Oxysol Great Soil Group - Ankasa, Boi, Tikobo - will require 200, 175 and 152 kilograms P per hectare, respectively to produce optimum dry matter yield. Mamfe series which belongs to the Forest Ochrosol Great Soil Group will also require 85 kilograms P per hectare to produce optimum yield. On the Forest Oxysol, Forest Ochrosol Rubrisol Intergrade Great Soil Gaoups - Koforidua, and Wacri - 78 and 72 kilograms P per hectare, respectively, will be needed to produce optimum yield. The Savanna Ochrosol soils - Oyarifa and Toje will need 260 and 144 kilograms P per hectare, respectively, whilst the Black Clay soil, Akuse will need 88 kilograms P per hectare to produce

optimum yield. Agawtaw also will require 74 kilograms P per hectare for optimum yield. This conclusion is tentative and must be confirmed by field trials to ascertain the beneficial effects in terms of crop yields and economics of these high phosphorus application rates.

The KH_2PO_4 phosphorus - carrier resulted in higher dry matter yields and P uptake on all the soils used than the K_2HPO_4 phosphorus-carrier. It is clear from this study that the $H_2PO^-_4$ ion is preferred by plants to the HPO_4^{--} ion.

On the basis of plant tissue concentrations of calcium, magnesium, iron and manganese, it is concluded that successive additions of phosphorus fertilizer to soils will probably induce calcium shortages in plant tissues. Of course, further research will have to be conducted both in the greehouse and in the field to ascertain the validity of this finding and also throw some light on the mechanism involved. Actual increases in magnesium and manganese availability are likely to occur with increased phosphorus additions. Availability of iron appear to be reduced with increased additions of P only on Boi and Tikobo soils. On Koforidua and Wacri soils however, iron availability appear to be enhanced by increased P additions.

Clay, silica and free iron oxide (Fe_2O_3) were all better correlated to adsorption maximum than pH, organic carbon, and free aluminium oxide (Al_2O_3). For the soils under investigation, therefore, clay, silica, and free iron oxide content appear to be factors which greatly influence phosphorus adsorption maximum. Bonding energy of the absorbent for the absorbate, was also better correlated to pH, free iron oxide, and silica. The correlation coefficients for pH, silica content and the bonding energy were negative. This points to the fact that the highly acidic soils with less silica content hold on to soil phosphorus with greater bonding energy than the alkaline or slightly acid soils with high silica content. The bonding energy of the absorbent for the absorbate was found to be a better index of uptake of applied phosphorus than the adsorption maximum. Thus soils with high bonding energy, no matter the value of the adsorption maximum, will still make less phosphorus available to plants for their growth and yield.

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