A STUDY OF SOIL PHOSPHORUS FORMS IN KIKUYU RED LOAM AND OF THEIR SURFACE ACTIVITY

JOSEPH KIPKORIR A. KETER

A thesis submitted in fulfilment for the Degree of M.Sc.
in the University of Nairobi.

1974

DECLARATION BY THE CANDIDATE:

This thesis is my original work and has not been presented for a degree in any other University.

JKeter

JOSEPH KIPKORIR A. KETER

DECLARATION BY THE UNIVERSITY SUPERVISORS

This thesis has been submitted for examination with our approval as University supervisors.

P. M. Ahn

P. A. Robins

ACKNOWLEDGEMENTS

The research for this thesis was carried out at the Coffee Research Station, Ruiru, Kenya. I am very grateful to Deutscher Akademischer Austauschdienst (German Academic Exchange Service) for their scholarship support and to the Board of Directors, Coffee Research Foundation, for providing the facilities which enabled this work to be completed.

I wish to express my sincere appreciation for the inspiration, guidance and helpful suggestions and criticisms tendered by Professor P.M. Ahn, of the Department of Soil Science, University of Nairobi, under whose supervision this investigation was conducted. I also wish to acknowledge my indebtedness to Dr. C. Bould, of Long Ashton Research Station, University of Bristol, England, who helped with the isotopic-exchange studies; to Professor P.A. Robins, of the Department of Chemistry, University of Nairobi, and to Dr. A.M. Kabaara, Director of Research, Coffee Research Foundation, for their advice and valuable suggestions.

Messrs A. Mathu and S. Kamau of the Agronomy Section, Coffee Research Station, gave valuable assistance in the statistical treatment of the data. Thanks are also due to Messrs B.S. Kimeu, G.M. Gatitu, R.Z. Patel, G. Manuya, S. Gathuku and the entire staff of the Chemistry Section, Coffee Research Station, for their general assistance. I also wish to express my sincere thanks to Messrs C. Mugane and G.K. Githaiga, of the Department of Soil Science, University of Nairobi, for their technical assistance.

Miss Ruth Githegi typed the thesis.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

FIGURE Page

CHAPTER I

INTRODUCTION

1.1 Scope of the Investigation

The importance of phosphorus in soil fertility has caused it to receive extensive attention from soil chemists. The emphasis that has been laid on the chemistry of phosphorus in the soils arises from its role as a plant nutrient and from the influence which the chemical form and reactions of this element have on its utilization by plants. It is, for example, necessary for root growth and sufficient wood production and particularly necessary for sound fruit formation and early maturation of berries (Tisdale and Nelson, 1956). Owing to the rather complex nature of the chemistry of phosphorus, in solution as well as in soil, methods of analytical determination have inevitably required demanding attention. There are two lines of study along which the extraction of phosphorus from soils has been considered: (i) the extraction of available phosphate from soil-P fractions with high specific surface activity; and (ii) determination of the total chemical form of each phosphate.

Objectives:

A study was initiated with the following objectives:

1. To study the disposition of native soil-P in Kikuyu Red Loam.
2. To establish the extent of reversion of applied fertilizer-P to soil natural forms.

3. To investigate the surface activity of the various soil-P fractions using ^{32}P.

The distribution of total, total organic, and the total of each of the chemical forms comprising aluminium phosphate, iron phosphate, calcium phosphate and occluded phosphate (the latter four constitute the total soil inorganic phosphorus) in a coffee plot and a profile was studied. Available phosphate was determined in samples of soil from plots treated respectively with phosphate, cattle manure and phosphate, phosphate and mulch, and in samples from untreated plots. More information about the soil was obtained with regard to fixation of applied water-soluble phosphate (potassium dihydrogen phosphate - KH_2PO_4) and the surface activity of the active soil inorganic forms consisting of aluminium phosphate, iron phosphate and calcium phosphate using ^{32}P for the activity studies.

The potential plant availability of the active soil-P fractions (aluminium phosphate, iron phosphate and calcium phosphate) was determined by labelling the soil-P fractions with ^{32}P and growing barley seeds in the labelled soil for three weeks. Assay of radioactivity in the barley seedlings and in the soil-P fractions was determined and the per cent uptake of ^{32}P by the seedlings from each of the soil-P fractions was finally calculated.

Attempts were made to give possible explanations for the patterns of distribution of soil phosphorus forms in the soil and the extent of fixation of applied water soluble phosphate.

Some broad conclusions were reached concerning the nature and abundance of the various soil phosphorus forms, the relative availability and potential plant availability of the soil-P fractions in the Kikuyu Red Loam soil.

Correlation of yield with possible plant and soil-P might in future studies be attempted taking into consideration some of the information obtained in this study.

1.2 The Soils Investigated

1.2.1 Geology

The main cofee-producing areas of Kenya, of which Ruiru is representative, are located on closely similar soil types, named by Gethin Jones (1949) the Kikuyu Series. The main soil type present, and that on which the coffee is grown, is the Kikuyu red and to a lesser extent the dark red friable clay (loam) soil. Both these soils are deep, porous and naturally well drained latosols derived from a volcanic parent material, Tertiary trachytic lava, by weathering *in situ*. They have a high pore space, a fairly high base holding capacity and a percentage of clay fraction, yet the field texture is that of a friable loam (Pereira, 1957). The difference between the two soils is that the Kikuyu Dark Red Loam has a greater depth of dark topsoil and is found on the flat tops of the lava flow ridges. It has a higher organic matter content and a greater degree of base saturation.

The highly porous surface soil has a good natural crumb structure and it is resistant to erosion. The soil depth may exceed 20 feet on the main ridges and will fall to two or less on the flanks immediately above the river valleys (Gethin Jones, 1949).

The soil holds 48" water in the top 10 ft. at field capacity and of this, 12" is available to plants (Pereira 1957). The rooting range of mature coffee trees is at least 15 ft., (Nutman, 1933), but the root system forms a dense surface root mat, filling the first 2 ft. of well-aerated top-soil.

The soils are dominated by kaolinite and halloysite and also contain in some cases, some gibbsite or goethite and, very often, small quantities of illite. They generally do not contain measureable quantities of amorphous substances. These soils fix phosphorus very strongly and an increase in plant available phosphorus is possible only when mineral phosphates are used in conjuction with organic manures or mulching materials (Mehlich, 1968). These soils are known to be fairly acidic and contain iron and aluminium complexes (Gethin Jones, 1953); these complexes can render the phosphorus insoluble.

Soil Classification

Gethin-Jones (1953), working with the Soil Survey Department, East African Agriculture and Forestry Research Organisation, classified and mapped the soils into seven soil series with additional phases to allow for seasonal impeded drainage (areas of topographical depression), steepness of slope, shallowness of soil and a combination of the latter two factors. Almost the entire coffee acreage is sited on the Kikuyu red and dark red loam soil types.

The Soil Series

1. Kikuyu dark red loam
2. Kikuyu red loam
3. Kikuyu red loam, steep phase
4. Kikuyu red loam, shallow phase
5. Kikuyu red loam, st. and sh. phase.
6. Kikuyu 'creep' soil
7. Ruiru gritty red loam
8. Kahawa gritty orange-brown loam
9. Vlei, grey-brown clay loam-clay
10. Alluvium, liable to flooding.

1.2.2 Relief

The Coffee Research Station at Ruiru (1°08'S., 36° 56' E. 1608 m alt.) is situated in an undulating region. The two estates comprising the station, namely Jacaranda and Rukera, are bounded in the north, east and south by two rivers which flow towards the south-east. In the north-west the boundary is formed with a neighbouring coffee estate.

Many areas in the region as a whole are made up of long, parallel ridges with small valleys 50 to 80 feet deep and about one mile apart. The valleys have cut through the deep soil and into the underlying lava. There is a sequence of soil conditions from the crest of the ridge to the stream; the soil becomes more shallow and contains decreasing amounts of organic matter and bases towards the stream. On the steep slopes near the streams the soils are shallow with soft laterite or murram occurring within a few feet of the surface. The better land always occurs on the more level top of the ridge.

1.2.3 Climate

The main coffee-producing areas of Kenya lie on the east of the East African Rift Valley and receive rainfalls of between 750 and 1500 mm per annum. The Coffee Research Station has a mean annual rainfall of 1048.1 mm; three quarters of the annual rainfall is normally concentrated into two intensive wet seasons with intervening hot dry periods which can be very severe. Hence the rainfall distribution is usually unfavourable.

At Ruiru the rainfall distribution follows the monsoon pattern, with two wet seasons which are known locally as the Long Rains (late March to early June) and the Short Rains (late October to mid-December). The mean annual rainfall of about 100 cm is typical of the drier districts producing coffee in Kenya.

1.2.4 Vegetation

The development of the vegetation over considerable areas of East Africa is influenced by man, but marked change resulting in extensive soil degeneration in certain areas is relatively of recent origin. In the past, for instance, fire was used and it still is used to retard the development of bush and maintain open grassland; also it was a means by which, in some grassland regions, undesirable coarse herbage was suppressed in favour of more readily utilizable phases of the succession (Edwards, 1951).

Six main regions of vegetation have been recognized in Kenya, occurring in some cases as several isolated masses and extending into the adjoining territories. Roughly one quarter of the country to the south-west is occupied by relatively moist vegetation types situated on elevated land, while the remainder, with the exception of the more tropical coastal belt, supports semi-desert bush and scrub.

The major plant communities which have been recognized at the coffee-growing areas around and extending considerably to the north of Ruiru constitute one of the six main regions of vegetation (the other similar region is the Lake Victoria basin) namely Scattered Tree Grassland (Low Tree - High Grass).

The community to which this name is given consists of grassland with herbage 5 to 8 feet in height, thickly scattered with small trees which are in the main 10 to 15 feet high. Larger trees some 30 feet in height occur occasionally, and a characteristic feature of wide regions is the existence of isolated small areas of tall forest trees (50 to 90 feet) evidently resulting from exceptional ground water conditions.

Typically, the small trees are broad-leaved and deciduous with characteristic, fissured, corky bark. The most general dominant is Combretum, frequently C. splendens. The grasses which contribute mainly to the "high grass" character of this vegetation are members of the genera Hyparrhenia and Cymbopogon, although the herbage is often complex and contains a considerable range of grasses (Edwards, 1951).

This vegetation appears to be a seral phase leading to forest (Edwards, 1951). The phase is maintained largely by the frequent passage of fire, in the absence of which factor thicket tends to replace the high grass between the scattered trees. This mainly refers to areas where tillage of crops and correct intensive management of grazing have not already occupied the land.

1.3 Previous work on these soils

The significance of phosphorus in East African soils was recognized by Birch (1949) who observed that one must measure and evaluate the different forms of phosphorus in research work in order to understand the function of phosphorus in soil fertility. Pereira and Jones (1954) reported the results of a number of years of field experiments, accompanied by soil and plant analyses, relating to the use of nitrogenous and phosphatic fertilizers, cattle manure, and grass mulches with coffee in Kenya. The Kikuyu Red Loam soil was included in the investigation. They observed that neither yield nor quality of the crop was affected by the usual dressings or by heavier dressings of either cattle manure or phosphates. Crop yields were sometimes increased when nitrogenous fertilizers were given at heavy rates.

The major studies on coffee in East Africa have been concerned with nitrogen. There is general agreement that nitrogen fertilizers increase the yield of coffee (Jones, Robinson and Wallis, 1960 (a); Robinson, 1957; Robinson and Hosegood, 1965).

Whereas applications of phosphorus fertilizers, manure and mulching materials have been shown to increase the levels of soil-P, no consistent yield response of coffee to phosphorus has been recorded (Jones, Robinson and Wallis, 1960 (a) and (b)). However, results of experiments carried out by the Coffee Research Station between 1959/67 and summarised by H.W. Mitchell (private communication) show that in a trial, involving lime, phosphate and mulch, started in 1964, P alone at 4½ cwt/acre of a 3:1 mixture of single superphosphate/diammonium phosphate increased clean coffee yield from 8.86 cwt to 10.69 cwt/acre in 1966. This was just below the 5 per cent significance level. Over the two years 1965 and 1966, the increase was 1.06 cwt/acre on yields of around 9 cwt/acre, again just failing to gain significance at 5 per cent probability level. No increases were recorded in the presence of lime. This is the first trial at the Coffee Research Station to show a response to phosphate. In an adjacent trial (in the absence of mulch) single superphosphate and a mixture of diammonium phosphate and single superphosphate caused significant decreases in yield amounting to 1.48 and 1.98 respectively in the absence of lime. Where lime was applied these decreases were small and nonsignificant. Single superphosphate without lime increased the yield significantly by 1.67 cwt in the presence of 100 lb/acre N but caused a decrease of 1.79 cwt with 200 lb N/acre. The yields were around 8 cwt/acre.

These data indicate that increases in yield can be achieved with phosphate fertilizers but that the conditions under which this occurs have yet to be worked out more precisely.

CHAPTER II

LITERATURE REVIEW

2.1 Forms of Phosphorus in Soils

Phosphorus occurs in soils in both organic and mineral combinations; its chemistry is complex owing to the ability of each phosphate ion to form a multiplicity of compounds of different composition and variable solubilities.

The total phosphorus content of a soil may vary over a broad range depending upon its organic matter content, the parent material, and the degree of weathering. In most mineral soils the phosphorus content falls between 0.02 and 0.5 per cent P and a general average of 0.5 per cent frequently is representative of soils compared to an average of 0.12 per cent P in the earth's crust (Jackson, 1964). Generally speaking, inorganic phosphorus is the preponderant form of soil phosphorus, although soils exist in which as much as 75 per cent of the total phosphorus is in organic combination (Black, 1953). In addition, the organic phosphorus content of mineral soils is usually higher in the surface horizon than it is in the sub-soil because of the accumulation of organic matter in the upper reaches of the soil profile.

The pH-solubility relationship of the soil phosphate when compared with those of known phosphate minerals (Chang and Jackson, 1957; Stelly and Pierre, 1943, and others) indicate that the inorganic phosphates are dominantly bonded to calcium in alkaline and calcareous soils, and mainly bonded to aluminium or iron in acid soils. In many parent rocks from which soils are formed it occurs mainly as calcium phosphate. Stelly and Pierre (1943) observed in some Iowa soils that the main calcium phosphate is fluorapatite - $Ca_{10}(PO_4)_6F_2$. This is the principal phosphatic constituent of mineral phosphates in the great deposits in North Africa, Florida and elsewhere, and which form the principal commercial sources of phosphates.

As weathering proceeds and acidity develops in soils, the phosphate becomes increasingly bonded to aluminium and iron ions released from silicate minerals by weathering (Ensminger, 1949; Low and Black, 1948; Haseman et al., 1950b; Kittrick and Jackson, 1954 and 1955). The phosphates formed have chemical properties which resemble those of the minerals variscite - $Al(OH)_2H_2PO_4$ or $AlPO_4.2H_2O$ (Cole and Jackson, 1951; Lindsay et al., 1959), strengite - $Fe(OH)_2H_2PO_4$ or $FePO_4.2H_2O$ (Chang and Jackson, 1957) and the isomorphous intermediate barrandite - $(Al, Fe)(OH)_2H_2PO_4$ or $(Al, Fe)PO_4.2H_2O$ (Cole and Jackson, 1951; Wright and Peech, 1960). In conditions where there is a high content of K or NH_4, as in fertilizer bands, these ions are incorporated as in taranakite - $K_3Al_5H_6(PO_4)_8.18H_2O$ or its ammonium analogues (Wada, 1959) or other (K, NH_4) salt such as $(K, NH_4)(Al, Fe)_3H_8(PO_4)_6.6H_2O$ (Haseman et al., 1950b; Lindsay and Stephenson, 1959). Dyal (1953) identified wavellite $Al_6(F, OH)_6(PO_4)_4.9H_2O$ in soils.

Jackson (1958) observed that as weathering in soils proceeds, some of the phosphate becomes occluded with hydrous iron (Chang and Jackson, 1957), thereby acquiring properties similar to those of dufrenite - $Fe_2(OH)_3PO_4$ in solid solution with FeOOH. It is recognized that occluded iron phosphate is abundant in Ferruginous Latosols.

The variscite - barrandite - strengite type of phosphates are considered to be the probable, principal crystalline compounds of aluminium and ferric phosphate in well drained soils. In water-logged or badly drained soils (which, as a result, provide reducing conditions) vivianite - $Fe_3(PO_4)_2.8H_2O$ forms in soils and, being fairly soluble, may be deposited in lower levels in the soil profile. This is the only iron phosphate mineral that has been found in crystals which are recognizable in the petrological microscope (Russell, 1961). Reduction of the ferric iron renders the oxides soluble and the phosphate becomes more available to plants, as to rice in paddy culture.

In their studies of inorganic phosphate transformations by chemical weathering in soils as influenced by pH, Hsu and Jackson (1960) found that the aluminium and iron phosphates have solubility approximately equal to calcium phosphate between pH 6 and 7 depending on the magnitude of cation activities from various solid phases such as gibbsite - aluminosilicates, hydrous iron oxide, calcium carbonate, exchangeable calcium, and possibly from soluble salts. Below this pH range, the aluminium and iron phosphates are more stable than calcium phosphate; above this range, the calcium phosphate is more stable than aluminium and iron phosphates, particularly in the presence of calcium carbonate. The calcium phosphates formed above this pH range (6 to 7) include hydroxyapatite - $Ca_{10}(PO_4)_6(OH)_2$, dicalcium phosphate - $CaHPO_4$, and complex calcium phosphates intermediate between these two, one of which is octocalcium phosphate (Lindsay and Moreno, 1960). Fluorapatite, which is sometimes added to soils in finely ground form as an amendment, is rapidly transformed into combination with aluminium and iron phosphate in acid soils (Joos and Black, 1950).

Organic soil phosphorus may occur as a constituent of either living or dead organic matter. One of the prominent organic phosphorus compounds is phytin, a calcium - magnesium salt of inositol phosphoric acid. It is widely distributed in plants and constitutes the form in which much of the phosphorus in seeds is stored, being about 75 per cent of the phosphorus content (Millar, 1955). It is recognized that the portion of the organic phosphorus in soils in the form of phytin varies considerably.

Other organic substances which contain phosphorus and are found in soils are the nucleoproteins. These are compounds of nucleic acids with proteins and are found in both plant and animal tissue. Phosphatides including lecithin are the third main group of organic compounds containing phosphorus which occur in soils.

These compounds are slowly mineralized to orthophosphate (Hemwall, 1957). Other compounds include choline, inosite, casein and ovovitellin. Of these the nucleic acid group is present in major proportion (Sauchelli, 1965).

The compounds that include the major portion of soil organic phosphorus still remain to be identified. If the maximum values for inositol phosphates and nucleic acids are taken, at least 50 per cent of the soil organic phosphorus occurs in unidentified compounds (Mortensen and Himes, 1964). Since the soil probably contains most types of organic compounds synthesized by biological organisms, the identification and characterization of these compounds will require the ingenuity and time of many chemists.

2.2 Fractionation of Soil Phosphorus

Considerable attempts have been made by many workers to characterize soil phosphorus compounds and the results achieved have presented improvements in precision and in accuracy of the methods. A lot still remains to be done to overcome some of the persistent difficulties experienced even in some of the most widely used of these methods.

Russell (1932), quoted by Dean (1938), classified soil phosphorus compounds into three groups:

(a) Inorganic phosphorus in neutral soils: probably a calcium phosphate: hydroxyapatite.

(b) Inorganic phosphorus in acid soils: presumably combinations with iron and aluminium oxides.

(c) Organic phosphorus compounds.

Fisher and Thomas (1935) attempted the fractionation of soil phosphate into three groups consisting of:

(a) Calcium, magnesium and manganese phosphates.

(b) Iron and aluminium phosphates and

(c) Adsorbed phosphate and apatite.

Their method was based upon the relative rates of solution of soil phosphorus compounds in buffered acid extractants. They extracted separate samples of soil with acetic acid - sodium acetate buffer at pH 5.0 for different periods of time and also with dilute sulphuric acid at pH 3.0.

Williams (1937) divided the soil phosphorus compounds, on the basis of their solubility in sodium hydroxide, into the following groups: (a) an alkali soluble fraction, said to include organic phosphorus, exchangeable phosphate and the more soluble inorganic phosphates such as those of the sesquioxides, dicalcium phosphate, $CaHPO_4$, and any water soluble phosphate; and (b) the alkali insoluble fraction consisting of the apatites and possibly titanium phosphate, and crystal lattice phosphorus.

Dean (1938) showed that by extraction with sodium hydroxide, followed by an acid, it is possible to divide the phosphorus compounds of soils into three broad fractions:

(1) Organic compounds soluble in sodium hydroxide.

(2) Inorganic compounds dissolved by extraction with sodium hydroxide followed by an acid.

(3) Insoluble compounds.

Bray and Dickman (1941) fractionated the soil phosphates into four classes:

(1) The easily replaceable phosphate and some of the "more tightly" adsorbed forms: these were extracted with 0.1 N NH_4F.

(2) and (3) The "more tightly" adsorbed phosphate which could slowly change to fraction (1) as the latter was removed: fraction (2) was extracted with 0.1N NH_4F in 0.01N HCl and fraction (3) with 1.0N neutral NH_4F.

(4) The "acid - soluble" phosphate: such forms as rock phosphate, apatite, and similar calcium or magnesium compounds as well as iron, aluminium or manganese phosphates. These were extracted with 0.5N NH_4F in 0.002 N H_2SO_4.

Ghani (1943 a) argued that the methods of extraction and determination of the fractions of soil phosphorus adopted by Dean (1938) were more or less empirical in nature. In view of this he made modifications in which the soil phosphorus was divided into five groups.

(1) Acetic acid-soluble: Mono-, di- and tricalcium phosphates.

(2) Alkali - soluble inorganic: Iron and aluminium phosphate.

(3) Alkali - soluble organic: Total organic phosphorus of the soil (nucleic acid, phytin, lecithin, etc.).

(4) Sulphuric acid - soluble: phosphates of apatite type.

(5) Insoluble.

N/2 acetic acid was used as a pre-treating agent for the removal of exchangeable bases before alkali extraction.

When it was discovered that some of the phosphates brought into solution by the acetic acid was readsorbed by the soil and then extracted in the sodium hydroxide extraction, thereby tending to give a lower amount extracted by acetic acid while giving a higher amount extracted by sodium hydroxide than was the real case, Ghani (1943 b) modified his first method; he suggested the use of 8-hydroxyquinoline as a means of blocking readsorption or precipitation of phosphate by active iron and aluminium during the acetic acid extraction.

Chirikov and Volkova (1941) fractionated total soil phosphorus into five groups; they classified the various fractions in order of decreasing availability on the basis of plant growth tests: (1) fraction soluble in solution of CO_2- alkali phosphates, acid phosphates and diphosphates of calcium and magnesium, $Mg_3(PO_4)_2$, and some phosphorites, (2) fraction soluble in 0.5N AcOH - some apatite, phosphorite and salts of alcohol phosphoric acids and sugar phosphoric acids, (3) fraction soluble in 0.5N HCl-phosphorite, apatite, $AlPO_4$, $FePO_4$, some of the more basic phosphates of iron and phytin, (4) fraction soluble in 0.2N NaOH - nucleins, nucleoproteins and similar compounds of humic acid, and (5) fraction insoluble in any of these solvents - titanium phosphates and P_2O_5 compounds of the unweathered minerals of the mother formation.

Williams (1950 a) adopted Ghani's (1943 b) 8-hydroxyquinoline method but made a further modification by omitting the final extraction with sulphuric acid. He extracted the phosphorus compounds in the soil with 2.5% acetic acid containing 1% 8-hydroxyquinoline and then with 0.1N sodium hydroxide. In his method, the partial fractionation procedure was as follows:

(1) Acetic acid - 8-hydroxyquinoline extractions:
  - Water soluble phosphates
  - Calcium phosphates
  - Hydroxy - and carbonate - apatite
  - Magnesium and manganese phosphates
  - To some extent chloro - and fluo - apatites.

(2) Sodium hydroxide extraction:
  - (a) Inorganic phosphates
    - Adsorbed phosphate
    - Basic iron and aluminium phosphates
    - Titanium phosphate
  - (b) Organic phosphorus.

(3) Insoluble in either extractant:
  - Chloro - and fluo - apatite
  - Crystal lattice phosphorus
  - Resistant phosphate minerals such as turquois, monazite and amblygonite.

Turner and Rice (1954) found that neutral ammonium fluoride can dissolve aluminium phosphate but not iron phosphate. Henceforth it was feasible to clearly separate aluminium phosphate from its combination with iron phosphate.

Studying the chemical characterization of phosphorus present in various Kansas soils, Bhangoo and Smith (1957) grouped the forms into four divisions:

(a) 0.1N HCl soluble phosphorus (calcium phosphate)

(b) cold-alkali - soluble phosphorus after removal of (a) (adsorbed phosphorus).

(c) hot-alkali - soluble phosphorus after removal of (a) and (b) (iron and aluminium phosphorus).

(d) organic phosphorus.

It was not until Chang and Jackson (1957) developed a suitable procedure that there was a method available for the fractionation of the soil inorganic phosphate discretely into the total amount of each of the major chemical forms as shown:

(1) Aluminium phosphate extracted with neutral 0.5N NH_4F.

(2) Iron phosphate extracted with 0.1 N NaOH.

(3) Calcium phosphate extracted with 0.5N H_2SO_4.

(4) Reductant soluble iron phosphate (iron oxide - occluded) extracted with $Na_2S_2O_4$ - citrate.

(5) Occluded aluminium phosphate extracted with neutral 0.5N NH_4F.

Alternative or addition to (5) is (6): occluded aluminium - iron phosphate extracted with 0.1N NaOH.

Chang and Jackson's (1957) fractionation procedure was still faced with an incomplete selective extraction of aluminium phosphate by neutral 0.5N NH_4F since iron phosphate was also slightly extractable and in the extraction of iron phosphate with 1.0 N NaOH aluminium phosphate and organic phosphorus were also extractable. 0.5N H_2SO_4 was also found to extract aluminium and iron phosphate considerably.

Working with both non-soil and soil systems Fife (1959 a and b) showed that the most general selective delineation of aluminium-bound soil phosphate by ammonium fluoride extractant is probably attainable at approximately pH 8.5 instead of pH 7 as recommended by Chang and Jackson (1957).

Glen et al. (1959) agreed with Fife's (1959 a and b) recommended pH of the ammonium fluoride solution used to extract aluminium phosphate but made further modification of Chang and Jackson's (1957) fractionation procedure with regard to the order of extraction of the different forms of soil inorganic phosphorus. The proposed method of Glen et al. (1959) was: (a) aluminium phosphate, soluble in 0.5N NH_4F, pH 8.2, (b) iron phosphate, soluble in 0.1N NaOH, extracted for 9 to 17 hours instead of 17 hours as originally proposed, (c) reductant soluble phosphate, soluble in $Na_2S_2O_4$ - citrate and (d) calcium phosphate, soluble in 0.5N H_2SO_4. The order was changed because the 0.5N H_2SO_4 used to extract calcium phosphate tends to remove some of the occluded phosphate.

Petersen and Corey (1966) modified Chang and Jackson's procedure to make it more suitable for the requirements of routine analysis of large numbers of samples. Dilutions were avoided by use of two molybdophosphoric reductants with different sensitivities. They eliminated the H_2O_2 treatment and increased the speed and convenience of the phosphorus determinations by determining the reductant soluble fraction by an isobutyl alcohol extraction following oxidation of dithionite and citrate with 0.25M $KMnO_4$.

Although the phosphate fractionation procedure of Chang and Jackson (1957) had been widely used to investigate the forms of native phosphate and the fate of applied phosphate in soils, certain workers have modified it in the light of subsequent findings concerning the effects of various extractants on pure compounds and on soils. Williams et al. (1967) modified it to include the determination of "residual inorganic P"; they also introduced a revised nomenclature for the other fractions. They used a modified version (Glen et al. (1959) already referred to above) of the original scheme as the starting point in a further revision of the procedure.

The procedure for the fractionation of soil inorganic phosphate and the nomenclature used by William et al. (1967) was as follows:

Stage No.	Treatment	Name of fraction
1	0.5M NH_4Cl for 30 min	easily soluble P
2	0.5M NH_4F, pH 8.2 for 24 hrs., with correction for resorption of phosphate from solution during extraction	NH_4F - P

Stage No.	Treatment	Name of fraction
3	0.1N NaOH + 1M NaCl for 17 hours	1st NaOH - P
4	extraction with dithionite citrate - bicarbonate	reductant - soluble P
5	1M NaOH for 17 hours	2nd NaOH - P
6	0.5N HCl for 1 hour	1st HCl - P
	followed by 1N HCl for 4 hr	2nd HCl - P
	if 1st HCl - P $>$ 20 ppm	sum = acid - extractab Ca - P
	ignition at 550°C for 1 hr., followed by 1 N HCl for 16 hrs	residual org. P
7	Na_2CO_3 fusion	residual inorg. P

Criticisms based on the behaviour of pure chemical compounds when shaken, often at high extraction ratios, with solutions containing large amounts of phosphate, do not necessarily make invalid the results obtained by using the Chang and Jackson procedure on the complex mixture of materials which makes up a soil. The phosphate in soil comes fairly quickly to a quasi-equilibrium; soluble phosphate mixed with moist soil does not remain in the water - soluble state for more than a few hours.

This is not to say that the Chang and Jackson fractionation always gives a precise deliniation of the various forms of inorganic soil phosphate; this was not claimed by the authors. Whatever its shortcomings, however, it has been used extensively.

2.3 Distribution of Phosphorus in the Soil

Knowledge about the distribution of forms of soil phosphorus naturally depends on the techniques for soil phosphorus fractionation. The study and improvements achieved in fractionation procedure have thrown more light on phosphorus distribution in the soil.

Dean (1938) grouped soil phosphorus forms into three broad fractions: organic, inorganic and insoluble phosphorus. Making use of his proposed system of fractionating the soil phosphorus, Dean (1938) analysed two sets of soil samples from the classical plots at Rothamsted and Woburn. He found that the largest fraction of the total soil phosphorus was in the insoluble form. It was also found that this fraction was not increased by the long-continued use of phosphatic fertilizers at Rothamsted and Woburn. He found relatively large amounts of organic phosphorus in the soils and observed that the amounts were closely related to the carbon contents.

Pearson et al. (1940) studied the vertical distribution of total and dilute acid - soluble phosphorus in twelve Iowa soil profiles. He found that in all the profiles studied total phosphorus decreased with depth to a minimum between the lower A and upper C horizons. Below this zone in 11 of the 12 soils, the amounts increased rapidly with depth to the bottom of the profile. In eight of the soils the concentration of phosphorus in the C horizon was more than double that in the lower A to upper B horizons.

Pearson and Simonson (1939) determined the amounts and distribution of organic phosphorus in seven Iowa soil profiles. They found the amounts ranged from 205 ppm to 393 ppm in the surface layers but they were as low as 8 ppm in the C horizons of some soils. The ratios of organic phosphorus to organic carbon and nitrogen were found to vary considerably within individual profiles as well as from one soil to another. Smaller variations occurred in the nitrogen - phosphorus ratio than in the carbon - phosphorus ratio; C:P ratio was between 100 and 200 and N:P ratio was between 8 and 16 for the soils.

Ghani and Aleem (1943 a) studied surface distribution of different forms of phosphorus in some Indian soils. They found that iron and aluminium phosphates were relatively high in acid soils and that they tended to decrease as the pH increased. They also found that on average, less than 10 per cent of the total soil phosphorus was in the apatite forms and in contrast to iron and aluminium phosphates, this fraction tended to increase with increase in pH.

The organic phosphorus was also found to occur most abundantly under acid conditions and decreased with increase in pH reaching a minimum at nearly neutral reactions and then increasing with increase in pH; this suggested that its accumulation in soil was mainly a function of microbiological activities.

The insoluble fraction came to a mean value of 25 per cent of the total and was related neither to pH nor to the sesquioxide content. In the majority of cases investigated by Ghani and Aleem (1943 a) it decreased in the soils as the organic phosphorus increased.

In their later study of the vertical distribution of various phosphorus fractions in a number of Indian soil profiles Ghani and Aleem (1943 b) found total phosphorus to be at a minimum in the intermediate layers of the profiles. They found iron and aluminium phosphates expressed as percentage of the total phosphorus to be at their maximum at the intermediate layers. In most of the soils organic phosphorus, organic carbon and nitrogen decreased with depth and on average, C:P ratios decreased with depth whereas the N:P ratio showed a maximum in the subsurface.

Williams (1950 b) made an examination of the native phosphorus in a series of red-brown earth and solonized brown (mallee) soils in South Australia. The investigation showed that only 15 per cent of the total soil phosphorus was extracted as inorganic phosphorus by the successive acetic acid and alkali extractions from the red-brown earth soils and 19 per cent from the solonized brown soils. Over 50 per cent of the mean total phosphorus in both groups of soils was insoluble in either extractant, and approximately 30 per cent was present as organic phosphorus. The organic phosphorus content of red-brown earth and solonized brown soils increased with increase in total nitrogen and the nitrogen - organic phosphorus ratio generally ranged from 15 to 23:1 for these two groups of soils.

Aldrich and Buchanan (1954) studied the phosphorus content of soils and their parent rocks in southern California.

They concluded that the phosphorus content of soil in southern California was apparently primarily determined by the phosphorus content of the parent rock material from which the soils were derived.

Paul (1954) investigated the phosphorus status of peat soils of British Guiana before and after cropping. Organic and inorganic alkali-soluble (iron and aluminium phosphate) forms constituted more than 70 per cent of the total phosphorus of these soils.

Studies on the total and organic phosphorus by Godfrey and Riecken (1954) in five virgin-like loess-derived soil profiles occurring along a traverse from south western Iowa to northern Missouri in the U.S.A. showed a decrease of total phosphorus in the profiles along the traverse in relation to the degree of profile development, and the vertical distribution was found to vary in a systematic manner also. They found that soil weathering action had reduced the amount of phosphorus in the A horizons of the soils in relation to the amount found in the C horizons. The phosphorus measured in the B horizons was less than in the A or C horizons.

It was also found that the organic phosphorus decreased in relation to the degree of soil profile development along the traverse and declined vertically in the profiles at a progressively greater rate with each succeeding more strongly developed profile.

Karim and Khan (1955) undertook an examination of the relationship of pH to the relative abundance of different forms of phosphorus in some soils of East Pakistan. In their investigation they found the following observations:

(1) "As the pH rose from 4.2 to 4.6, the organic phosphorus increased; with further rise of pH from 4.6 to 5.6, this form decreased, to increase again with still further rise of pH, that is, above pH 5.6.

(2) The sesquioxide - bound phosphorus steadily rose with pH up to 5.6, but the rate of rise at pH above 5.3 was much greater than that at pH below 5.3. With the increase in pH from 5.6 to 6.2 R_2O_3-P decreased.

(3) The adsorbed phosphorus increased with a rise in pH from 4 to 5.3, but as the pH went above 5.3, this form steadily decreased."

Karim and Khan suggested further that the critical influence of pH 5.3 and 5.6 might be due to changes in the state of Fe and Al with the change of pH of the medium.

Williams and Saunders (1956), in a contribution to a long-term investigation of the phosphorus relationship of the soil associations in north-east Scotland, reached the following conclusions with regard to the distribution of phosphorus in profiles and particle-size fractions:

(a) "The total soil P decreases down all the profiles, reflecting mainly a marked fall in the organic P.

(b) The clay and silt together contain 85 per cent and more of the total soil organic P, but the sands also contain appreciable amounts, present in coarse particles of organic matter, and it is unlikely that this phosphorus is completely extracted by alkaline reagents. In the topsoils the proportions of the total P in organic form are 27-67 per cent for the soils and 50-65 per cent for the clays and silts.

(c) The P contents of the fractions vary widely depending on the soil, but the total P is normally highest in the clay and lowest in the coarse sand, the main exceptions being the gleyed subsoils where the fine sands are richer than the clays.

(d) The phosphorus in the sands is largely inorganic and in about half of the samples, including most of the basic igneous soils and the gleyed subsoils, the fine sand is richer in inorganic P than the clay.

(e) In the topsoils the course sands account for 12-22 per cent total soil inorganic P and the fine sands for 18-50 per cent giving total of 34-62 per cent in the combined sands. The tendency is for these proportions to increase with depth and in the gleyed subsoils the value of the combined sands are of the order of 70-80 per cent.

(f) The inorganic P in the sands, particularly the fine sand, is very highly soluble in 0.2N H_2SO_4 and appears to be largely calcium-bound. For most of the samples, 50 per cent of the inorganic P extracted by this reagent is derived from the sands, but the composition and significance of the values vary widely depending on the distribution of phosphorus over the fractions.

(g) The main effect of parent material is that the sands, particularly the fine sands, are richer in phosphorus and account for higher proportions of the total soil P in the basic igneous rocks. These soils are also relatively rich in aluminium and iron.

(h) The results emphasize the importance of drainage conditions in the phosphorus relationships of the soils. In general, poor drainage is reflected in: (i) much lower total organic P, lower total P, but rather higher total inorganic P; (ii) a very abrupt fall in organic P with depth; (iii) higher P contents for the sands, but much lower contents in the clays; (iv) higher amounts and proportions of the soil inorganic P present as sand and correspondingly lower amounts and proportions as clay; (v) higher acid-soluble inorganic P in the soils, reflecting both the higher amounts and higher solubility of the phosphorus in the sands".

Bhangoo and Smith (1957) fractionated total P contained in both surface soil and subsoil of seven virgin Kansas soil sites. They found that on the average, iron and aluminium phosphates accounted for somewhat more than half of the total

P in surface material and about two-thirds of the total P in subsoils. Organic P generally made up about one-third of the total P contained in surface soil material.

Nye and Bertheux (1957) determined the abundance of phosphorus in surface and profile samples from a range of agriculturally important soils in the forest and savannah regions of the Gold Coast (Ghana). In the surface soils they found that although the total phosphorus was low, its distribution among the soil fraction was normal for slightly acid soils. Soils developed over basic rocks had more total phosphorus, and a lower proportion of acid soluble phosphorus than soils over quartzose rocks and forest soils had more total phosphorus and more phosphorus in each of the fractions than savannah soils.

There was a close relationship between the organic phosphorus content and the organic carbon content. The C/P ratio averaged 233 in forest and 247 in savannah and the N/P ratio was 21.6 in forest and 19.5 in savannah. The higher amount of organic phosphorus found in the forest soils was attributed to the increased amount of organic matter in the forest soils.

In the profile samples, Nye and Bertheux (1957) found that in thoroughly leached soils the acid-soluble phosphate (mainly calcium phosphate) decreased sharply, and the alkali-soluble inorganic phosphate (mainly iron and aluminium phosphates) rather more slowly with depth. They also found that in the forest total phosphorus is greatest in the surface but found no consistent change with depth in the savannah. The incompletely leached profiles differed in showing a sharp rise in the acid-soluble phosphorus and the total phosphorus in the subsoil. The level of organic phosphorus fell less than expected down the profile, and the C/P ratio, like the C/N ratio, decreased in the subsoil.

The Chang and Jackson (1957) soil phosphorus fractionation procedure which had made use of improvement in the removal of iron oxide coatings from soils and clays by Aguilera and Jackson's (1953) use of dithionite-citrate reduction-chelation technique offered a means by which it was estimated that many soils contain about 40% of reductant soluble phosphorus.

Chang and Jackson (1958) investigated the soil phosphorus in some widely different soil types using the fractionation procedure they had developed (Chang and Jackson, 1957). They found that the distribution of soil phosphorus measured the degree of chemical weathering, the chemical weathering sequence being calcium phosphate, aluminium phosphate, iron phosphate, and occluded phosphate which includes reductant soluble iron phosphate and aluminium-iron phosphate occluded in iron oxides.

Chang and Jackson (1958) concluded in their investigations that the formation of the various discrete chemical forms of phosphate in the soil is apparently related to soil factors such as pH, activities of various cations, solubility products of the various phosphates, degree of chemical weathering, and fertilizer practice.

Walker and Adams (1958) analyzed twenty-two grassland soils to a depth of 21 inches for carbon, nitrogen, sulphur, and organic and total phosphorus. The soils had been formed from a few parent materials differing widely in phosphorus content. They found a close relationship between total phosphorus content of the soils and the phosphorus content of the parent materials; organic phosphorus content of the soils was on the average a very high fraction of the total phosphorus. The carbon, nitrogen, and sulphur contents were also closely related to organic phosphorus (C:N:S: organic P = 120:10:1.3:2.7, on the average for 20 of the soils to a depth of 21 inches), and as the phosphorus is the only one of these four elements that must be supplied by the parent material, the workers concluded that in this particular climatic zone the major factor governing accumulation of organic matter is phosphorus content of the parent material.

Whereas observations have been made by certain workers that total phosphorus tends to decrease with increasing profile depth Hamilton and Lessard (1960) reported the reverse to be true when they fractionated the phosphorus of a Canadian soil. They found that the total phosphorus content of the soil layers varied from 425 ppm of soil in the 6-12 inch layer to 538 ppm in the 18-24 inch layer. The contribution of calcium phosphates to total phosphorus increased from 41.1 per cent in the surface layer to 88.4 percent in the 18-24 inch layer. Aluminium phosphate was higher in the 0-6 inch layer and accounted for 5 per cent or less of the phosphorus in the sub-surface layers. Iron phosphate concentration was negligible for all layers. "Residual phosphates", which are comprised of occluded iron and aluminium phosphates, formed a substantial percentage of total phosphorus in the surface soil. Organic phosphorus decreased with depth of soil profile.

Bates and Baker (1960) studied the distribution of phosphorus of a Nigerian forest profile and of the sand fractions and aggregate fractions of the fine earth. They found that the soil phosphorus was accumulated in the surface soil. Below 2 inches there was a marked fall in total phosphorus, reflecting a large decrease in the amount of organic phosphorus. Thereafter the total phosphorus was found to be fairly constant down the profile. The concentration of phosphorus in the iron concretions was found to be considerably higher than in the surrounding fine earth. In the gravel horizon, 12-30 in., over 80 per cent of the total phosphorus at this level was immobilized in the concretions.

Hesse (1962) studied the distribution of phosphorus in a mangrove swamp mud in Sierra Leone and found the concentration of various fractions as follows: water-soluble phosphorus (2 ppm), aluminium phosphate (6 ppm), iron phosphate (29 ppm) reductant soluble iron phosphate (nil), calcium phosphate (25 ppm), organic phosphorus (485 ppm). Thus organic phosphorus constituted 87 per cent of the total and the remainder was almost entirely associated with iron and calcium. Hesse concluded that since the swamp muds are comparatively unweathered the absence of occluded forms of phosphorus is expected. Hesse (1963) further examined the distribution of phosphorus in the mangrove swamp muds collected from Warri, Nigeria, and obtained results similar to the ones he had found in Sierra Leone mangrove swamp mud, nearly 76 per cent of the total phosphorus was in organic forms and the remainder was in association mostly with calcium and iron.

Dormaar and Webster (1963) studied the status of organic phosphorus in some Alberta soils. They found that in all profiles the total organic phosphorus content decreased with increasing depth. They concluded that for the soils which they studied, organic phosphorus formed an integral part of the organic matter.

Dahnke et al. (1964) studied the phosphorus fractions in selected soil profiles of El Salvador, Central America, as related to their development. They found that in the younger soils a greater proportion of the total phosphorus was found in the organic and the readily available forms, while in the older soils nearly all the phosphorus was found as occluded iron phosphate and in unweathered minerals.

It can be appreciated that the inorganic and organic phosphorus content of soils is being constantly subjected to the influence of many active factors, among which may be mentioned:

(1) the character of the parent material;

(2) the nature of the processes that cause soils to evolve such as climate, vegetation and microbes;

(3) soil texture;

(4) temperature and moisture;
and (5) age of the soil.

2.4 Available Phosphorus in Soils

Owing to the complex nature of the chemistry of phosphorus in soils, particularly its interaction with other elements and their compounds, only a small fraction is available for plant growth. Consequently the problem of the determination of that readily available phosphorus in the soil has been under consideration and investigation by soil chemists for many years. This has given rise to several methods, one of the earliest of which was that of Truog (1930) in which the readily available phosphorus of the soil was extracted with a 0.002N solution of sulphuric acid, buffered with ammonium sulphate to a pH of 3. Bray and Kurtz (1945) introduced their Nos. 1 and 2 methods in view of the then prevailing concepts about the available forms of phosphorus; there was a general division of certain soil phosphates into the adsorbed forms and the easily acid-soluble forms. Method No. 1 (for adsorbed phosphorus) used an extraction solution made up of 0.03N NH_4F and 0.025N HCl; method No. 2 used an extraction solution of 0.03N NH_4F and 0.1N HCl and was supposed to extract mainly acid-soluble and adsorbed phosphorus. Olsen et al. (1954), quoted and outlined by Jackson (1958), advocated the use of 0.5N $NaHCO_3$ extractant of pH 8.5 to determine the available phosphorus status on both acid and alkaline soils. Working on Southern Rhodesian soils, Saunder (1956) suggested the use of hot 0.1N caustic soda for determination of available phosphorus in tropical soils. He claimed that the phosphorus extracted by this reagent gave excellent correlations with crop response. Al-Abbas and Barber (1964 a and b) correlated soil phosphorus fraction with plant available phosphorus (that is, phosphorus uptake by millet in their experiments) and were able to develop a soil test in which available phosphorus was extracted with a solution of 0.3N NaOH and 0.5N $Na_2C_2O_4$.

Chai and Caldwell (1959) and Pratt and Garber (1964) compared some of the methods which had been proposed for the determination of available phosphorus in the soil since it was appreciated that each of the methods had both advantages and disadvantages. It seems that there is no one method of determining available phosphorus which is completely satisfactory for all soils. It is recognised that the usefulness of any given method must take into consideration the correlation of results with crop responses to fertilizer application in practice. Weir (1962) evaluated several phosphorus soil test methods, on some Jamaican soils, in terms of correlation between the test results and measured yield response of cauliflower to phosphorus fertilizer. He observed that in the order of decreasing precision of estimating the available phosphorus of soils, the methods are as follows: (1) 0.002N sulphuric acid method of Truog; (2) 0.1N hydrochloric acid method of Bray; (3) 0.5M $NaHCO_3$ method of Olsen et al.; (4) 10 per cent sodium acetate method of Morgan; and (5) 0.1N caustic soda method of Saunder.

In their study of the availability to plants of the phosphoric acid of different forms of soil phosphate, Chirikov and Volkova (1941) fractionated the total soil phosphorus into five groups on the basis of solubility in chemical extractants, and then classified the various fractions in order of decreasing availability on the basis of plant growth tests. The sodium hydroxide-soluble fraction, containing most of the organic phosphorus together with some inorganic phosphorus, was placed in the fourth group as it appeared to be of no value. Williams (1950 c) conducted a similar experiment with five soils, in which removal of 7.5 ppm of phosphorus from the soil by a wheat crop was accompanied by a reduction of 8.1 ppm in soil phosphorus extracted in three fractions, distributed as follows, 4.5 ppm in the acetic acid - soluble inorganic fraction, 2.5 ppm in the alkali-soluble inorganic fraction, and 1.0 ppm in the organic fraction. In other experiments, he found that the phosphorus in the soil fractions was correlated significantly with the phosphorus percentage in wheat plants in the case of the acetic acid-soluble and alkali-soluble inorganic fractions, but not in the case of the organic fraction.

These results of Chirikov and Volkova (1941) and Williams (1950 c) clearly showed that availability of soil phosphorus to plants is primarily a matter of the inorganic phosphorus status, and that organic phosphorus is of little or no importance. However, it was shown by Eid, Black and Kempthorne (1951) that soil organic phosphorus may be of significance in the phosphorus nutrition of the crop when it mineralizes to the inorganic form; Eid, Black and Kempthorne (1951) showed that the process of mineralization of organic phosphorus proceeds several times faster at 35°C than at 20°C indicating that much more mineralized organic phosphorus is available at high soil temperature than at low soil temperature.

The inorganic phosphorus fractions that are considered to be significantly available for plant growth are calcium, aluminium, and iron phosphates; the occluded phosphates are believed to be unavailable due to the iron oxide coating, rendering them insoluble. Dean (1938) reported that this insoluble fraction (now mainly referred to as occluded form of phosphate) did not change after over 50 years of fertilization at Rothamsted and Woburn indicating its relative lack of importance in problems of phosphate absorption. When amounts of P extracted by several chemical methods were related to quantities of the different forms of P, Chang and Juo (1963) found that the degree of correlation was dependent upon the dominating forms of soil P. Al-Abbas and Barber (1964 b) found that the iron phosphate fraction accounted for the available P and subsequently developed a chemical method for the selective dissolution of iron-P. Tripathi et al. (1970) related chemical tests for P to soil P forms and observed that many of the P soil tests, currently used as a basis for fertilizer recommendations, extract some of each P form in amounts that vary according to the extracting solution employed.

Russell (1961) noted that the assumption that there is a fairly definite pool of available phosphate in the soil fails for soils in which most of the potentially available phosphate is in the soil organic matter, such as exhausted soils very low in available mineral phosphate which have recently been fertilized with farmyard manure, or many tropical soils on old land surfaces. In these soils the organic phosphate is mineralized in flushes, in phase with the flushes of decomposition of the soil's organic matter. In view of this, simple chemical extraction methods are unsuitable for measuring the phosphate supply available to the crop and though an incubation technique is more suitable, the supply depends on the concordance in time between the crops requirements for the phosphate and its production from the organic matter. It is likely that the amount of organic phosphate mineralized can be estimated from the readily extractable and oxidisable organic matter, and that the proportion actually liberated in the field, or the relative importance of the organic to the inorganic phosphates, is greater the higher the soil temperature during the growing season (Eid, Black and Kempthorne, 1951).

It is accepted that the amount of phosphate available to a crop not only depends on the amount present per gram of soil but also depends on the volume of the soil tapped by the root system of the crop. Hence, everything which increases the rate of growth of the root system, such as good husbandry practices, balanced manuring, and even sometimes starter doses of phosphate placed near a seedling, will increase the speed with which the roots will ramify through the soil; and everything which encourages deeper rooting, such as moderate droughts at suitable periods during the growing season will also increase the volume of soil accessible to the crop. These realities underline the great caution needed when using the phosphate status of soil, as measured in the laboratory or greenhouse, for predicting field responses.

Liming acid soils is a common practice in the humid regions of the temperate zone and the studies of various workers indicate that lime helps to increase the availability of P to plants. It is not clear as yet to what extent this applies to tropical soils. Abdul (1964) conducted field studies over a 2-year period on experimental plots at El Zamorano, Honduras, to study the effects of lime on the availability of soil P. Highly significant yield increases of corn, sorghum, beans and cowpea green manure were obtained when the acid soil (pH 5.5) was limed to raise the pH to 6.5. The highest yields in all crops were obtained when lime and P were used together. The results of the analysis of soil P at the end of 2 years showed that the major part of the potentially available P in Zamorano soils is in the organic form; Abdul (1964) suggested that liming of these acid soils liberated soil P from the organic fraction and increased the efficiency of the applied P for crop use.

Dalton et al. (1952) determined by plant uptake the relative availability of the phosphate precipitated by iron and aluminium under acid conditions and the effectiveness of organic matter in making available to plants the phosphate fixed in acid soils or contained in rock phosphate; it had long been known by practical farmers that as soil organic matter decreased, there was also a parallel increase in the phosphate requirements for high production of crops. Dalton et al. (1952) concluded in their investigations that organic matter added to the soil as an amendment is effective in increasing the availability of soil phosphate and that easily decomposable organic matter is more effective in this regard than are organic substances that decompose slowly. They observed that the fixation products of phosphate with iron and aluminium are relatively poor sources of phosphate for plants. Rock phosphate was found to serve as a very good source of phosphate for ladino clover although it was less efficient than soluble phosphate. The efficiency of the rock phosphate was increased by the presence of sucrose, glucose, and citrus pectin but not by starch; these organic substances had been chosen because they contain insignificant amounts of phosphorus; are normally found in plant residues; and are metabolized by soil micro-organisms to produce such organic acids as citric, oxalic, tartaric, malic, malonic and galacturonic, all of which had been shown to be effective in replacing fixed phosphate (Struthers and Sieling,1950). Dalton et al. (1952) attributed the activity of the organic matter in making soil phosphate available to the ability of certain metabolic products of microbiological decomposition to form stable complex molecules with iron and aluminium that are responsible for phosphate fixation in acid soils.

Acquaye (1963) in Ghana found that nitrogen and phosphorus increased the mineralization of the soil organic phosphorus sufficiently to explain the high correlation between cocoa yield response and organic phosphorus content of the top soil in nitrogen and phosphorus treated plots.

Acidic red lateritic soils are usually known to be deficient in available phosphorus and even if any soluble phosphates are added to such soils they become largely fixed and non-available to plants. This has given rise to the belief that added phosphates make insoluble compounds of ferric phosphates with iron salts in the ferric state. In view of this, Islam and Elahi (1954) kept red lateritic soils from a Dacca farm, East Pakistan, under water-logged condition (a reducing condition) and studied the effect this had upon the conversion of Fe^{3+} into Fe^{2+} state and the change of readily soluble phosphorus. They observed that by water-logging alone the amounts of ferrous iron and readily soluble phosphorus increased and the addition of oxidizable organic matter increased this transformation. Among the added oxidizable substances, green manure was particularly helpful in effecting the reduction of ferric salts into ferrous and also making the soil phosphorus more easily soluble. Islam and Elahi (1954) pointed out that whatever may be the mechanism of this reduction (Fe^{3+} to Fe^{2+}), water-logging seems to mobilize the fixed phosphorus in the soil and make it more available to the plants. The addition of organic matter such as green manure will also make the phosphorus more available.

Islam and Choudhury (1960) studied the distribution of iron, manganese and phosphorus in the paddy soil profiles in Dacca, East Pakistan. They found that under water-logged conditions there was a higher concentration of phosphorus over the initial concentration at the surface layers than at the lower layers. They believed that this was caused by its movement as partners (i.e. salts) of iron and manganese, and its distribution pattern has been determined by them. Under water-logged conditions iron and manganese, because of their ability to exist in different valence states, not only determine their own distribution pattern in the paddy soil profile and availability to plants, but also exert great influence on the distribution and availability to plants of other nutrients, particularly phosphorus and of sulphur.

Shapiro (1958a) measured the effect of flooding on the availability of soil and applied phosphorus and nitrogen to rice on rice soils and other soils. He found that flooding increased the yield, phosphorus uptake, and nitrogen uptake by rice. These increases occurred with both a lowland (Colusa) and an upland (Korean) variety of japonica rice. Flooding increased the availability of soil nitrogen. The applied phosphorus and nitrogen were both utilized more efficiently under flooded conditions. Shapiro (1958b) made further subsequent investigation into the effect of organic matter and flooding on availability of soil and synthetic phosphates and was able to show that the addition of spent brewer's hops to soil increased both the inorganic and organic phosphorus content of the flooded soil solution for all sampling dates. As he had found before, flooding increased the measured availability of both soil and applied phosphorus. In his view, reduction is the more important effect of both flooding and organic matter.

Basak and Bhattacharya (1962) conducted studies on phosphate transformations in rice soil in West Bengal, India. They observed that water-logged soils have a tendency to show a unique capacity for regenerating an increasing quantity of available phosphoric acid during the active period of crop life. They suggested that the source of its supply and the cause of its regeneration were probably in the release of phosphoric acid from the mineralization of organic phosphorus and the reductive transformation of iron and aluminium phosphate under anaerobiosis developed due to water-logging. The amount of phosphoric acid regeneration from these sources seemed to be large enough to provide heavy insurance against any possible shortage in its requirement by a heavy crop.

Sperber (1958) has shown that sulphides in the soil may reduce ferric phosphate to black ferrous sulphide and release available phosphate; the sulphides were produced mainly by micro-organisms. Sesquioxides, which might compete with ferric phosphate for any hydrogen sulphide formed, would greatly hinder release of phosphates by this mechanism, but in water-logged siliceous soils, low in sesquioxides but high in hydrogen sulphide, release of phosphate might be of importance.

2.5 Phosphorus Fixation and its Mechanism

Phosphate fixation or retention by soils has been known and studied for many years. It has been the object of considerable study to develop practices that will increase the efficiency of applied phosphate fertilizers and of residual soil phosphates in crop production.

Phosphate fixation is a general term which refers to the removal of phosphate from solution by soils - the conversion of soluble phosphate to less soluble form. The term has been variously defined by some workers. Davis (1935) stated that phosphate fixation is taken to imply the following phenomenon: "When a solution of orthophosphates is applied to soil, there is a decrease in the concentration of phosphates in the solution". Dean (1949) defines 'fixed phosphorus' as the soil phosphorus which has become attached to the solid phase of soils. Midgley (1940) defines 'phosphate fixation' as the conversion of soluble form to a less soluble form. Wild (1950) stated that 'phosphate fixation' is used to describe any change that phosphorus undergoes in contact with the soil, which reduces the amount that the plant roots can absorb. Dean (1949) noted that in some instances the term 'phosphate fixation' has been used to designate a change in the degree of availability of soil phosphorus but pointed out that changes in availability are not sufficiently specific to warrant quantitative interpretation. It does not necessarily follow that a change in solubility will mean a change in availability.

Many concepts have been advanced to explain the process involved in the fixation of phosphorus. Davis (1935) groups these theories as follows: (1) Cations of soluble salts present in the soil, or cations replaced from the soil by those present in the solution form precipitates with the phosphate ions. (2) By double decomposition, relatively insoluble soil minerals react to form insoluble phosphates. (3) Phosphates are adsorbed at the extensive soil-solution interface. (4) Phosphates are adsorbed by the soil minerals to form complex systems in one or more of the solid soil phases. Kardos (1964) classified the types of reactions by which phosphorus becomes fixed into three general groups: adsorption, isomorphous replacement, and double decomposition involving solubility - product relations and stated that in all the reactions the phosphorus is involved as one or more of the ionic forms into which orthophosphoric acid may dissociate.

From a consideration of the ionization constants of H_3PO_4, Buehrer (1932), quoted by Kardos (1964), has calculated the relation of pH to the relative concentration of the undissociated H_3PO_4 and the three ionic species $H_2PO_4^-$, HPO_4^{2-} and PO_4^{3-}. His work provided clear evidence that all phosphate reaction systems will be fundamentally influenced by the hydrogen ion activity in the systems.

Murphy (1939) did considerable work with kaolinite and found that grinding greatly increased its capacity to retain applied phosphate, which is quite indicative of adsorption.

Low and Black (1950) plotted the amount of phosphorus fixed by kaolinite against the equilibrium concentration of phosphorus in dilute solution. The plot produced a typical adsorption curve, which would be represented by the Freundlich adsorption equation $x/m = kc^{\frac{1}{n}}$ where x is the amount of the solute adsorbed, m is the weight of the adsorbent (hence x/m = amount of phosphorus adsorbed), k is a proportionality constant, c is the concentration of the solute in the equilibrium solution, and n is a constant. They also found that the degree of adsorption was increased by increasing temperature, and hence, concluded that adsorption was chemical.

Kurtz, De Turk and Bray (1946) investigated the nature of the reactions responsible for the removal of phosphate ions from solution by soils. They found that phosphate adsorption curves for different soils were similar in shape and could be expressed by an equation of the Freundlich type.

Rennie and McKercher (1959) found that adsorption of phosphorus by four Saskatchewan soils of differing colloid content showed close agreement with the Langmuir isotherm when final phosphorus solution concentrations were less than 20 µg P/ml. They noted that phosphorus adsorption data on soils have commonly been described by the Freundlich isotherm (Davis, 1935; Kurtz, De Turk and Bray, 1946; Russell and Low, 1954) but maintain that this equation is not specific, in that it applies to a wide range of equilibrium phosphorus concentrations. In contrast, the Langmuir isotherm has a sound theoretical derivation, is specific for smaller amounts of adsorbed phosphorus and more dilute equilibrium phosphorus concentrations (more likely to be encountered in normal fertilizer applications of phosphorus), and an adsorption maximum can be calculated. Olsen and Watanabe (1957), and Fried and Shapiro (1956) had shown that constants calculated from the Langmuir isotherm permit a sound theoretical approach to some of the problems of phosphorus retention in soils.

The Langmuir adsorption equation may be written in the form:

$$\frac{x}{m} = \frac{kbc}{1 + kc}$$

In linear form this equation becomes

$$\frac{c}{x/m} = \frac{1}{kb} + \frac{c}{b},$$

where c = the final solution concentration (equilibrium concentration) in μg P/ml, $\frac{x}{m}$ = μg P adsorbed per g of soil b = the adsorption maximum and k = a constant related to the bonding energy of the soil colloids for the phosphorus. A straight line plot of $\frac{c}{x/m}$ against c can be assumed to be indicative of an adsorption reaction.

Hsu (1964) treated a slightly acid soil with dilute phosphate solutions of pH 7 in order to study the mechanisms of phosphate fixation. The results obtained indicated that the relationship between the phosphate fixed and the concentration of phosphate in solution followed the Langmuir adsorption isotherm. One of the phosphated soil samples was successively extracted ten times with 0.0015 N KCl solution. It was found that the phosphate desorption again followed the Langmuir adsorption isotherm.

Wada (1959) studied the reaction of ammonium phosphate with soil clays, that is, allophane and halloysite; from the reaction he reported the formation of an ammonium taranakite. He observed high phosphate retention by halloysite at pH 7.0. X-ray analysis revealed that the 10.1 Å spacing of halloysite shifted to 13.2 Å. A type of physical adsorption of ammonium phosphate between the silicate layers of halloysite, probably forming a monolayer of $(NH_4)_2HPO_4$, was suggested by Wada as a probable mechanism of the reaction.

The iron and aluminium oxides and hydroxides have been recognized by many workers as playing a significant role in phosphorus fixation in acid soils by forming iron and aluminium phosphate compounds. Toth (1937) demonstrated that the removal of the free iron oxide content of soil colloids reduces the magnitude of phosphorus fixation, and deduced from this that these compounds must be partially responsible for phosphorus fixation. Many other workers have shown that fixation of phosphorus by acid soils is directly related to their content of iron and aluminium (Coleman, 1944 and 1945; Doughty, 1930 and 1935; Ellis and Truog, 1955; Ghani and Islam, 1946; Kanwar, 1956; Kittrick and Jackson, 1955; Volk and McLean, 1963; Hinga 1973). Most of these workers convincingly demonstrated that removal of the iron and aluminium oxides from the soils investigated considerably lowered the phosphate fixing capacity of the soils. Coleman et al.

(1960) found that the amounts of phosphate sorbed by sixty subsoil samples from the North Carolina Piedmont were correlated with exchangeable aluminium content. The removal of exchangeable aluminium by salt-leaching reduced phosphate-sorption by soils that contained appreciable quantities of this ion.

After the fixation of phosphorus as iron or aluminium phosphates further immobilization of these fractions could result from the formation of occluded phosphate as described by Chang and Jackson (1957).

Many workers have shown that when phosphate reacts with iron, aluminium and other elements in the soil precipitates of definite crystalline structure are formed (Ford, 1933; Haseman et al. 1950 a and b; Kittrick and Jackson, 1955 and 1956; Wada, 1959).

Through fixation studies with the clay minerals montmorillonite, illite, and kaolinite and the minerals gibbsite ($Al(OH_3)$ and goethite ($Fe(OH)_3$), Haseman et al. (1950 b) showed that the mechanism of fixation by each of these minerals was identical. They found that all were characterized by two stages of fixation, one progressing at a rapid rate and the other at a much slower rate. They concluded that both stages of fixation proceed through the same chemical reaction, that the rapid fixation results from the reaction of phosphate with readily available aluminium and iron, and that the slow fixation results from the reaction with aluminium and iron released through decomposition of the respective minerals.

With regard to the problem of phosphorus fixation by kaolinite, Low and Black (1948) hypothesized that kaolinite dissociates into aluminium and silicate ions in accordance with the solubility product principle and that phosphate precipitates the aluminium, thereby disturbing the equilibrium and causing more clay to dissolve. As evidence in support of the hypothesis, it was found that the addition of both phosphate and 8-hydroxyquinoline to kaolinite produced a considerable increase in the concentration of silica in the solution. Kittrick and Jackson (1954) and Tamini et al. (1964) made similar observations in their experiments.

Fassbender (1969) analysed 107 samples of tropical soil from Central America. He reported that the P-fixation capacity determined under laboratory conditions varied between 9.7 and 94.1 per cent of the P added and correlated positively with organic matter, clay, free Fe_2O_3 and axtractable aluminium and negatively with pH. It was demostrated with ^{32}P that P-fixation consists of H_2PO_4-adsorption and precipitation of less soluble iron and aluminium phosphates, which is much more important. The latter contributed more than 90 per cent of the P-fixation.

Phosphorus fixation in alkaline and calcareous soils is usually attributed to the formation of phosphate compounds of calcium. In addition, however, the iron and aluminium compounds discussed in relation to fixation in acid soils are also responsible for some fixation in soils of higher pH. Although calcium has been known for a long time to be a factor in causing fixation in high pH soils, the exact compounds are still unknown.

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 phosphate 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 phosphorus fixation.

Cole et al. (1953) investigated the nature of phosphate sorption by calcium carbonate and suggested that when soluble phosphate fertilizers are added to calcareous soils, the reaction with calcium carbonate consisted of rapid monolayer sorption on calcium carbonate surfaces.

Stout (1939) indicated that phosphation of kaolinite and halloysite was primarily a displacement of hydroxyl by phosphate from a determination of the water loss in a system: clay mineral + KH_2PO_4 + dehydration at 150°C. The loss of water by this system, in excess of the sum of the water lost by the clay mineral alone and the KH_2PO_4 alone, was approximately equivalent to the milliequivalents of phosphate fixed.

Additional support of the hydroxyl replacement mechanism was given by Kelly and Midgley (1943), who found a 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. The materials used included $Fe(OH)_3$, finely ground kaolin, and a fine sand known to be a very high phosphate fixing soil.

Although the theory of hydroxyl replacement mechanism is strongly supported, there is also evidence that silicate replacement by phosphate may be important in phosphate fixation. Definite evidence of the displacement of silicate from soil colloids by phosphate was reported by Toth (1937), who found that as the phosphate fixation on each of four soil colloids increased, the amount of silica in the supernatant liquid increased. Other workers who made similar observations include Low and Black (1950). Thus phosphate fixation could be accounted for by the isomorphous replacement of hydroxyl and silicate ions of clay, and other soil minerals by phosphate ions.

The complexity of the organic phase in soil is chiefly reponsible for the lack of extensive critical evidence concerning the possible role of organic matter in phosphorus fixation.

Doughty (1935) studied phosphate fixation in soils, particularly as influenced by organic matter. He concluded in his investigations that soil organic matter as such has only a minor role, if any, in the fixation of phosphorus in difficultly available form when soluble phosphatic fertilizers are applied to a soil.

Studying the adsorption of phosphorus by four Saskatchewan soils, Rennie and McKercher (1959) observed that organic matter appeared to be equally as important as the inorganic colloids in determining the phosphorus adsorption capacity of the soils.

Weir (1972) quantitatively characterized the behaviour of native and applied phosphates in two Jamaican soils by studying the adsorption of added phosphate, the release of native bound phosphate, and the availability of released and applied phosphorus to maize plants grown on these soils. He observed that phosphate adsorption closely followed the Langmuir isotherm when the phosphorus solution concentrations were less than about 20 to 25 ppm. Additions of a commercial organic product, 'Aqua Humus', resulted in a marked reduction of the amount of phosphorus fixed by both soils.

Kardos (1964) considered the types of reactions by which phosphorus becomes fixed, namely adsorption, isomorphous replacement, and double decomposition involving solubility-product relations. He observed that in general, the overall effect of the organic phase in soils has been found to be such as to decrease phosphorus fixation.

The Fate of Phosphate Applied to Soil

The development of the methods of fractionation of inorganic soil phosphorus into four principal forms, namely, aluminium phosphate, iron phosphate, calcium phosphate and occluded phosphate, has made it possible for more detailed examination of the fate of applied phosphate to be made.

Chang and Jackson (1958) studied soil phosphorus fractions in some representative soils. They found that the application of phosphate fertilizer to a silt loam in Wisconsin greatly increased the amount of aluminium and iron phosphate at three lime levels; only a slight increase of calcium phosphate occurred, at the highest lime level. The amount of occluded phosphate remained unchanged by liming or fertilization. They attributed the relatively small increase of calcium phosphate through phosphate application partly to crop removal but showed it to be due mostly to formation of the less soluble iron and aluminium phosphates.

Yuan et al. (1960) studied the forms of newly fixed phosphorus in three acid sandy soils of Florida. They found that over 80 per cent of the added phosphorus was retained by the soils as aluminium and iron phosphates. Less than 10 per cent was in the water-soluble and calcium phosphate forms.

Chang and Chu (1961) studied the fate of added soluble phosphate in six Taiwan soils, with pH ranging from 5.3 to 7.5 kept at field moisture capacity for 3 days. They found that the added phosphate was mainly fixed as aluminium phosphate, followed by iron phosphate and calcium phosphate. After keeping under the same conditions for 100 days, the amount of iron phosphate increased while that of aluminium phosphate decreased. In two latosols the amount of iron phosphate surpassed that of aluminium phosphate. They further found that under flooded conditions for 100 days, iron phosphate became the dominant form of phosphate fixed in all six soils.

Le Mare (1968) conducted experiments on the effects of phosphate applied to a Buganda acid clay loam. He found that triple superphosphate applied at 8 cwt per acre or less was converted within 2 years to a very insoluble form, having a solubility similar to that of variscite; with 16 cwt per acre the phosphate concentration was much greater than with the smaller dressing after this period and the soils appeared supersaturated with variscite.

2.6 Surface Activity of Inorganic Soil Phosphorus

Experimental work with radioactive phosphorus (McAuliffe et al., 1948) has established the principle that the inorganic phosphate ions in the soil solution are in continuous exchange with inorganic phosphate ions held by the solid phase of soil. They suggested that this principle can be applied to a soil system to measure what they called the surface phosphate-p^{31}. They claimed that soil surface phosphate thus estimated corresponds to the level of phosphatic fertility measured by anion exchange, modified Truog solubility or Neubauer's growth experiments.

In the technique employed by McAuliffe et al. (1948), soil was suspended in water for 4 days to allow the phosphorus in the solid phase to come to equilibrium with solution phase. A trace of ^{32}P was then added in a small volume of water, thereby avoiding any substantial net movement of phosphorus either to or from the solid phase during the subsequent period of equilibration. The exchange that takes place between solution phase ^{32}P and solid phase ^{31}P may be represented by the equation of McAuliffe et al., (1948):

$$^{32}P\ (\text{solution}) + {}^{31}P\ (\text{solid}) \rightleftharpoons {}^{32}P\ (\text{solid}) + {}^{31}P\ (\text{solution})$$

At equilibrium:

$$\frac{^{32}P\ (\text{Solid})}{^{32}P\ (\text{solution})} = \frac{^{31}P\ (\text{solid})}{^{31}P\ (\text{solution})}$$

Therefore ^{31}P (Solid) $= \dfrac{^{32}P\ (\text{Solid}) \times {}^{31}P\ (\text{solution})}{^{32}P\ (\text{Solution})}$

Thus the isotopically exchangeable phosphorus of the soil (^{31}P solid) can be estimated by determining the phosphorus level in solution (^{31}P solution) and the amount of ^{32}P left in solution (^{32}P solution). Since the amount of ^{32}P added is known, the amount of ^{32}P on the solid (^{32}P solid) can be calculated by difference.

Russell et al. (1954) and Fried (1957) suggested that instead of using carrier-free ^{32}P, a solution of sodium, potassium or calcium orthophosphate tagged with ^{32}P can be used. They indicated that the technique is relatively independent of the amount of phosphorus added in the equilibrating solution. When the amount of carrier-phosphate added is appreciable, isotopic dilution calculations should be made using the formula :

$$^{31}P\ (\text{solid}) = {}^{31}P\ (\text{added}) \times \frac{1 - y}{y}$$

$$\text{where } y = \frac{\text{specific activity of the solution at time of sampling}}{\text{specific activity of the added phosphorus}}$$

The ^{32}P exchangeable soil phosphorus determined by this concept was referred to as Pe by Wiklander (1950). The notation given for the phosphate estimated by isotopic exchange by Russell et al. (1954) was E_t (E for exchange and 't' for time of exchange) which in later publications they referred to simply as E. Various other investigators (Talibudeen 1957, 1958; Seatz, 1954; Amer et al., 1955; Arambarri and Talibudeen, 1959a, b, c; Rennie and McKercher, 1959; Amer, 1962; Fife, 1962 and Fried and Broeshart, 1967) have used this procedure for determining the surface or exchangeable phosphorus in soil.

Kinetic studies of the isotopic exchange of phosphate between the soil surface and the soil solution by McAuliffe et al. (1948), Wiklander (1950), Russell et al. (1954) and Talibudeen (1957, 1958) suggest that, in general, two distinct sets of reactions are involved which consist of rapid and slow rate-forming processes. These workers proposed that only the rapid processes contributed to the surface phosphorus value and therefore the time of equilibration 't' should be selected so that the contribution of the slow rate-forming processes is negligible. McAuliffe et al. (1948) shook 5 g of soil in 25 ml distilled water for 4 days, tagged the solution with 1 ml of carrier-free ^{32}P and determined the radioactivity in solution at various times. They found that the surface phosphorus estimated increased logarithmically with respect to time till an equilibration period of 20 hours, after which the rate of increase was slow and linear. They observed that if perfect equilibrium is established between solid-phase phosphate ions and the phosphate ions of the solution phase within this period of 20 hours, the curve plotted for surface phosphate with respect to time should be flat after 20 hours. The continued increase of the estimated surface phosphate after this time was understood as a demonstration of the existence of phosphate ions of lower exchangeability in the solid phase.

Wiklander (1950) treated soil with an orthophosphate solution tagged with ^{32}P instead of carrier-free ^{32}P, the solution phase being sampled at various times to determine its specific activity. The surface phosphorus was calculated taking account of phosphate added in the form of carrier. He concluded that the isotopic exchange was governed by the law of mass action, and that, in general, the logarithm of the exchange constant approached the equilibrium value of unity logarithmically with respect to time.

Seatz (1954) studied the phosphate activity measurements in soils by treating 1 g soil with 10 ml water for 4 days and then added 1 ml carrier-free ^{32}P. The suspension was shaken intermittently and the radioactivity in the solution was measured at various time intervals up to 7 days. The fractional activity in the solid was plotted against the logarithm of time. The curve obtained revealed two inflexion points after 1 and 36 hours which were assumed to be associated with phosphate fraction of varying abilities to dissociate. He observed that the curves indicated that equilibrium or near-equilibrium was not attained for most soils even after 7 days, suggesting the difficulty of calculating an equilibrium value for labile phosphorus in the soil.

Russell et al. (1954) shook 10 g soil with 200 ml of solution containing 5 mg labelled orthophosphate and determined the ^{31}P and ^{32}P contents at various times. For the two soils used, they showed that isotopic equilibrium was not attained even after 20 days in one case and 50 days in the other.

From the observations made by many workers, it can be appreciated that in isotope exchange of phosphates in soil perfect equilibrium between added ^{32}P and the surface phosphate is not readily established within any reasonable period of equilibration, probably due to the gradual diffusion of phosphate ions in the solid inorganic phosphate and/or due to exchange involving phosphate ions other than 'true surface phosphate'. However, there is agreement among the investigators that the isotopic exchange of phosphate in soil comprises rapid exchange as well as slow exchange processes, and only the rapid processes contribute to the true surface phosphorus value.

The solid (i.e. surface) phosphorus in exchange with solution-phase phosphorus includes the solid phases of aluminium phosphate, iron phosphate, and calcium phosphate. The occluded phosphate does not take part in the exchange reaction, since it is coated by iron oxide (Chu and Chang, 1966).

Chu and Chang (1966) studied the surface activity of inorganic soil phosphorus fractions of seven soil samples in Taiwan, using the equation of McAuliffe et al.,(1948). The samples included latosols and alluvial soils of a wide pH range.

They evaluated the specific surface activity of the respective phosphate species, that is, the percent of surface phosphate to the total phosphate of the respective species, using the following equations:

$$\text{specific activity of surface aluminium phosphate} = \frac{\text{surface aluminium phosphate (ppm)}}{\text{total aluminium phosphate (ppm)}} \times 100$$

$$\text{specific activity of surface iron phosphate} = \frac{\text{surface iron phosphate (ppm)}}{\text{total iron phosphate (ppm)}} \times 100$$

$$\text{specific activity of surface calcium phosphate} = \frac{\text{surface calcium phosphate (ppm)}}{\text{total calcium phosphate (ppm)}} \times 100$$

Chu and Chang (1966) found that surface aluminium and iron phosphates of these soils were much greater than surface calcium phosphate. They observed that the specific surface activity of these phosphate species follows the decreasing order of aluminium phosphate, iron phosphate, and calcium phosphate. They also found that although the total amount of calcium phosphate in calcareous soils is very large, its specific surface activity is extremely low. They explained the phenomena by the distribution of the various inorganic phosphate species in the different particle separates of soils. They noted that aluminium and iron phosphates are more concentrating in the clay, while calcium phosphate is more concentrating in the sand and silt, particularly in the less-weathered calcareous alluvial soils.

Rotini and El-Nennah (1971-72) evaluated the relative availability of inorganic phosphorus fractions in eight Italian soil samples using isotopic exchange and solubility criteria. They claimed that the isotopic exchange studies indicated that surface iron phosphate was predominant in all the soils and that there was no simple or direct relationship between the surface P-fractions and their respective quantity of total phosphorus.

In all the soils, the specific surface activity of the various fractions, that they believed controlled their availability to plants, ranked in the order:

Al-P > Fe-P > Ca-P. They noted that the lowest specific surface activity of Ca-P was in the calcareous samples.

CHAPTER III

MATERIALS AND METHODS

3.1 Soil Sampling and Sample Preparation

The first set of soil samples was taken from a plot of coffee planted before 1920, a level area of good soil depth. A manurial trial on this plot was started in 1950 and stopped in 1969. (Spacing of the trees is 10 ft. by 10 ft. The plot is unshaded). The object of the trial was to investigate the response of coffee to high rates of application of nitrogenous fertilizer, phosphatic fertilizer and cattle manure. The layout is two replications of a 2^3 factorial design. Each plot consists of one row of ten trees.

Over the first 12 years nitrogen increased the coffee yield significantly but the cattle manure and phosphate treatments had no significant effect. Over the seven year period 1962-68 there were no significant differences between treatments in their effect on the average yield of clean coffee, but there were significant interactions between treatments in their effect on the yield of Grade 'A' coffee. Cattle manure interacted negatively with mulch (not quite significant) and with phosphate but positively with nitrogen. (Coffee Research Foundation, Kenya, Results of Field Experiments - 1968/69).

Treatments

Nitrogen

- N No nitrogen

+ N 102 kg N per hectare per annum in two applications, April and May.

Nitrogen was applied as ammonium sulphate 1950-56, as urea 1957-59 and as ammonium nitrate 1960-69.

Phosphate

- P No phosphate

+ P 102 kg citric-soluble P_2O_5 per hectare, applied before the Long Rains in March.

Phosphate was applied as double superphosphate from 1950-56 and as basic slag from 1957-69.

Cattle manure

- C No manure

+ C 4-20 litre tins of composted cattle manure per tree applied in March.

Since March 1969 no further applications of basic slag, composted cattle manure and mulch were made but the nitrogen treatment was continued at double the rate, i.e., 204 kg N per hectare.

Sampling of soil

In order to ensure a composite sample that would be representative of the volume sampled, forty cores were taken from each plot. Four cores were randomly taken around each tree, each at a distance of 50 cm from the base of the stem, using a soil auger. Adjacent distances between the cores were kept approximately equal as much as possible. The topsoil was taken at 0-15 cm depth and the subsoil at 15-30 cm depth.

All the samples were air-dried in small cartons, ground in a mortar with a pestle and passed through 2 mm and 0.5 mm sieves successively. The respective samples were thoroughly mixed before taking sub-samples for analysis.

The second set of soil samples was taken from a soil profile, a pit on the Research Station measuring 3 ft x 6 ft. and 20 ft. deep. A site had been chosen on the basis that it had not been cultivated for a considerable period and had a low degree of erosion and surface drainage. Soil samples were taken, starting from the bottom of one wall, at intervals of 50 cm. The intervals were narrowed at the top, the surface horizon sampled being 0-8 cm.

The third set of soil samples was taken from an irrigation trial plot which had never received phosphate fertilizer. The object of the trial was to determine the effect of the various recommended cultural practices and the interactions between them. Bulk samples were taken from the irrigation trial in order to suffice for pot culture seedling studies.

The plots from which the first and third samples were taken are as follows:-

Plot 11 (1) : A control plot - no P.
Plot 27 (1) : A control plot - no P.
Plot 4 P : Received phosphate.
Plot 19 P : Received phosphate.
Plot 9 CP : Received cattle manure and phosphate.

Plot 31 CP : Received cattle manure and phosphate

Plot 14 PM : Received phosphate and mulch, napier grass

Plot 29 PM : Received phosphate and mulch, napier grass

Plot 14 : Irrigation trial plot.

3.2 Laboratory Determination of Phosphorus

3.2.1 Total Phosphorus: Total phosphorus was determined by perchloric acid digestion as outlined by Jackson (1958). A 1-g sample of soil was weighed and transferred to a 100 ml conical flask. Then 15 ml of 60 per cent $HClO_4$ was added and the digestion was carried out at about 130°C. in a fume cupboard. A funnel was used to reflux the $HClO_4$ during the digestion in the flask.

When the digestion was completed, the flask was cooled and 25 ml of distilled water added; the solution was transferred through a filter to a 100 ml volumetric flask and volume made to the mark. The phosphorus in the extract was determined by development of the molybdenum blue colour.

3.2.2 Inorganic Phosphorus Fractions: These were determined by the method of Chang and Jackson (1957).

(i) Aluminium Phosphate:

A 0.5 g sample of soil was placed in a 50 ml centrifuge tube and extracted with 25 ml of 1N NH_4Cl for 30 minutes on a shaking machine. The suspension was centrifuged and the supernatant solution discarded. To the NH_4-soil in the centrifuge tube, 25 ml of neutral 0.5 N NH_4F was added and the suspension extracted on a shaking machine for 1 hour. The suspension was centrifuged and the clear supernatant solution was decanted for the determination of phosphorus. Phosphorus was determined colorimetrically in an aliquot of the extract by Jackson's (1958) method II in a chloromolybdic acid system. 0.8 M boric acid was used to reduce interference from fluoride ions in the extract.

(ii) Iron Phosphate:

The soil sample saved after the extraction of aluminium phosphate was washed twice with 12.5 ml portions of saturated NaCl solution. It was then extracted with 25 ml of 0.1 N NaOH on a shaking machine for 17 hours. The soil suspension was centrifuged and the supernatant decanted into another centrifuge tube. Since the extract was usually highly coloured with organic matter, 1 ml of 2N H_2SO_4 and a few drops of concentrated H_2SO_4 were added to flocculate the organic colloids. The suspension was then centrifuged and the clear solution collected.

Phosphorus was determined colorimetrically in an aliquot of the clear extract by Jackson's (1958) method I in a sulphomolybdic acid system.

(iii) Calcium Phosphate:

The soil sample saved after the extraction of iron phosphate was washed twice with 12.5 ml portions of saturated NaCl solution. It was then extracted with 25 ml of 0.5 N H_2SO_4 for one hour on a shaking machine. The suspension was centrifuged and the supernatant solution decanted. An aliquot of the extract was taken for determination of phosphorus as for iron phosphate.

(iv) Reductant Soluble Iron Phosphate:

The soil sample saved after the extraction of calcium phosphate was washed twice with 12.5 ml portions of saturated NaCl solution. It was then suspended in 20 ml of 0.3M sodium citrate solution and then 0.5 g of solid sodium dithionite ($Na_2S_2O_4$) was added. The suspension was heated in a water bath at 80-90°C. with constant stirring for 15 minutes. The supernatant solution after centrifugation was collected in a 50 ml volumetric flask. The soil was washed twice with 12.5 ml portions of saturated NaCl solution, the washings being combined with the extract in the 50 ml flask.

The solution in the flask was made up to volume. A 2 ml aliquot of this solution was oxidized with 30 per cent hydrogen peroxide. After oxidation phosphorus was determined as iron phosphate.

(v) Occluded Aluminium-Iron Phosphate:

The soil residue saved after the extraction of reductant soluble iron phosphate was extracted with 25 ml of 0.1 N NaOH on a shaking machine for 17 hours. The phosphorus in the solution was determined in the same way as iron phosphate.

3.2.3 Organic Phosphorus: Organic phosphorus was determined by the method of Legg and Black (1955). A 0.5 -g sample of soil was placed in a beaker and ignited at 240°C for 1 hour. The ignited sample was transferred to a 50 ml centrifuge tube. Each of the samples in the tubes was extracted with 4 ml of concentrated HCl on a steam plate for 10 minutes, the final temperature of the solution being about 70°C. Additional 4 ml of concentrated HCl was added to the tubes, after they were removed from the steam plate, and allowed to stand at room temperature for 1 hour. 20 ml of water was added and the suspension mixed. The suspensions were centrifuged, the extracts poured into 100 ml volumetric flasks and made to volume. The inorganic phosphorus was immediately determined in these solutions in a chloromolybdic acid system.

The difference in content of inorganic P found in the extracts of the ignited and nonignited samples was taken as an estimate of the content of organic P in the soil.

3.2.4 Available Phosphorus: Available phosphorus was determined by the method of Olsen et al. (1954) as outlined by Black et al. (1965). A 5-g sample of soil was extracted with 1 teaspoon of carbon black and 100 ml of 0.5 M $NaHCO_3$ (pH 8.5) for 30 minutes in a shaking machine. The suspension was filtered and the phosphorus in the extract colorimetrically determined in a chloromolybdic acid system.

3.2.5 Fixation of Applied Water Soluble Phosphorus

A 5 ml aliquot of a 400 ppm standardized solution of potassium dihydrogen phosphate (KH_2PO_4) was added to a 10 g soil sample in a 250 ml beaker to give 200 micrograms of phosphorus per gram of soil. The soil was allowed to come to dryness at room temperature over a three day span and then fractionated for phosphorus. Another set of the same soils was similarly treated but left to stand at room temperature for thirty days. During that period they were kept approximately at field capacity by periodic watering and finally allowed to come to dryness by the end of the thirty days; the soils were then fractionated for phosphorus.

Water soluble (saloid-bound), aluminium, iron and calcium phosphate fractions were extracted with 1N NH_4Cl, 0.5 N NH_4F, 0.1 N NaOH, 0.5 N H_2SO_4, respectively.

The phosphorus fixed was taken as the difference between the concentrations of phosphorus added to the soil and the phosphorus recovered as water soluble after the three-and thirty-day periods.

3.2.6 Surface Activity of Inorganic Phosphorus Fractions

Some of the soils which had been previously characterised for P-fractions by chemical analysis were used for this study. The method adopted for this investigation was that of Chu and Chang (1966), using ^{32}P. The quantities of surface aluminium, iron and calcium phosphate involved in exchange with inorganic orthophosphate in the solution phase were estimated by the following procedure. 0.5 g of soil was suspended in 25 ml of water in a centrifuge tube for 1 day to allow the phosphate in the solid phase to come to equilibrium with the solution phase. 1 ml of carrier-free ^{32}P solution was added into the soil suspension and the equilibration continued for 2 days, then the solution was analyzed for its total content of P by vanadomolybdophosphoric yellow colour method (Jackson, 1958) and ^{32}P in solution by a Geiger-Muller counter. The latter determination was done by evaporating to dryness an aliquot of the radioactive solution on a planchet using an infra-red lamp and taking the counts. These are designated as P 31 and P 32 solution in equations (1), (2) and (3) below. The phosphorus of the soil in the tube was fractionated using the method of Chang and Jackson (1957). The radioactivity of each extract was counted with the Geiger-Muller counter. These are designated as P 32 surface of the respective species of phosphates in equation (1), (2) and (3). With all the values on the right side of the equations determined, the surface P on the left side of the equation was calculated.

The equilibrium (referred to above) taking place between solution phase ^{32}P and solid-phase ^{32}P may be represented by the equation of McAuliffe et al. (1948).

$$\text{P 31 surface} = \frac{\text{P 32 surface} \times \text{P 31 solution}}{\text{P 32 solution}}$$

Since

$$\text{P 31 surface} = \text{Al-P 31 surface} + \text{Fe-P 31 surface} + \text{Ca-P 31 surface.}$$

$$\text{P 32 surface} = \text{Al-P 32 surface} + \text{Fe-P 32 surface} + \text{Ca-P 32 surface.}$$

When the foregoing equation is rearranged it can be represented as follows:

$$\text{P 31 surface} = (\text{Al-P 32 surface} + \text{Fe-P 32 surface} + \text{Ca-P 32 surface}) \times \frac{\text{P 31 solution}}{\text{P 32 solution}}$$

Since

$$\frac{\text{Al-P 32 surface}}{\text{Al-P 31 surface}} = \frac{\text{Fe-P 32 surface}}{\text{Fe-P 31 surface}} = \frac{\text{Ca-P 32 surface}}{\text{Ca-P 31 surface}}$$

Therefore

$$\text{Al-P 31 surface} = \text{Al-P 32 surface} \times \frac{\text{P 31 solution}}{\text{P 32 solution}} \quad (1)$$

$$\text{Fe-P 31 surface} = \text{Fe-P 32 surface} \times \frac{\text{P 31 solution}}{\text{P 32 solution}} \quad (2)$$

$$\text{Ca-P 31 surface} = \text{Ca-P 32 surface} \times \frac{\text{P 31 solution}}{\text{P 32 solution}} \quad (3)$$

To evaluate the specific surface activity of the respective phosphate fractions, that is, the per cent of surface phosphate to the total phosphate of the respective fractions, the following equations were used for calculation.

Specific activity of surface aluminium phosphate =

$$\frac{\text{surface aluminium phosphate (ppm)}}{\text{total aluminium phosphate (ppm)}} \times 100 \quad (4)$$

Specific activity of surface iron phosphate =

$$\frac{\text{surface iron phosphate (ppm)}}{\text{total iron phosphate (ppm)}} \times 100 \qquad (5)$$

Specific activity of surface calcium phosphate =

$$\frac{\text{surface calcium phosphate (ppm)}}{\text{total calcium phosphate (ppm)}} \times 100 \qquad (6)$$

Background correction: All the count rates of ^{32}P solution determined on the Geiger-Muller counter were corrected for the background count rate registered on the counter. The latter could have come from such varied sources as cosmic radiation, natural radioactivity in the vicinity, artificial radioactivity (fallout), and thermal or other circuit noise. The gross sample count rate (m_g) always includes some background count rate (m_b). The net observed counting rate (m_o) due to sample activity alone was thus

$$m_o = m_g - m_b \qquad (7)$$

Decay correction: After the background correction of all the counts, the reduction of radioactivity of all the samples due to radioactive decay was corrected using the data for ^{32}P (Wang and Willis, 1965).

3.3 Laboratory Determinations of Soil Properties

3.3.1 Mechanical Analysis: The particle size distribution of soil samples was determined by the pipette method.

3.3.2 Soil Reaction (pH): This was determined electrometrically by means of the glass electrode according to the procedure outlined by Jackson (1958).

3.3.3 Cation Exchange Capacity and Exchangeable Cations

(a) The cation exchange capacity was determined by the neutral normal ammonium acetate method. The adsorbed ammonium was displaced by distillation with magnesium oxide (Jackson, 1958).

(b) Exchangeable calcium, magnesium, potassium, sodium and manganese were determined from normal ammonium acetate leachate directly by flame emission, as outlined by Jackson (1958), using Unicam SP90A Atomic Absorption Spectrophotometer.

(c) Total Exchangeable Metallic Cations were determined by adding together exchangeable calcium, magnesium, potassium, sodium and manganese. Per cent base saturation of the soil was calculated as follows:

$$\% \text{ saturation} = \frac{S}{T} \times 100$$

where S = total exchangeable metallic cations as m.e./100 g of soil and

T = cation exchange capacity as m.e./100 g of soil.

(d) Exchangeable aluminium was extracted from soil with normal KCl solution as outlined by Black et al. (1965). The exchangeable aluminium was determined by the aluminon method of Chenery (1955).

3.3.4 Organic Carbon and Total Nitrogen

(a) The Organic Carbon was determined by the Walkley - Black method as outlined by Jackson (1958). The organic matter was oxidized by chromic acid in the presence of excess H_2SO_4, the excess of standard chromic acid being back titrated with a ferrous solution. For "correction" of % carbon, assuming that recovery was 77 per cent as found by Walkley, the results were multiplied by 100/77. The percentage of organic matter was calculated by multiplying the "corrected" percentage of organic carbon by the conventional factor of 1.72 (58% C occurs in soil organic matter).

(b) Total Nitrogen was determined by the Kjeldhal method as outlined by Jackson (1958).

3.4 Pot - Culture Seedling Studies

Some of the soils which had been previously characterised for P fractions and surface activity were used for the experiment. In every experimental pot 600 g of soil (2 mm sieved) was diluted thoroughly with 600 g of sand (2 mm sieved) which had been washed successively with dilute acid, dilute alkali and water. The mixture in the pots (except the controls) were respectively equilibrated with an orthophosphate (KH_2PO_4) solution tagged with ^{32}P by thoroughly mixing and allowing to equilibrate for three days.

At the end of the three-day equilibration period, sixty barley seeds were planted at a depth of 1 cm in each pot. To each of the pots nutrient solutions containing nitrogen, potassium, magnesium, calcium and sulphur were added. Periodic nutrient application was maintained throughout the three weeks of the experiment and the moisture conditions were kept reasonably constant at about 80 per cent field capacity.

At the end of three weeks seedlings were harvested and the total ^{32}P uptake determined. Known weights of the residual soil were refractionated after harvesting the seedlings and the residual ^{32}P in the various soil-P fractions was determined.

The residual soil which was taken for radiochemical assay and refractionation was separated as much as possible from sand by sieving. The assaying was done on planchets using a Geiger-Muller counter. Known weights of the plant material which had been milled were similarly assayed.

Dead Time Correction for Observed Activity

This correction was necessary for counts higher than about 5000 per 100 sec. ; hence it was not necessarily applicable to the surface activity studies. The calculation used was that outlined by Taylor (1957). It is known that a radiation counting assembly requires a definite time to clear the pulse created by each radiation particle. During this period, other incident radiation is either not detected or not differentiated. The results of this failure to resolve two incident radiation particles that are closely spaced in time is coincidence loss; disintegrations are not evenly spaced in time. The minimum time interval between which two events can be registered is termed the resolving time (or dead time) of the counter. This short interval is usually of the order of 100 microseconds.

The following equation was used for dead time correction:

$$n_t = n_o + n_t n_o t$$

giving

$$n_t = \frac{n_o}{1 - n_o t}$$

whence the true counting rate (n_t) could be calculated from the observed counting rate (n_o). t was the resolving time of the recorder = 167 microseconds.

Self - absorption correction: This was done for the barley seedlings but not for the soil. The procedure adopted was that outlined by Wang and Willis (1965). The correction was found essential for the plant material because it was observed that the radioactivity measurements made on a series of samples of increasing thickness (hence of mass) but of constant specific activity did not increase linearly as was expected. Evidently beta particles from the lower layers of plant samples on the planchets were absorbed to some extent by the overlying sample material. This correction was found to be unnecessary for the soil samples since the weights taken for radioactivity measurements had comparatively small thicknesses so that self-absorption was nil or negligible.

The method for the correction of the self-absorption effect among the counting barley samples involved the use of a self-absorption graph. This involved the preparation and assay of a series of the samples (of constant specific activity), by varying masses (hence thickness). A curve was prepared of the normal specific activity of the samples plotted against the sample mass. Correction factors could then be read from this curve for self-absorption at any sample mass - Fig. 3.

Uptake of Phosphorus

The per cent uptake of ^{32}P by the seedlings from each of the soil-P fractions was calculated. The percent of the total phosphorus in the plant derived from the fertilizer (KH_2PO_4) was also calculated.

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Soil Properties

4.1.1 Mechanical Analysis

Table 1 (a-f) shows the particle size distribution of the plot and the soil profile samples.

Though the profile appeared uniform below the topsoil there are in fact considerable variations between horizons, particularly as regards silt and clay (which are largely reciprocal , that is, horizons with less clay have more silt). In general clay rises to a maximum of over 80% at 50-190 cm but then falls off below this to 40-50% in the next 3 metres (where silt increases to almost as much as, and, in one horizon, more than, the clay) with a further small rise in clay content to about 60% at 540-620 cm. Sand is fairly constant, at only about 3-5% in most horizons, though with odd rises in a few horizons, particularly in the 240-290 cm horizon where it reaches about 23%.

The high clay content of the station soils is clearly related to the nature of the parent rock - a volcanic, Tertiary trachytic lava, which was weathered *in situ*. Trachytes contain as essential minerals an alkali-feldspar — either orthoclose, sanidine or very sodic plagioclase - and a ferro-magnesian mineral which may be a pyroxene, amphibole or dark mica. Along the eastern shoulders of the Rift Valley in southern Kenya (Nairobi - Ruiru areas) all the trachytic lavas are strongly sodic varieties (Williams, 1969). They range from undersaturated phonolitic types containing small amounts of modal nepheline to over-saturated quartz trachytes (pantelleritic trachytes). Aenigmatite, soda-pyroxenes and alkali amphiboles are common. Under conditions of warmth and long-continued leaching under acid conditions, there has been the almost complete decomposition of the original rock minerals with the loss of silica and with accumulation of secondary iron and aluminium compounds; that is, soil weathering towards laterization (Gethin-Jones, 1953).

The texture of the plot samples appears somewhat variable. Slightly over-half the samples have over 50% clay, with three having between 70 and 80%, but some are lower with 4 sampling horizons falling below the 40% limit of clay texture. Since both the plot and soil profile are supposed to be on an area of fairly uniform soils the wide variations in silt/clay ratios of the plot samples are probably a reflection of differing extents of leaching clay downwards to below 30 cm depth.

TABLE Ia

PARTICLE SIZE DISTRIBUTION: PLOT SAMPLES

Plot No.	Sampling Depth (cm)	% Total sand (2000 - 60 µ)*	% Total silt (60 - 2 µ)*	% Total clay (less than 2 µ)*
11(1)	0-15	6.85	30.67	62.48
11(1)	15-30	7.58	36.73	55.69
27(1)	0-15	8.08	28.33	63.59
27(1)	15-30	6.94	24.79	68.27
14	0-15	2.86	16.64	80.50
14	15-30	1.46	19.23	79.31

* µ = micron

TABLE Ib

PARTICLE SIZE DISTRIBUTION: PLOT SAMPLES

Plot No.	Sampling Depth (cm)	% Total sand (2000 - 60 µ)	% Total silt (60 - 2 µ)	% Total clay (less than 2 µ)
4P	0-15	14.54	47.36	38.10
4P	15-30	5.89	19.72	74.39
19P	0-15	12.18	51.69	36.13
19P	15-30	8.40	36.54	55.06
9 CP	0-15	10.00	46.82	43.18
9 CP	15-30	10.73	44.64	44.63

TABLE Ic

PARTICLE SIZE DISTRIBUTION: PLOT SAMPLES

Plot No.	Sampling Depth (cm)	% Total sand (2000 - 60 µ)	% Total silt (60 - 2 µ)	% Total clay (less than 2 µ)
31 CP	0-15	8.83	52.48	38.69
31 CP	15-30	4.43	58.13	37.44
14 PM	0-15	12.08	46.64	41.28
14 PM	15-30	10.15	40.09	49.76
29 PM	0-15	12.38	54.10	33.52
29 PM	15-30	9.28	31.64	59.08

TABLE Id

PARTICLE SIZE DISTRIBUTION: SOIL PROFILE SAMPLES

Sampling Depth (cm)	% Total sand (2000 - 60 µ)	% Total silt (60 - 2 µ)	% Total clay (less than 2 µ)
0-8	4.01	37.61	58.38
8-15	4.57	43.96	51.47
15-30	3.74	26.45	69.81
30-50	4.25	18.74	77.01
50-90	3.13	14.03	82.84
90-140	4.70	13.10	82.20

4.1.2 Soil reaction

Table II (a - q) shows the pH of the soils studied. The pH values of the plots which did not receive any fertilizer treatment or mulch material are lower than those which were fertilized and/or mulched, with those of the control plots (11 and 27) varying between 5.8 and 6.3, and those of the treated plots varying between 6.2 (4P 15 - 30 cm) and 7.2 (29PM 0 - 15 cm). These are pH values in water. The higher reaction of the plots which received phosphate fertilizer as compared with the lower values of the plots which did not, might be accounted for by the alkalinity of basic slag which was applied to the former plots. Moreover the highest pH values of the mulched plots, partly being due to basic slag, are also probably due to reduction of soil acidity by mulching; this effect was observed by Robinson and Hosegood (1965). The acid reaction of plot 14 is most probably due to lack of application of basic material (basic slag), absence of mulch, and progressive removal of bases by intense irrigation (plot 14 is an irrigation trial).

There were appreciable decreases in pH values of all the samples when they were determined in 0.01 M $CaCl_2$ solution. The difference between pH/water and pH/$CaCl_2$ averages about one unit. Measurement of pH in a soil-water suspension is influenced by the presence of soluble salts. Use of a salt such as 0.01 M KCl or Ca Cl_2 tends to mask the variability of pH caused by differences in the salt concentration of the soil solution and gives a more precise estimate of the acidity status of the soil than that measured in a soil-water suspension. The concentration of soluble salts which can influence measurement of pH in a soil-water suspension is assumed to be negligible with respect to the amount of salt added in the solution.

The top horizons of the soil profile are more acidic than those below them, ranging between 4.9 (in the 30-50 cm horizon) and 5.5 (in the 0-15 cm horizon). From the 30-50 cm horizon, the pH progressively increases down the profile to a maximum value of 8.0 in the 590-620 cm horizon. The increase in pH with increasing depth is greater in the horizons between 90 and 340 cm - depths than in the horizons below, where the pH is fairly constant at about pH 7.9.

As in the case of the plot samples there were appreciable decreases in the pH values of all the profile samples when they were determined in 0.01 M $CaCl_2$ solution; the differences averaged about one unit. The general trend of pH/$CaCl_2$ down the profile is similar to that of pH/water except for the lower values of the former.

The average degree of base saturation of plots which received phosphate fertilizer (basic slag) and mulch exceeds 100%, the highest being 109% (14 PM 0-15 and 29 PM 0-15). These figures are considerably higher than those of the untreated plots. The lowest base saturation is 49% (plot 14 0-15). As expected, there is a clear relationship between base saturation and soil pH; the pH increases with

TABLE IIa

CHEMICAL PROPERTIES: PLOT SAMPLES

Plot No. Sampling depth (cm)	11 (1) 0 - 15	11 (1) 15 - 30
pH (soil: water 1:2)	6.3	6.1
pH (soil: 0.01M $CaCl_2$ 1:2)	5.0	5.2
C.E.C.* (m.e/100 g)	32.4	30.0
Exchangeable Cations		
(m.e./100 g)		
Calcium	12.50	12.00
Magnesium	5.33	5.12
Potassium	3.79	3.22
Sodium	0.48	0.48
Manganese	0.84	0.51
Aluminium	0.24	0.14
% Base Saturation	70.80	71.10
% Organic Matter	6.93	5.87
% Carbon	4.03	3.41
% Nitrogen	0.31	0.26
Carbon: Nitrogen Ratio	13.00	13.11

* Cation Exchange capacity.

TABLE IIb

CHEMICAL PROPERTIES: PLOT SAMPLES

Plot No. Sampling depth (cm)	27 (1) 0 - 15	27 (1) 15 - 30
pH (soil:water 1:2)	5.9	5.8
pH (soil:0.01M $CaCl_2$ 1:2)	5.2	5.0
C.E.C. (m.e/100 g)	26.3	22.8
Exchangeable Cations		
(m.e./100 g)		
calcium	12.50	10.50
Magnesium	4.92	4.10
Potassium	3.53	2.71
Sodium	0.52	0.48
Manganese	0.73	0.47
Aluminium	0.17	0.14
% Base Saturation	84.41	80.08
% Organic matter	6.59	5.57
% Carbon	3.83	3.24
% Nitrogen	0.28	0.23
Carbon: Nitrogen Ratio	13.67	14.08

TABLE II c

CHEMICAL PROPERTIES: PLOT SAMPLES

Plot No. Sampling depth (cm)	14 0 - 15	14 15 - 30
pH (soil:water 1:2)	4.8	5.0
pH (soil:0.01M $CaCl_2$ 1:2)	3.9	4.3
C.E.C. (m.e/100 g)	22.6	19.0
Exchangeable Cations		
(m.e./100 g)		
Calcium	7.50	7.00
Magnesium	1.64	2.05
Potassium	1.23	1.02
Sodium	0.21	0.43
Manganese	0.55	0.18
Aluminium	0.43	0.28
% Base Saturation	49.24	56.21
% Organic Matter	5.47	4.49
% Carbon	3.18	2.61
% Nitrogen	0.25	0.19
Carbon:Nitrogen Ratio	12.72	13.73

TABLE IId

CHEMICAL PROPERTIES: PLOT SAMPLES

Plot No Sampling depth (cm)	4 P 0 - 15	4 P 15 - 30
pH (soil:water 1:2)	6.9	6.2
pH (soil:0.01M $CaCl_2$ 1:2)	6.1	5.2
C.E.C. (m.e./100 g)	26.6	22.6
Exchangeable Cations (m.e./100 g)		
Calcium	18.00	12.00
Magnesium	2.87	2.25
Potassium	3.07	2.30
Sodium	0.61	0.43
Manganese	0.22	0.38
aluminium	0.16	0.17
% Base Saturation	93.12	76.81
% Organic Matter	6.23	5.04
% Carbon	3.62	2.93
% Nitrogen	0.29	0.20
Carbon:Nitrogen Ratio	12.48	14.65

TABLE IIe

CHEMICAL PROPERTIES: PLOT SAMPLES

Plot No. Sampling depth (cm)	19 P 0 - 15	19 P 15 - 30
pH (soil:water 1:2)	6.9	6.6
pH (soil:0.01M $CaCl_2$ 1:2)	6.0	5.6
C.E.C. (m.e./100 g)	29.0	26.4
Exchangeable Cations (m.e./100 g)		
Calcium	17.50	14.00
Magnesium	4.30	4.51
Potassium	3.68	3.17
Sodium	0.61	0.91
Manganese	0.13	0.07
Aluminium	0.21	0.31
% Base Saturation	90.41	85.83
% Organic Matter	6.98	5.38
% Carbon	4.06	3.13
% Nitrogen	0.33	0.26
Carbon : Nitrogen Ratio	12.30	12.03

TABLE IIf

CHEMICAL PROPERTIES: PLOT SAMPLES

Plot No. Sampling depth (cm)	9 CP 0 - 15	9 CP 15 - 30
pH (soil:water 1:2)	6.6	6.7
pH (soil:0.01M $CaCl_2$ 1:2)	5.4	5.6
C.E.C. (m.e./100 g)	36.4	34.2
Exchangeable Cations		
(m.e./100 g)		
Calcium	20.50	15.50
Magnesium	6.56	6.15
Potassium	5.37	6.14
Sodium	0.65	0.61
Manganese	0.40	0.29
Aluminium	0.14	0.14
% Base Saturation	91.97	83.88
% Organic Matter	11.08	7.22
% Carbon	6.44	4.20
% Nitrogen	0.49	0.32
Carbon:Nitrogen Ratio	13.14	13.12

TABLE II g

CHEMICAL PROPERTIES: PLOT SAMPLES

Plot No. Sampling depth (cm)	31 CP 0 - 15	31 CP 15 - 30
pH (soil:water 1:2)	6.7	6.7
pH (soil:0.01M $CaCl_2$ 1:2)	5.8	5.8
C.E.C. (m.e./100 g)	34.0	32.0
Exchangeable Cations (m.e./100 g)		
Calcium	21.00	17.00
Magnesium	7.38	6.15
Potassium	5.12	5.37
Sodium	0.74	0.61
Manganese	0.25	0.15
Aluminium	0.10	0.21
% Base Saturation	101.44	91.50
% Organic Matter	10.65	7.52
% Carbon	6.19	4.37
% Nitrogen	0.50	0.35
Carbon:Nitrogen Ratio	12.38	12.48

TABLE IIh

CHEMICAL PROPERTIES: PLOT SAMPLES

Plot No. Sampling depth (cm)	14 PM 0 - 15	14 PM 15 - 30
pH (soil:water 1:2)	7.1	6.6
pH (soil:0.01M $CaCl_2$ 1:2)	6.3	5.8
C.E.C. (m.e./100 g)	28.8	24.0
Exchangeable Cations (m.e./100 g)		
Calcium	21.00	14.00
Magnesium	5.74	3.48
Potassium	3.94	4.60
Sodium	0.56	0.39
Manganese	0.20	0.16
Aluminium	0.17	0.17
% Base Saturation	109.16	94.29
% Organic Matter	7.59	5.50
% Carbon	4.41	3.20
% Nitrogen	0.33	0.22
Carbon:Nitrogen Ratio	13.36	14.54

TABLE IIi

CHEMICAL PROPERTIES: PLOT SAMPLES

Plot No. Sampling depth (cm)	29 PM 0 - 15	29 PM 15 - 30
pH (soil:water 1:2)	7.2	6.9
pH (soil:0.01M $CaCl_2$ 1:2)	6.6	6.1
C.E.C. (m.e./100 g)	30.4	25.8
Exchangeable Cations (m.e./100 g)		
Calcium	22.00	16.50
Magnesium	5.74	4.51
Potassium	4.81	5.12
Sodium	0.74	0.61
Manganese	0.09	0.05
Aluminium	0.17	0.16
% Base Saturation	109.80	103.83
% Organic Matter	8.08	6.31
% Carbon	4.70	3.67
% Nitrogen	0.33	0.25
Carbon: Nitrogen Ratio	14.24	14.68

TABLE IIj

CHEMICAL PROPERTIES: SOIL PROFILE SAMPLES

Sampling depth (cm)	0 - 8	8 - 15
pH (soil:water 1:2)	5.5	5.5
pH (soil:0.01M $CaCl_2$ 1:2)	4.8	4.7
C.E.C. (m.e./100 g)	24.6	22.2
Exchangeable Cations (m.e./100 g)		
Calcium	8.90	5.50
Magnesium	5.74	3.93
Potassium	3.02	2.10
Sodium	1.30	0.76
Manganese	0.16	0.07
Aluminium	0.10	0.07
% Base Saturation	77.72	55.67
% Organic Matter	5.28	3.53
% Carbon	3.07	2.05
% Nitrogen	0.43	0.28
Carbon:Nitrogen Ratio	7.13	7.62

TABLE IIk

CHEMICAL PROPERTIES: SOIL PROFILE SAMPLES

Sampling depth (cm)	15 - 30	30 - 50
pH (soil:water 1:2)	5.0	4.9
pH (soil:0.01M $CaCl_2$ 1:2)	4.4	4.0
C.E.C. (m.e./100 g)	20.0	18.6
Exchangeable Cations (m.e./100 g)		
Calcium	4.80	3.90
Magnesium	3.28	2.79
Potassium	1.48	0.87
Sodium	0.63	0.52
Manganese	0.08	0.03
Aluminium	0.10	0.35
% Base Saturation	51.35	43.60
% Organic Matter	2.53	1.77
% Carbon	1.47	1.03
% Nitrogen	0.23	0.13
Carbon:Nitrogen Ratio	6.39	7.92

TABLE II 1

CHEMICAL PROPERTIES: SOIL PROFILE SAMPLES

Sampling depth (cm)	50 - 90	90 - 140
pH (soil:water 1:2)	5.0	5.2
pH (soil:0.01M $CaCl_2$ 1:2)	3.9	4.2
C.E.C. (m.e./100 g)	13.0	13.4
Exchangeable Cations (m.e./100 g)		
Calcium	3.70	3.30
Magnesium	2.54	3.11
Potassium	0.33	0.23
Sodium	0.48	0.39
Manganese	0	0
Aluminium	0.42	0.45
% Base Saturation	54.23	52.46
% Organic Matter	1.15	0.64
% Carbon	0.67	0.37
% Nitrogen	0.12	0.08
Carbon:Nitrogen Ratio	5.38	4.62

TABLE IIm

CHEMICAL PROPERTIES: SOIL PROFILE SAMPLES

Sampling depth (cm)	140 - 190	190 - 240
pH (soil:water 1:2)	5.8	6.2
pH (soil:0.01M $CaCl_2$ 1:2)	4.8	5.3
C.E.C. (m.e./100 g)	13.8	14.4
Exchangeable Cations (m.e./100 g)		
Calcium	3.70	4.80
Magnesium	3.77	4.26
Potassium	0.23	0.20
Sodium	0.52	0.70
Manganese	0	0
Aluminium	0.24	0.05
% Base Saturation	59.56	69.16
% Organic Matter	0.67	0.69
% Carbon	0.39	0.40
% Nitrogen	-	-
Carbon:Nitrogen Ratio	-	-

TABLE IIn

CHEMICAL PROPERTIES: SOIL PROFILE SAMPLES

Sampling depth (cm)	240 - 290	290 - 340
pH (soil:water 1:2)	6.9	7.7
pH (soil:0.01M $CaCl_2$ 1:2)	5.8	6.5
C.E.C. (m.e./100 g)	16.6	17.4
Exchangeable Cations		
(m.e./100 g)		
Calcium	6.10	10.10
Magnesium	4.59	5.08
Potassium	0.18	0.18
Sodium	1.00	1.91
Manganese	0	0
Aluminium	0	0
% Base Saturation	71.50	99.25
% Organic Matter	0.41	0.36
% Carbon	0.24	0.21
% Nitrogen	-	-
Carbon:Nitrogen Ratio	-	-

TABLE IIo

CHEMICAL PROPERTIES: SOIL PROFILE SAMPLES

Sampling depth (cm)	340 - 390	390 - 440
pH (soil:water 1:2)	7.8	7.8
pH (soil:0.01M $CaCl_2$ 1:2)	6.7	6.7
C.E.C. (m.e./100 g)	17.0	16.0
Exchangeable Cations		
(m.e./100 g)		
Calcium	11.10	10.90
Magnesium	5.57	5.90
Potassium	0.18	0.15
Sodium	1.98	1.98
Manganese	0	0
Aluminium	0	0
% Base Saturation	110.76	118.31
% Organic Matter	0.31	0.29
% Carbon	0.18	0.17
% Nitrogen	-	-
Carbon:Nitrogen Ratio	-	-

TABLE IIp

CHEMICAL PROPERTIES: SOIL PROFILE SAMPLES

Sampling depth (cm)	440 - 490	490 - 540
pH (soil:water 1:2)	7.9	7.9
pH (soil:0.01M $CaCl_2$ 1:2)	6.8	6.7
C.E.C. (m.e./100 g)	14.2	13.4
Exchangeable Cations (m.e./100 g)		
Calcium	8.90	7.50
Magnesium	6.23	6,56
Potassium	0.15	0.18
Sodium	1.59	1.26
Manganese	0	0
Aluminium	0	0
% Base Saturation	118.80	115.67
% Organic Matter	0.14	0.14
% Carbon	0.08	0.08
% Nitrogen	-	-
Carbon:Nitrogen Ratio	-	-

TABLE IIq

CHEMICAL PROPERTIES: SOIL PROFILE SAMPLES

Sampling depth (cm)	540 - 590	590 - 620
pH (soil:water 1:2)	7.9	8.0
pH (soil:0.01M $CaCl_2$ 1:2)	6.9	6.8
C.E.C. (m.e./100 g)	13.2	13.0
Exchangeable Cations		
(m.e./100 g)		
Calcium	6.70	6.80
Magnesium	7.05	7.21
Potassium	0.20	0.33
Sodium	1.15	1.24
Manganese	0	0
Aluminium	0	0
% Base Saturation	114.39	119.84
% Organic Matter	0.14	0.03
% Carbon	0.08	0.02
% Nitrogen	-	-
Carbon:Nitrogen Ratio	-	-

an increase in the degree of base saturation. A base saturation of over 100% means that exchangeable cations are in excess of the cation exchange capacity.

The percentage base saturation of the horizons above 290 cm of the profile is almost half that of the lower horizons, the lowest and highest values being 44% and 120% respectively. In general, the pH increases with an increase in the degree of base saturation.

4.1.3 Cation Exchange Capacity and exchangeable cations

Cation exchange capacity and exchangeable cations of the soils are shown in Table II (a-q). In all the plots, cation exchange capacity is higher for the 0-15 cm horizon than for the 15 - 30 cm. The plots which received cattle manure (and phosphate fertilizer) have the highest values of exchange capacity, reaching 36.4 m.e. per 100 g in 9 CP (0-15). The lowest values are in the untreated plots (and plot 4P which received phosphate fertilizer only). However, one of the untreated plots (11) has a considerably high cation exchange capacity, being 32.4 and 30 m.e. per 100 g in the top - and subsoils respectively.

Evidently the magnitude of cation exchange capacity is related to the amount of organic matter in all plots. The higher the content of the latter, the higher is the former, for example, plot 9 CP (0-15) with 11% organic matter has an exchange capacity of 36.4 m.e. per 100 g;

plot 31 CP (0-15) with approximately 11% organic matter has an exchange capacity of 34.0 m.e. per 100 g; plot 14 (0-15) with about 5% organic matter has an exchange capacity of 22.6 m.e. per 100 g, and 14 (15-30) with about 4% organic matter has an exchange capacity of 19 m.e. per 100 g (the latter values being the lowest, respectively, in the plots). The high cation exchange capacity of the 0-15 cm horizon in comparison with the 15-30 cm horizon is chiefly due to a higher content of organic matter in the topsoil.

The cation exchange capacity of the plot samples does not appear to bear a direct relation to the per cent clay, although the latter must naturally be contributing to the exchange capacity. This indicates that organic matter contributes predominatly to the magnitude of the cation exchange capacity, a smaller percentage being due to the clay content.

Exchangeable calcium and magnesium are markedly low in plot 14 (about 7 and 2 m.e./100 g respectively) which has a low reaction. Exchangeable calcium is highest in the P plots, particularly where cattle manure and phosphate or mulch and phosphate were applied, with values just over 20 m.e. per 100 g. Exchangeable magnesium is highest in the plots where cattle manure and phosphate (basic slag) were applied. In general exchangeable calcium and magnesium are more in the topsoil than in the subsoil. The low levels of exchangeable calcium, magnesium, potassium and sodium in plot 14 are probably due to leaching intensfied by irrigation as was pointed out with regard to percent base saturation.

In general exchangeable potassium is very high, being over 5 m.e. throughout plots 9 and 31 CP. This is unusually high by normal standards and reflects the fact that East African rocks are often high in this element. Soil analyses of comparable plantation samples tend to confirm that much of the Kenya coffee acreage is situated on soils containing adequate quantities of exchangeable potassium. A large proportion of these soils is derived from parent material of volcanic origin. Excessive application of Napier grass mulch, which contains very high levels of potassium, may lead to potassium-induced magnesium deficiency.

Exchangeable sodium occurs fairly uniformly in the plots; exchangeable aluminium is also low and uniform. The part it plays on the exchange complex is quite small; the soils are not acidic enough to contain high concentrations of aluminium. Exchangeable aluminium ranges between 0.10 and 0.43 m.e. (the corresponding pH (in water) being 6.7 and 4.8 respectively). Exchangeable manganese is often uneven in soils and the slight variations in the plots are not unexpected.

The highest cation exchange capacity of the profile samples is that of the topsoil (0-8 cm horizon), being about 25 m.e. per 100 g. In general, the exchange capacity of the top 4 horizons (0-50 cm) is higher than that of any horizon below them; this is apparently due to the amount of organic matter which is considerably higher in the top 4 horizons than in any horizon below them. There is a decreasing trend from the top (24.6 m.e.) to the 50-90 cm horizon (13.0 m.e.)

and then an increase from the 90-140 cm horizon (13.4 m.e.) downwards to the 290-340 cm horizon (17.4 m.e.). Furthermore, the exchange capacity progressively decreases from the 340-390 cm horizon (17.0 m.e.) all the way down to 13.0 m.e. at the bottom of the profile. This parallels an increase in clay.

The trend of cation exchange capacity down the soil profile generally follows the downward decrease in the percentage organic matter content. There is a slight exception to this between the horizons 140-190 cm and 440-490 cm where the exchange capacity is a little higher than the three horizons just above, although the percentage organic matter decreases progressively downwards. The very low percentage organic matter (0.03%) at the bottom of the soil profile affords an opportunity to calculate the apparent cation exchange capacity of clay fraction, since it can be reasonably assumed that this amount of organic matter contributes insignificantly to the exchange capacity of the soil. In view of this 13 m.e. C.E.C. per approximately 58% clay is apparently equivalent to about 22 m.e. C.E.C. per 100 g clay, at the 590-620 cm horizon. The apparent cation exchange capacity of the clay fraction in the 540-590 cm horizon (where percentage organic matter is 0.14) is also about 22 m.e. per 100 g clay. This is not taking into consideration the adsorptive capacity of humus that might be present or of silt which has a much lower adsorptive capacity than clay.

Exchangeable calcium, magnesium, potassium and sodium are all higher in the topsoil than in the subsoil to about

2 metres and this appears to reflect plant action, but below 2 metres calcium, magnesium and, to a lesser extent, sodium, rise again to a maximum at about 4 metres where totals are a little above those in the topsoil. The increase in the lowest horizons might be partly due to leaching down from horizons above, but may also simply reflect the supply of cations from the parent rock. Exchangeable manganese is found in small amounts at the top of the profile and was not detected in the rest of the horizons below; this is also true of exchangeable aluminium. The higher amounts of manganese in the topsoil may be due to plant action. With regard to exchangeable aluminium, it is noticeable that when the pH reached 6.9 (in water) exchangeable aluminium ceased to be detectable: this is usual for a neutral soil.

4.1.4 Organic Carbon and Total Nitrogen

Table II (a-q) shows percentages of organic carbon and total nitrogen. The carbon figures are corrected Walkley Black values. The plot samples show higher percentages of organic matter than the corresponding horizons of the profile soil. The variability of the percentages within the samples of the plot is possibly due to unequal amounts of cattle manure and plant material added and also to their varying degree of decay and ease of incorporation with the soil. The soil profile gives a different but expected pattern of distribution of organic matter and of total nitrogen: the percentage of the former decreases all the way downwards, from 5.2 to 0.03. This phenomenon is undoubtedly due to addition of organic matter mainly at the top.

The differences in C:N ratios between the profile and the plot samples are unusually large. The profile has a surprisingly low C:N ratio in the topsoil, though the decrease with depth is normal. The plots, on the other hand, all have a generally consistently high C:N ratio, irrespective of treatment. These differences might be explained by the following considerations.

Raw organic material of plant residues has a C:N ratio of 20 to 30:1 for plant parts relatively high in nitrogen but as high as up to 90:1 for straw or cellulose rich woody parts (Ahn, 1970). Micro-organisms, on the other hand, have a much higher protein content and C:N ratios which may be as low as 4 to 9:1. Soil humus is derived from both plant and animal residues: lower C:N ratios therefore generally indicate higher microbial populations and more rapid mineralization, whereas the higher (or wider) C:N ratios suggest slower mineralization and a greater content of little-altered plant remains.

The carbon : nitrogen ratio of the profile samples decreases from 30-50 cm horizon to the 90-140 cm horizon (total nitrogen was not determined for the samples below 140 cm). This decrease suggests variability in the constitution of the soil organic matter downwards, a feature which has been observed by others. Russell (1961) partly attributed this apparent fall to the inclusion of ammonium ions held by the clay in a form in which they can only be displaced by treatment with a strong acid. This narrowing of the carbon: nitrogen ratio with depth was also observed by Stevenson (1959) who attributed it to a combination of two factors, one of which he shared with Russell (1961); according to Stevenson (1959), the narrowing was due to: (a) an increase, with depth, in the relative amount of the soil nitrogen as fixed ammonium, and (b) the presence of relatively higher amount of nitrogen - rich constituents in the organic matter of the subsoil as compared with the surface soil.

TABLE III

AVAILABLE PHOSPHORUS DETERMINED BY OLSEN'S METHOD (0.5 M $NaHCO_3$, pH 8.5). AMOUNTS GIVEN IN PPM

PLOT SAMPLES

Plot No.	Sampling depth (cm)	Available P
11 (1)	0 - 15	13.3
11 (1)	15 - 30	11.3
27 (1)	0 - 15	9.3
27 (1)	15 - 30	8.5
4P	0 - 15	26.2
4P	15 - 30	18.0
19 P	0 - 15	19.0
19 P	15 - 30	14.0
9 CP	0 - 15	29.8
9 CP	15 - 30	20.8
31 CP	0 - 15	30.0
31 CP	15 - 30	19.5
14 PM	0 - 15	23.2
14 PM	15 - 30	16.3
29 PM	0 - 15	23.3
29 PM	15 - 30	14.5

4.2 Distribution of Phosphorus in the Soils

The distribution of fractions of inorganic phosphorus of the plot samples is shown in table IV (a-h) and that of the horizons of the soil profile is shown in table V (a-h). The means of different forms of soil phosphorus are shown in table VI (a-e) and VII (a-e). The percentages are shown in table VIII - XI.

Each soil sample was replicated three times (i.e. a, b and c) in the determination of fractions of inorganic phosphorus. The results of the replicated samples are in good agreement indicating thorough mixing of each sample prior to sub-sampling; this good agreement in the results of the replicated samples is also partly due to careful extraction and colorimetric determination procedures.

4.2.1 Total P in plots:

The total phosphorus for the control plots where no phosphate fertilizer was added ranged between 285 and 430 ppm in the two sampling depths whereas, as was expected, plots 4P and 19P which received double superphosphate and basic slag had a higher range of 428 to 974 ppm. The apparent relative increase of total P is greater for 0-15 than 15-30 cm. The difference appears to reflect the phosphate fertilizers added to the latter plots over the years. Plots 9 CP and 31 CP to which were applied cattle manure besides the phosphate fertilizers had an even higher range of total phosphorus: 694 to 1143 ppm in the two sampling depths. The difference between these plots and 4P and 19P is largely attributable to a higher percentage

TABLE IVa

DISTRIBUTION OF FORMS OF INORGANIC PHOSPHORUS (ppm)

PLOT 11 (1)-CONTROL

Sampling depth	0 - 15 cm			15 - 30 cm		
Replicates	a*	b*	c*	a*	b*	c*
Aluminium phosphate	16	18	15	11	13	12
Iron phosphate	65	63	64	26	26	33
Calcium phosphate	17	18	20	6	13	10
Reductant soluble iron phosphate	90	83	83	68	60	70
Occluded aluminium-iron phosphate	63	67	64	48	51	53
Added total inorganic phosphate	251	249	246	159	163	178

* a, b and c = replicated samples; this refers to tables IV and V.

of organic phosphorus in the former, that is, 9 CP and 31 CP. The effect of mulch in contributing to the total phosphorus content of the soil in plots 14 PM and 29 PM is somewhat similar to that of cattle manure. In these plots, however, organic phosphorus is less than in the CP plots, and inorganic phosphorus is more in the 0-15 cm layers.

Table XIV shows the analysis of variance of total phosphorus in the plots. There is a highly significant difference between the amounts in the two sampling depths.

TABLE IVb

DISTRIBUTION OF FORMS OF INORGANIC PHOSPHORUS (ppm)

PLOT 27 (1)-CONTROL

Sampling depth	0 - 15 cm			15 - 30 cm		
Replicates	a	b	c	a	b	c
Aluminium phosphate	20	22	19	13	12	14
Iron phosphate	50	53	46	28	31	38
Calcium phosphate	13	16	11	6	8	8
Reductant soluble iron phosphate	30	28	28	50	60	55
Occluded aluminium-iron phosphate	35	35	38	46	50	49
Added total inorganic phosphate	148	154	142	143	161	164

Limited mobility of phosphate ions in the soil may account for this difference. There is a significant difference between treatments whereas the interaction of the treatments with sampling depths is least significant.

4.2.2 Total P in the profile: There is not much variability in the amounts of total phosphorus down the profile. The decrease from 284 ppm at the surface to 230 ppm in the 30-50 cm horizon is largely accounted for by a decrease in organic phosphorus although there is an increase in total occluded phosphate. The relatively uniform total phosphorus down the

TABLE IVc

DISTRIBUTION OF FORMS OF INORGANIC PHOSPHORUS (ppm)

PLOT 4 P

Sampling depth	0 - 15 cm			15 - 30 cm		
Replicates	a	b	c	a	b	c
Aluminium phosphate	74	80	72	77	80	75
Iron phosphate	265	271	274	150	148	153
Calcium phosphate	226	240	236	59	66	69
Reductant soluble iron phosphate	181	194	194	68	73	63
Occluded aluminium-iron phosphate	63	61	55	48	43	51
Added total inorganic phosphate	809	846	831	402	410	411

profile reinforces the appearance of uniformity of the deep subsoil. Totals are somewhat less than those for the control plots. Total occluded phosphate contributes predominantly to the downward trend of increase in total phosphorus and has been observed by others; Nye and Bertheux (1957) found in some forest and savannah soils of Ghana that insoluble (occluded) phosphate increased with depth.

The amounts of total phosphorus in the soils studied show that they are not too different from what has been observed in

TABLE IVd

DISTRIBUTION OF FORMS OF INORGANIC PHOSPHORUS (ppm)

PLOT 19 P

Sampling depth	0 - 15 cm			15 - 30 cm		
Replicates	a	b	c	a	b	c
Aluminium phosphate	86	91	89	84	88	85
Iron phosphate	239	238	250	98	95	101
Calcium phosphate	165	168	163	44	48	43
Reductant soluble iron phosphate	35	43	33	23	30	20
Occluded aluminium-iron phosphate	69	61	55	56	50	50
Added total inorganic phosphate	594	601	590	305	311	299

other parts of the world. Nye and Bertheux (1957) found a mean of 130 ppm of total phosphorus for surface horizons of some Ghana soils developed on sandstones, a mean of 215 ppm for those developed on sandstones or sandy clays, a mean of 266 ppm for those developed on granite, gneiss or schist and a mean of 509 ppm for those developed from basic igneous or metamorphic rocks - all these values being for the forest region of Ghana. In the fine earth fraction of a Western Nigerian forest soil profile developed from coarse granitic

TABLE IVe

DISTRIBUTION OF FORMS OF INORGANIC PHOSPHORUS (ppm)

PLOT 9 CP

Sampling depth	0 - 15 cm			15 - 30 cm		
Replicates	a	b	c	a	b	c
Aluminium phosphate	154	150	159	98	100	103
Iron phosphate	334	346	346	268	266	266
Calcium phosphate	228	238	243	141	136	136
Reductant soluble iron phosphate	70	60	60	58	50	50
Occluded aluminium-iron phosphate	89	95	100	64	60	75
Added total inorganic phosphate	875	889	908	629	612	630

rocks and coarse gneisses, Bates and Baker (1960) obtained the following concentrations for total phosphorus: 553 ppm (0-2"), 210 ppm (2-7"), 283 ppm (7-12").

An important feature to note in the present study is the high percentage of the total P which is occluded, reinforcing the general view that analysis of total P alone in such soils has little value, and perhaps none in predicting phosphorus availability.

TABLE IVf

DISTRIBUTION OF FORMS OF INORGANIC PHOSPHORUS (ppm)

PLOT 31 CP

Sampling depth	0 - 15 cm			15 - 30 cm		
Replicates	a	b	c	a	b	c
Aluminium phosphate	164	159	166	103	95	99
Iron phosphate	320	309	320	206	199	201
Calcium phosphate	238	237	253	110	116	122
Reductant soluble iron phosphate	88	100	103	50	50	55
Occluded aluminium-iron phosphate	88	75	75	31	35	38
Added total inorganic phosphate	898	880	917	500	495	515

4.2.3 Forms of inorganic P in plots: In the plots, there is considerable variability within each fraction of inorganic phosphorus in the sampling depths. Application of phosphate fertilizer and mulch or cattle manure greatly increased the accumulation of calcium phosphate and aluminium phosphate when compared to the levels of these two fractions in the untreated (control) plots. Although it is true that iron phosphate was also increased by the fertilizer treatments, it is noticeable that the rates of increase were lower than those of calcium and aluminium phosphates since the untreated plots contained

TABLE IVg

DISTRIBUTION OF FORMS OF INORGANIC PHOSPHORUS (ppm)

PLOT 14 PM

Sampling depth	0 - 15 cm			15 - 30 cm		
Replicates	a	b	c	a	b	c
Aluminium phosphate	208	201	208	150	163	160
Iron phosphate	298	285	300	140	148	144
Calcium phosphate	363	357	351	90	95	94
Reductant soluble iron phosphate	73	70	70	35	33	38
Occluded aluminium-iron phosphate	116	115	110	64	70	70
Added total inorganic phosphate	1058	1028	1039	479	509	506

much higher amounts of iron phosphate than the other two fractions. In the PM plots, however, calcium phosphate is much higher than iron and aluminium phosphate in the 0-15 but not in the 15-30 cm sampling layers. Mulch, besides phosphate fertilizers, probably accounts for this difference. Although the treatments might have had some effect on total occluded phosphate (for example this fraction is higher in 31 CP, 9 CP and 14 PM than in the controls) it is interesting to observe that the percentages of this fraction in the untreated plots are much higher than the percentages in the

TABLE IVh

DISTRIBUTION OF FORMS OF INORGANIC PHOSPHORUS (ppm)

PLOT 29 PM

Sampling depth	0 - 15 cm			15 - 30 cm.		
Replicates	a	b	c	a	b	c
Aluminium phosphate	145	150	142	126	133	128
Iron phosphate	248	246	230	149	143	141
Calcium phosphate	459	465	471	180	182	179
Reductant soluble iron phosphate	60	48	50	35	28	28
Occluded aluminium-iron phosphate	58	64	70	58	56	65
Added total inorganic phosphate	970	973	963	548	542	541

fertilized plots. This means that the fertilizer treatments or mulching or both did not have any noticeable effect on the relatively insoluble form. This observation was also made by Dean (1938); he found that the insoluble (occluded) phosphate did not change after over 50 years of fertilization at Rothamsted and Woburn indicating that it is relatively unimportant in problems of phosphate absorption.

TABLE Va

DISTRIBUTION OF FORMS OF INORGANIC PHOSPHORUS (ppm) SOIL PROFILE SAMPLES

Sampling depth	0 - 8 cm			8 - 15 cm		
Replicates	a	b	c	a	b	c
Aluminium phosphate	10	9	10	7	7	8
Iron phosphate	41	43	43	38	36	34
Calcium phosphate	14	13	12	8	10	7
Reductant soluble iron phosphate	44	41	45	51	48	54
Occluded aluminium-iron phosphate	39	39	42	47	51	50
Added total inorganic phosphate	148	145	152	151	152	153

Table XIV (a-d) shows the analysis of variance of aluminium phosphate, iron phosphate, calcium phosphate and total occluded phosphate respectively. There are highly significant differences between the amounts of iron phosphate in the 0-15 and 15-30 cm sampling horizons; the same applies for calcium phosphate in the two horizons. As was mentioned concerning total phosphorus in the two sampling horizons (0-15 and 15-30 cm), these respective differences can be attributed to limited mobility of phosphate ions in the soil. The significant differences

TABLE Vb

DISTRIBUTION OF FORMS OF INORGANIC PHOSPHORUS (ppm)

SOIL PROFILE SAMPLES

Sampling depth	15 - 30 cm			30 - 50 cm		
Replicates	a	b	c	a	b	c
Aluminium phosphate	12	10	10	12	11	10
Iron phosphate	28	29	31	33	31	28
Calcium phosphate	11	10	13	9	9	11
Reductant soluble iron phosphate	56	50	53	54	57	59
Occluded aluminium-iron phosphate	50	55	53	52	55	60
Added total inorganic phosphate	157	154	160	160	163	168

between the concentrations of aluminium phosphate in the two sampling horizons may also be due to limited mobility of phosphate ions in the soil. The fertilizer treatments with or without mulching must have contributed to these differences but had no significant effect on the occluded phosphate.

Considering the 0-30 cm layer of the control plots, the means of the various inorganic phosphate fractions are as follows:

Ca-PO_4	12.0 ppm	Fe-PO_4	43.5 ppm
Al-PO_4	15.3 ppm	Occluded-PO_4	108.8 ppm

These data are graphically shown in Fig. 1.

TABLE Vc

DISTRIBUTION OF FORMS OF INORGANIC PHOSPHORUS (ppm)

SOIL PROFILE SAMPLES

Sampling depth	50 - 90 cm			90 - 140 cm		
Replicates	a	b	c	a	b	c
Aluminium phosphate	11	9	9	12	13	11
Iron phosphate	71	69	73	78	76	81
Calcium phosphate	9	8	10	18	16	16
Reductant soluble iron phosphate	85	79	83	88	87	82
Occluded aluminium-iron phosphate	97	101	103	93	96	99
Added total inorganic phosphate	273	266	278	289	288	289

<u>4.2.4 Inorganic P in the profile</u>: Table VII (a-e) shows the means of inorganic phosphate fractions in the profile samples. The forms of phosphorus as percentages of total phosphorus are presented in table XI (a-e). Considering the 0-30 cm layer, the means of the various inorganic phosphate fractions are as follows:

Ca-PO_4	10.6 ppm
Al-PO_4	9.3 ppm
Fe-PO_4	35.6 ppm
Occluded-PO_4	96.3 ppm

TABLE Vd

DISTRIBUTION OF FORMS OF INORGANIC PHOSPHORUS (ppm)

SOIL PROFILE SAMPLES

Sampling depth	140 - 190 cm			190 - 240 cm		
Replicates	a	b	c	a	b	c
Aluminium phosphate	14	13	15	11	11	13
Iron phosphate	69	70	76	68	66	64
Calcium phosphate	28	25	28	8	9	9
Reductant soluble iron phosphate	99	103	105	98	102	96
Occluded aluminium-iron phosphate	84	81	77	94	90	91
Added total inorganic phosphate	294	292	301	279	278	273

Although the amount of aluminium phosphate is slightly less than that of calcium phosphate, these figures tend to suggest the degree of chemical weathering of the soil - graphically shown in Fig. 1. The change in the ratio of calcium phosphate to aluminium phosphate down the profile suggests that if Chang and Jackson's (1958) weathering sequence is correct there are differences between horizons: calcium phosphate is generally a little higher than aluminium phosphate in the upper horizons but less than it in the deeper parts of the profile.

TABLE Ve

DISTRIBUTION OF FORMS OF INORGANIC PHOSPHORUS (ppm)

SOIL PROFILE SAMPLES

Sampling depth	240 - 290 cm			290 - 340 cm		
Replicates	a	b	c	a	b	c
Aluminium phosphate	12	10	11	13	10	14
Iron phosphate	31	29	28	29	33	28
Calcium phosphate	8	9	8	13	14	13
Reductant soluble iron phosphate	104	111	108	112	107	106
Occluded aluminium-iron phosphate	99	96	102	103	101	100
Added total inorganic phosphate	254	255	257	270	265	261

Chang and Jackson (1958) found that the distribution of soil inorganic phosphorus in soils measured the degree of chemical weathering, the chemical weathering sequence being calcium phosphate, aluminium phosphate, iron phosphate, and occluded phosphate. They found that three horizons: one Chernozem profile, a Dark Brown soil, and the calcareous C_1 horizon of a Grey-Brown Podzolic soil contained 68-95 per cent of their inorganic phosphorus in the form of calcium phosphate, the other forms decreasing exponentially in the sequence.

TABLE Vf

DISTRIBUTION OF FORMS OF INORGANIC PHOSPHORUS (ppm)

SOIL PROFILE SAMPLES

Sampling depth	340 - 390 cm			390 - 440 cm		
Replicates	a	b	c	a	b	c
Aluminium phosphate	23	25	24	15	17	18
Iron phosphate	33	36	33	31	32	34
Calcium phosphate	12	13	11	7	8	8
Reductant soluble iron phosphate	116	113	114	119	124	126
Occluded aluminium-iron phosphate	105	101	109	125	130	128
Added total inorganic phosphate	289	288	291	297	311	314

The inorganic phosphorus of two Latosols, however, increased exponentially in the order calcium phosphate (1%), aluminium phosphate (0-3%), iron phosphate (10-13%), and occluded (reductant soluble) phosphate 66-78%. The Kikuyu Red Loam soil offers an example similar to these two Latosols studied by Chang and Jackson, suggesting that it is strongly weathered. The absence of flooding and water-logging in this soil means that reducing conditions are generally eliminated, thus

TABLE Vg

DISTRIBUTION OF FORMS OF INORGANIC PHOSPHORUS (ppm)

SOIL PROFILE SAMPLES

Sampling depth	440 - 490 cm			490 - 540 cm		
Replicates	a	b	c	a	b	c
Aluminium phosphate	10	11	8	6	8	7
Iron phosphate	29	27	31	29	30	31
Calcium phosphate	6	7	6	5	6	7
Reductant soluble iron phosphate	122	127	121	129	128	134
Occluded aluminium-iron phosphate	119	121	123	123	125	123
Added total inorganic phosphate	286	293	289	292	297	302

allowing for continued presence of high percentages of occluded phosphate. Although even well drained soils can be subject to very temporary reducing conditions when momentarily saturated, this may not affect the soil to a large extent as far as the high percentages of occluded phosphate are concerned.

TABLE Vh

DISTRIBUTION OF FORMS OF INORGANIC PHOSPHORUS (ppm)

SOIL PROFILE SAMPLES

Sampling depth	540 - 590 cm			590 - 620 cm		
Replicates	a	b	c	a	b	c
Aluminium phosphate	11	10	11	10	8	7
Iron phosphate	28	31	33	27	25	26
Calcium phosphate	3	4	4	5	6	6
Reductant soluble iron phosphate	131	128	133	137	132	136
Occluded aluminium-iron phosphate	127	130	127	131	138	130
Added total inorganic phosphate	300	303	308	310	309	305

The highly significant differences in the distribution of the various inorganic phosphorus fractions, that is, aluminium phosphate, iron phosphate, calcium phosphate and occluded phosphate down the profile (table XV(a-d) are probably due to controlling factors which include the activities of the various ions in the soil, in turn reflecting soil pH, age, drainage, and mineralogical nature.

TABLE VIa

MEANS OF FORMS OF SOIL PHOSPHORUS (ppm)

PLOT SAMPLES

Plot No. (controls) Sampling depth (cm)	11 (1) 0 - 15	11 (1) 15-30	27 (1) 0 - 15	27 (1) 15-30
Aluminium phosphate	16	12	20	13
Iron phosphate	64	28	50	32
Calcium phosphate	18	10	13	7
Total occluded phosphate	150	117	65	103
Added total inorganic phosphate	248	167	148	155
Organic phosphorus	175	146	162	140
Total phosphorus	430	317	312	285

4.2.5 Organic P in plots: The percentage distribution of organic phosphorus is less than 50 per cent in all the coffee plots except in one of the controls, where it forms 51.9 per cent of total phosphorus. The low percentages of organic phosphorus in the treated plots is evidently explained by sharp increases of inorganic phosphorus fractions caused by application of the fertilizers. Table XIVe shows the analysis of variance of organic phosphorus in the plots; the variability in its distribution is shown to be due to treatments rather than depths.

TABLE VIb

MEANS OF FORMS OF SOIL PHOSPHORUS (ppm)

PLOT SAMPLES

Plot No. Sampling depth (cm)	4P 0 - 15	4P 15 - 30	19 P 0 - 15	19 P 15 - 30
Aluminium phosphate	75	77	89	86
Iron phosphate	270	150	242	98
Calcium phosphate	234	65	165	45
Total occluded phosphate	250	115	99	76
Added total inorganic phosphate	829	407	595	305
Organic phosphorus	164	117	183	107
Total phosphorus	974	538	795	428

4.2.6 Organic P in the profile: The percentage of organic phosphorus in the profile decreases progressively with depth, the maximum being 44.7 per cent at the surface horizon and the minimum being less than 2.8 per cent below the 390-440 cm horizon; the decline is obviously related to decreasing amounts of organic matter, as was true of organic carbon and total nitrogen. Dormaar and Webster (1963) also found that the total organic phosphorus content decreased with increasing depth in all profiles they studied.

TABLE VIc

MEANS OF FORMS OF SOIL PHOSPHORUS (ppm)

PLOT SAMPLES

Plot No.	9 CP	9 CP	31 CP	31 CP
Sampling depth (cm)	0 - 15	15 - 30	0 - 15	15 - 30
Aluminium phosphate	154	100	163	99
Iron phosphate	342	267	316	202
Calcium phosphate	236	138	243	116
Total occluded phosphate	158	119	176	87
Added total inorganic phosphate	890	624	898	504
Organic phosphorus	274	178	256	179
Total phosphorus	1143	789	1134	694

The importance of organic phosphorus depends on the level of available inorganic phosphate, the lower the latter the more important the former is likely to be. Russell (1961) noted that there are a number of tropical soils in which the major part of the potentially plant available phosphate is in the organic matter in the surface soil, so that if the surface gets washed away by rain, or removed by some other cause, the subsurface soil which now becomes the surface is so low in phosphate, and usually in many other elements as well, that crop growth becomes exceedingly slow unless large amounts of phosphate fertilizer are added.

TABLE VId

MEANS OF FORMS OF SOIL PHOSPHORUS (ppm)

PLOT SAMPLES

Plot No.	14 PM	14 PM	29 PM	29 PM
Sampling depth (cm)	0 - 15	15 - 30	0 - 15	15 - 30
Alumininium phosphate	206	158	146	129
Iron phosphate	294	144	241	144
Calcium phosphate	357	93	465	180
Total occluded phosphate	185	103	117	90
Added total inorganic phosphate	1042	498	969	543
Organic phosphorus	191	101	188	149
Total phosphorus	1208	610	1172	687

Since the soil phosphorus which is of immediate importance in the nutrition of crops comes from the inorganic fraction, the distribution of this fraction in the soils is agriculturally significant; it is widely believed that organic phosphorus assumes importance in plant growth only after it mineralizes. One of the important factors which controls the rates of mineralization of the phosphate in organic matter is the number of times the soil becomes really dry between re-wettings, since drying or heating it and re-wetting it

TABLE VIe

MEANS OF FORMS OF SOIL PHOSPHORUS (ppm)

PLOT SAMPLES

Plot No.	14	14
Sampling depth (cm)	0 - 15	15 - 30
Aluminium phosphate	25	21
Iron phosphate	109	83
Calcium phosphate	20	17
Total occluded phosphate	158	137
Added total inorganic phosphate	312	258
Organic phosphorus	137	98
Total phosphorus	461	365

results in a flush of decomposition of the soil humus. Rates of humus mineralisation following the wetting of a dry soil were studied by Birch (1958, 1959 and 1960). Other factors which influence the rates of mineralization of the phosphate in organic matter include temperature, for the warmer the soil the more rapid the rate of decomposition can be, and any factor which affects the species and numbers of the various microorganisms involved in humus decomposition.

TABLE VIIa

MEANS OF FORMS OF SOIL PHOSPHORUS (ppm)

SOIL PROFILE SAMPLES

Sampling depth (cm)	0 - 8	8 - 15	15 - 30
Aluminium phosphate	10	7	11
Iron phosphate	42	36	29
Calcium phosphate	13	8	11
Total occluded phosphate	83	100	106
Added total inorganic phosphate	148	151	157
Organic phosphorus	127	94	62
Total phosphorus	284	256	233

TABLE VIIb

MEANS OF FORMS OF SOIL PHOSPHORUS (ppm)

SOIL PROFILE SAMPLES

Sampling depth (cm)	30 - 50	50 - 90	90 - 140
Aluminium phosphate	11	10	12
Iron phosphate	31	71	78
Calcium phosphate	10	9	17
Total occluded phosphate	113	182	182
Added total inorganic phosphate	165	272	289
Organic phosphorus	52	33	16
Total phosphorus	230	294	299

TABLE VIIc

MEANS OF FORMS OF SOIL PHOSPHORUS (ppm)

SOIL PROFILE SAMPLES

Sampling depth (cm)	140 - 190	190 - 240	240 - 290
Aluminium phosphate	13	12	11
Iron phosphate	72	66	29
Calcium phosphate	27	9	8
Total occluded phosphate	183	191	207
Added total inorganic phosphate	295	278	255
Organic phosphorus	18	18	14
Total phosphorus	320	292	277

TABLE VIId

MEANS OF FORMS OF SOIL PHOSPHORUS (ppm)

SOIL PROFILE SAMPLES

Sampling depth (cm)	290 - 340	340 - 390	390 - 440
Aluminium phosphate	12	24	17
Iron phosphate	30	34	32
Calcium phosphate	13	12	8
Total occluded phosphate	209	219	251
Added total inorganic phosphate	264	289	308
Organic phosphorus	12	9	9
Total phosphorus	283	302	322

TABLE VIIe

MEANS OF FORMS OF SOIL PHOSPHORUS (ppm)

SOIL PROFILE SAMPLES

Sampling depth (cm)	440-490	490-540	540-590	590-620
Aluminium phosphate	10	7	11	8
Iron phosphate	29	30	31	26
Calcium phosphate	6	6	4	6
Total occluded phosphate	244	254	259	268
Added total inorganic phosphate	289	297	305	308
Organic phosphorus	Trace	Trace	Trace	Trace
Total phosphorus	292	290	309	304

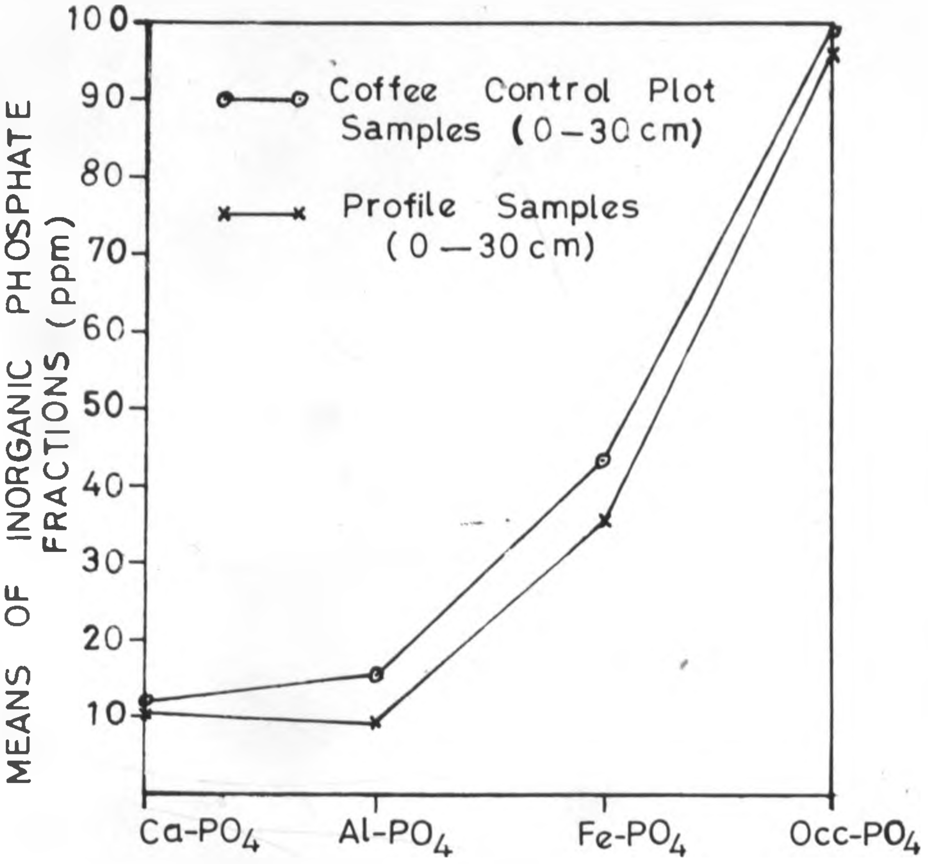


Fig. 1 — THE MEANS OF THE CHEMICAL FORMS OF INORGANIC SOIL PHOSPHATE PLOTTED AS A CHEMICAL WEATHERING SEQUENCE.

TABLE VIIIa

FORMS OF INORGANIC PHOSPHORUS AS PERCENTAGES OF ADDED TOTAL INORGANIC PHOSPHORUS

PLOT SAMPLES

Plot No. (controls) Sampling depth (cm)	11(1) 0-15	11(1) 15-30	27(1) 0-15	27(1) 15-30
Aluminium phosphate	6.5	7.2	13.5	8.4
Iron phosphate	25.8	16.8	33.8	20.6
Calcium phosphate	7.3	6.0	8.8	4.5
Total occluded phosphate	60.4	70.0	43.9	66.5

TABLE VIIIb

FORMS OF INORGANIC PHOSPHORUS AS PERCENTAGES OF ADDED TOTAL INORGANIC PHOSPHORUS

PLOT SAMPLES

Plot No. Sampling depth (cm)	4 P 0-15	4 P 15-30	19 P 0-15	19 P 15-30
Aluminium phosphate	9.0	18.9	15.0	28.2
Iron phosphate	32.6	36.9	40.7	32.1
Calcium phosphate	28.2	16.0	27.7	14.8
Total occluded phosphate	30.2	28.2	16.6	24.9

TABLE VIIIc

FORMS OF INORGANIC PHOSPHORUS AS PERCENTAGES OF ADDED TOTAL INORGANIC PHOSPHORUS

PLOT SAMPLES

Plot No. Sampling depth (cm)	9 CP 0-15	9 CP 15-30	31 CP 0-15	31 CP 15-30
Aluminium phosphate	17.3	16.0	18.2	19.6
Iron phosphate	38.4	42.8	35.2	40.1
Calcium phosphate	26.5	22.1	27.0	23.0
Total occluded phosphate	17.8	19.1	19.6	17.3

TABLE VIIId

FORMS OF INORGANIC PHOSPHORUS AS PERCENTAGES OF ADDED TOTAL INORGANIC PHOSPHORUS

PLOT SAMPLES

Plot No. Sampling depth (cm)	14 PM 0-15	14 PM 15-30	29 PM 0-15	29 PM 15-30
Aluminium phosphate	19.8	31.7	15.1	23.8
Iron phosphate	28.2	28.9	24.9	26.5
Calcium phosphate	34.3	18.7	48.0	33.1
Total occluded phosphate	17.7	20.7	12.0	16.6

TABLE IXa

FORMS OF INORGANIC PHOSPHORUS AS PERCENTAGES OF ADDED TOTAL INORGANIC PHOSPHORUS SOIL PROFILE SAMPLES

Sampling depth (cm)	0 - 8	8 - 15	15 - 30
Aluminium phosphate	6.8	4.6	7.0
Iron phosphate	28.4	23.8	18.5
Calcium phosphate	8.8	5.3	7.0
Total occluded phosphate	56.0	66.2	67.5

TABLE IXb

FORMS OF INORGANIC PHOSPHORUS AS PERCENTAGES OF ADDED TOTAL INORGANIC PHOSPHORUS SOIL PROFILE SAMPLES

Sampling depth (cm)	30 - 50	50 - 90	90 - 140
Aluminium phosphate	6.7	3.7	4.2
Iron phosphate	18.8	26.1	27.0
Calcium phosphate	6.1	3.3	5.9
Total occluded phosphate	68.4	66.9	62.9

TABLE IXc

FORMS OF INORGANIC PHOSPHORUS AS PERCENTAGES OF ADDED TOTAL INORGANIC PHOSPHORUS

SOIL PROFILE SAMPLES

Sampling depth (cm)	140-190	190-240	240-290
Aluminium phosphate	4.4.	4.3	4.3
Iron phosphate	24.4	23.7	11.3
Calcium phosphate	9.2	3.2	3.1
Total occluded phosphate	62.0	68.7	81.2

TABLE IXd

FORMS OF INORGANIC PHOSPHORUS AS PERCENTAGES OF ADDED TOTAL INORGANIC PHOSPHORUS

SOIL PROFILE SAMPLES

Sampling depth (cm)	290-340	340-390	390-440
Aluminium phosphate	4.5	8.3	5.5
Iron phosphate	11.4	11.8	10.4
Calcium phosphate	4.9	4.2	2.6
Total occluded phosphate	79.2	75.7	81.5

TABLE IXe

FORMS OF INORGANIC PHOSPHORUS AS PERCENTAGES OF ADDED TOTAL INORGANIC PHOSPHORUS

SOIL PROFILE SAMPLES

Sampling depth (cm)	440-490	490-540	540-590	590-620
Aluminium phosphate	3.5	2.4	3.6	2.6
Iron phosphate	10.0	10.1	10.2	8.4
Calcium phosphate	2.1	2.0	1.3	1.9
Total occluded phosphate	84.4	85.5	84.9	87.0

TABLE Xa

FORMS OF PHOSPHORUS AS PERCENTAGES OF TOTAL PHOSPHORUS

PLOT SAMPLES

Plot No. (controls) Sampling depth (cm)	11(1) 0-15	11(1) 15-30	27(1) 0-15	27(1) 15-30
Aluminium phosphate	3.7	3.8	6.4	4.6
Iron phosphate	14.9	8.8	16.0	11.2
Calcium phosphate	4.2	3.2	4.2	2.5
Total occluded phosphate	34.9	36.9	20.8	36.1
Added total inorganic phosphate	57.7	52.7	47.4	54.4
Organic phosphorus	40.7	46.1	51.9	49.1

TABLE Xb

FORMS OF PHOSPHORUS AS PERCENTAGES OF TOTAL PHOSPHORUS

PLOT SAMPLES

Plot No. Sampling depth (cm)	4 P 0-15	4 P 15-30	19 P 0-15	19 P 15-30
Aluminium phosphate	7.7	14.3	11.2	20.1
Iron phosphate	27.7	27.9	30.4	22.9
Calcium phosphate	24.0	12.1	20.8	10.5
Total occluded phosphate	25.7	21.4	12.5	17.8
Added total inorganic phosphate	85.1	75.7	74.8	71.3
Organic phosphorus	16.8	21.7	23.0	25.0

TABLE Xc

FORMS OF PHOSPHORUS AS PERCENTAGES OF TOTAL PHOSPHORUS

PLOT SAMPLES

Plot No. Sampling depth (cm)	9 CP 0-15	9 CP 15-30	31 CP 0-15	31 CP 15-30
Aluminium phosphate	13.5	12.7	14.4	14.3
Iron phosphate	29.9	33.8	27.9	29.1
Calcium phosphate	20.6	17.5	21.4	16.7
Total occluded phosphate	13.8	15.1	15.5	12.5
Added total inorganic phosphate	77.9	79.1	79.2	72.6
Organic phosphorus	24.0	22.6	22.6	25.8

TABLE Xd

FORMS OF PHOSPHORUS AS PERCENTAGES OF TOTAL PHOSPHORUS

PLOT SAMPLES

Plot No. Sampling depth (cm)	14 PM 0-15	14 PM 15-30	29 PM 0-15	29 PM 15-30
Aluminium phosphate	17.1	25.9	12.5	18.8
Iron phosphate	24.3	23.6	20.6	21.0
Calcium phosphate	29.6	15.2	39.7	26.2
Total occluded phosphate	15.3	16.9	10.0	13.1
Added total inorganic phosphate	86.3	81.6	82.7	79.0
Organic phosphorus	15.8	16.6	16.0	21.7

TABLE XIa

FORMS OF PHOSPHORUS AS PERCENTAGES OF TOTAL PHOSPHORUS

SOIL PROFILE SAMPLES

Sampling depth (cm)	0 - 8	8 - 15	15 - 30
Aluminium phosphate	3.5	2.7	4.7
Iron phosphate	14.8	14.1	12.4
Calcium phosphate	4.6	3.1	4.7
Total occluded phosphate	29.2	39.1	45.5
Added total inorganic phosphate	52.1	59.0	67.4
Organic phosphorus	44.7	36.7	26.6

TABLE XIb

FORMS OF PHOSPHORUS AS PERCENTAGES OF TOTAL PHOSPHORUS SOIL PROFILE SAMPLES

Sampling depth (cm)	30 - 50	50 - 90	90 - 140
Aluminium phosphate	4.8	3.4	4.0
Iron phosphate	13.5	24.1	26.1
Calcium phosphate	4.3	3.1	5.7
Total occluded phosphate	49.1	61.9	60.9
Added total inorganic phosphate	71.7	92.5	96.7
Organic phosphorus	22.6	11.2	5.4

TABLE XIc

FORMS OF PHOSPHORUS AS PERCENTAGES OF TOTAL PHOSPHORUS SOIL PROFILE SAMPLES

Sampling depth (cm)	140-190	190-240	240-290
Aluminium phosphate	4.1	4.1	4.0
Iron phosphate	22.5	22.6	10.5
Calcium phosphate	8.4	3.1	2.9
Total occluded phosphate	57.2	65.4	74.7
Added total inorganic phosphate	92.2	95.2	92.1
Organic phosphorus	5.6	6.2	5.1

TABLE XId

FORMS OF PHOSPHORUS AS PERCENTAGES OF TOTAL PHOSPHORUS SOIL PROFILE SAMPLES

Sampling depth (cm)	290-340	340-390	390-440
Aluminium phosphate	4.2	7.9	5.3
Iron phosphate	10.6	11.3	9.9
Calcium phosphate	4.6	4.0	2.5
Total occluded phosphate	73.9	72.5	78.0
Added total inorganic phosphate	93.3	95.7	95.7
Organic phosphorus	4.2	3.0	2.8

TABLE XIe

FORMS OF PHOSPHORUS AS PERCENTAGES OF TOTAL PHOSPHORUS SOIL PROFILE SAMPLES

Sampling depth (cm)	440-490	490-540	540-590	590-620
Aluminium phosphate	3.4	2.4	3.6	2.6
Iron phosphate	9.9	10.3	10.0	8.6
Calcium phosphate	2.1	2.1	1.3	2.0
Total occluded phosphate	8 83.6	87.6	83.8	88.2
Added total inorganic phosphate	99.0	102.4	98.7	101.3
Organic phosphorus	Trace	Trace	Trace	Trace

4.3 Carbon, nitrogen and organic phosphorus ratios

Carbon, nitrogen and organic phosphorus ratios are shown in table XII (a-c). The carbon:organic phosphorus ratios are nearly all between 200 and 250. In the profile they are between about 200 and 240; hence this variation is not very large. In Finnish cultivated mineral soils, Kaila (1950) found the ratio organic carbon:organic phosphorus to be about 100-150 and suggested that if it were possible to determine the available amounts of humus carbon and of soil organic phosphorus instead of the total amounts, the corresponding ratio might be found to be more constant. The values obtained in the present study are comparable to the ratios reported for Iowa soils by Pearson and Simonson (1939) and that for Ghana soils obtained by Nye and Bertheux (1957).

Smaller variations occurred in the nitrogen:organic phosphorus ratio than in the carbon:organic phosphorus ratio in the plots but there were large variations in the nitrogen:organic phosphorus ratio in the soil profile. This large variation is presumably caused by a more rapid decrease in organic phosphorus content in relation to nitrogen, with increasing depth of the profile. The Iowa soils studied by Pearson and Simonson (1939) had a nitrogen: organic phosphorus range of 8 to 16, which is much lower than that of the profile in the present study. For the surface soils of Ghana, Nye and Bertheux (1957) reported nitrogen:organic phosphorus ratio up to 43. A high

TABLE XIIa

CARBON, NITROGEN, ORGANIC PHOSPHORUS RATIOS

PLOT SAMPLES

Plot No. & Sampling depth (cm)	C:N	C:P	N:P	C:N:P
11 (1) 0 - 15	13.00	230	17.71	230:17.71:1
11 (1) 15 - 30	13.11	233	17.80	233:17.80:1
27 (1) 0 - 15	13.67	236	17.28	236:17.28:1
27 (1) 15 - 30	14.08	231	16.42	231:16.42:1
14 0 - 15	12.72	232	18.24	232:18.24:1
14 15 - 30	13.73	266	19.38	266:19.38:1
4 P 0 - 15	12.48	220	17.68	220:17.68:1
4 P 15 - 30	14.65	250	17.09	250:17.09:1
19 P 0 - 15	12.30	221	18.03	221:18.03:1
19 P 15 - 30	12.03	292	24.29	292:24.29:1

TABLE XIIb

CARBON, NITROGEN, ORGANIC PHOSPHORUS RATIOS

PLOT SAMPLES

Plot No. & Sampling depth (cm)		C:N	C:P	N:P	C:N:P
9 CP	0 - 15	13.14	235	17.88	235:17.88:1
9 CP	15 - 30	13.12	236	17.97	236:17.97:1
31 CP	0 - 15	12.38	241	19.53	241:19.53:1
31 CP	15 - 30	12.48	244	19.55	244:19.55:1
14 PM	0 - 15	13.36	230	17.27	230:17.27:1
14 PM	15 - 30	14.54	316	21.78	316:21.78:1
29 PM	0 - 15	14.24	250	17.55	250:17.55:1
29 PM	15 - 30	14.68	246	16.77	246:16.77:1

TABLE XII c

CARBON, NITROGEN, ORGANIC PHOSPHORUS RATIOS
SOIL PROFILE SAMPLES

Sampling depth (cm)	C:N	C:P	N:P	C:N:P
0 - 8	7.13	241	33.85	241:33.85:1
8 - 15	7.62	218	29.78	218:29.78:1
15 - 30	6.39	237	37.09	237:37.09:1
30 - 50	7.92	198	25.00	198:25.00:1
50 - 90	5.38	203	36.36	203:36.36:1
90 - 140	4.62	231	50.00	231:50.00:1
140 - 190	-	216	-	-
190 - 240	-	222	-	-
240 - 290	-	171	-	-
290 - 340	-	175	-	-
340 - 390	-	200	-	-
390 - 440	-	188	-	-

nitrogen:organic phosphorus ratio indicates more nitrogen in proportion to organic phosphorus.

Much higher carbon:organic phosphorus ratios and nitrogen:organic phosphorus ratios have been reported for other soils possibly suggesting deficiencies of phosphorus in such soils. The ratios for surface Kikuyu Red clays are lower than a number of those reported, indicating that total P in relation to nitrogen and organic carbon is not as low in the case of the Kikuyu Red soil as it is in the cases of the other soils reported.

4.4 Available phosphorus

Table III shows the available phosphorus status of the coffee plot samples investigated and table XIII shows correlation between available phosphorus and inorganic phosphorus fractions. All the correlations were found to be significant. The correlation coefficient between iron phosphate and available phosphorus tends to confirm the observation of Al-Abbas and Barber (1964b) that the iron phosphate fraction was the main contributor to the available phosphorus.

The significant correlation between available phosphorus and occluded phosphate is of a doubtful nature, as also noted by John (1972).

TABLE XIII

CORRELATION BETWEEN AVAILABLE PHOSPHORUS, DETERMINED BY OLSEN'S METHOD, AND INORGANIC PHOSPHORUS FRACTIONS

PLOT SAMPLES

Fraction	Correlation Coefficient(r)	Remarks
Aluminium phosphate	+0.72***	Significant at the 0.1% level
Iron phosphate	+0.96***	Significant at the 0.1% level
Calcium phosphate	+0.75***	Significant at the 0.1% level
Occluded phosphate	+0.67**	Significant at the 1% level

TABLE XIV a

DISTRIBUTION OF ALUMINIUM PHOSPHATE IN THE PLOT SAMPLES

Analysis of Variance

Factor	D.F.	Sum of squares	Mean square	F ratio
Replicates	1	175.5625	175.5625	
Treatments (T)	3	47503.6875	15834.5625	24.25*
Error (a)	3	1959.1875	653.0625	
1st aggregate	7	49638.4375		
Depth (D)	1	2545.1875	2545.1875	41.01*
T x D	3	2048.0625	682.6875	11.00**
Error (b)	4	248.2500	62.0625	
Total	15	54479.9375		

** = Significant at the 1% level

* = Significant at the 5% level.

L.S.D. Treatments	L.S.D. Depths
0.1% = 253.53	0.1% = 33.91
1 % = 105.54	1 % = 18.13
5 % 57.50	5% = 10.93

TABLE XIV b

DISTRIBUTION OF IRON PHOSPHATE IN THE PLOT SAMPLES

Analysis of Variance

Factor	D.F.	Sum of squares	Mean square	F ratio
Replicates	1	3422.2500	3422.2500	12.62*
Treatments (T)	3	118992.5000	39664.1667	146.32*
Error (a)	3	813.2500	271.0833	
1st aggregate	7	123228.0000		
Depth (D)	1	35532.2500	35532.2500	96.72***
T x D	3	6803.2500	2267.7500	6.17^{NS}
Error (b)	4	1469.5000	367.3750	
Total	15	167033.000		

*** = significant at the 0.1% level

* = significant at the 5% level.

NS = not significant

L.S.D. Treatments	L.S.D. Depths
0.1% = 150.46	0.1% = 82.51
1% = 68.00	1% = 44.12
5% = 37.04	5% = 26.60

TABLE XIV c

DISTRIBUTION OF CALCIUM PHOSPHATE IN THE PLOT SAMPLES

Analysis of Variance

Factor	D.F.	Sum of squares	Mean square	F ratio
Replicates	1	430.5625	430.5625	
Treatments (T)	3	143910.6875	47970.2291	40.86*
Error (a)	3	11128.1875	3709.3958	
1st aggregate	7	155469.4375		
Depth (D)	1	72495.5625	72495.5625	314.60***
T x D	3	36440.1875	12146.7291	52.71**
Error (b)	4	921.7500	230.4375	
Total	15	265326.9375		

*** = significant at the 0.1% level

** = significant at the 1% level

* = significant at the 5% level

L.S.D. Treatments	L.S.D. Depths
0.1% = 556.58	0.1% = 65.35
1% = 251.54	1% = 34.94
5% = 137.03	5% = 21.07

TABLE XIV d

DISTRIBUTION OF TOTAL OCCLUDED PHOSPHATE IN THE PLOT SAMPLES

Analysis of Variance

Factor	D.F.	Sum of squares	Mean square	F ratio
Replicates	1	9216.0000	9216.0000	7.00^{NS}
Treatments (T)	3	1856.2500	618.7500	
Error (a)	3	3948.5000	1316.1666	
1st aggregate	7	15020.7500		
Depth (D)	1	9506.2500	9506.2500	6.58^{NS}
T x D	3	3807.2500	1269.0833	0.88^{NS}
Error (b)	4	5777.5000	1444.3750	
Total	15	34111.7500		

NS = not significant

L.S.D. Treatments	L.S.D. Depths
0.1% = 331.54	0.1% = 163.61
1% = 149.84	1% = 87.49
5% = 81.62	5% = 52.75

TABLE XIV e

DISTRIBUTION OF ORGANIC PHOSPHORUS IN THE PLOT SAMPLES

Analysis of Variance

Factor	D.F.	Sum of squares	Mean squares	F ratio
Replicates	1	20.25000	20.2500	
Treatments (T)	3	15138.7500	5046.2500	22.6373*
Error (a)	3	668.7500	222.9166	
1st aggregate	7	15827.7500		
Depth (D)	1	14161.0000	14161.0000	3.37 NS
T x D	3	1914.0000	638.0000	
Error (b)	4	16790.7500	4197.6875	
Total	15	32865.7500		

* = significant at the 5% level

NS = not significant.

L.S.D. Treatments	L.S.D. Depths
0.1% = 136.44	0.1% = 279.92
1% = 61.66	1% = 149.15
5% = 33.59	5% = 89.93

TABLE XIV f

DISTRIBUTION OF TOTAL PHOSPHORUS IN THE PLOT SAMPLES

Analysis of Variance

Factor	D.F.	Sum of squares	Mean square	F ratio
Replicates	1	15750.2500	15750.2500	3.40 NS
Treatments (T)	3	947481.5000	315827.1666	68.27**
Error (a)	3	13879.2500	4626.4166	
1st aggregate	7	977111.0000		
Depth (D)	1	497025.0000	497025.0000	246.04***
T x D	3	119908.5000	39969.5000	19.79*
Error (b)	4	8080.5000	2020.1250	
Total	15	1602125.0000		

*** = significant at the 0.1% level
** = significant at the 1% level
* = significant at the 5% level
NS = not significant.

L.S.D. Treatments	L.S.D. Depths
0.1% = 621.58	0.1% = 193.49
1% = 280.92	1% = 103.47
5% = 153.03	5% = 62.38

TABLE XV a

DISTRIBUTION OF ALUMINIUM PHOSPHATE IN THE SOIL PROFILE SAMPLES

Analysis of Variance

Factor	D.F.	Sum of squares	Mean square	F ratio
Replicates	2	1.5788	0.7894	0.55^{NS}
Depths	15	748.8496	49.9233	34.76^{***}
Error	30	43.0879	1.4362	

*** = significant at the 0.1% level

NS = not significant

L.S.D.

0.1% = 3.57

1% = 2.69

5% = 2.00

TABLE XV b

DISTRIBUTION OF IRON PHOSPHATE IN THE SOIL PROFILE SAMPLES

Analysis of Variance

Factor	D.F.	Sum of squares	Mean square	F ratio
Replicates	2	5.1750	2.5875	0.5786^{NS}
Depths	15	15299.4666	1019.9644	228.0830***
Error	30	134.1584	4.4719	

*** = significant at the 0.1% level

NS = not significant

L.S.D.

0.1% = 6.29

1% = 4.75

5% = 3.52

TABLE XV c

DISTRIBUTION OF CALCIUM PHOSPHATE IN THE SOIL PROFILE SAMPLES

Analysis of Variance

Factor	D.F.	Sum of squares	Mean square	F ratio
Replicates	2	0.8250	0.4125	0.38^{NS}
Depths	15	1376.3666	91.7577	84.68^{***}
Error	30	32.5084	1.0836	

*** = significant at the 0.1% level

NS = not significant

L.S.D.

0.1% = 3.10
1% = 2.34

5% = 1.74

TABLE XV d

DISTRIBUTION OF TOTAL OCCLUDED PHOSPHATE IN THE SOIL PROFILE SAMPLES

Analysis of Variance

Factor	D.F.	Sum of squares	Mean square	F ratio
Replicates	2	49.4018	24.7009	2.11^{NS}
Depths	15	167340.6101	11156.0406	952.79***
Error	30	351.2649	11.7086	

*** = significant at the 0.1% level

NS = not significant

L.S.D.

0.1% = 10.18

1% = 7.68

5% = 5.70

4.5 Fixation of Applied Water Soluble Phosphate

The amounts of 200 ppm of potassium dihydrogen phosphate applied to the unfertilized soils and then fixed as aluminium phosphate, iron phosphate and calcium phosphate three and thirty days after treatment are shown in table XVI (a,b). The total phosphorus fixed is taken as the difference between the total quantity added and that recovered by N NH_4Cl extractant, the latter being considered to be water soluble.

Total phosphorus fixed: There are small but consistent differences between total and applied phosphate fixed, after three and after thirty days, by the plot soils and by the soil profile; this indicates similarities in general properties of the soils. There are, however, larger differences between the amounts fixed in three and in thirty days respectively, for each soil; more phosphorus was fixed in thirty days than in three days. The rates at which phosphorus fixed increased from three to thirty days are almost the same for the soils; this gives another indication of similarities in their general properties which include soil texture, clay content, inorganic phosphorus content and exchangeable aluminium content. Figure 2 (a-d) shows fixation and recovery patterns for potassium dihydrogen phosphate by the soils.

Phosphorus Fixed as Aluminium Phosphate: In all the samples investigated for the fixation of applied water soluble phosphorus, the fixed phosphorus was mostly in the form of ammonium fluoride - soluble phosphate, that is, aluminium phosphate. The amounts fixed in this form increased from three days to thirty days; this was also true of iron phosphate. Chang and Chu (1961), Yuan et al. (1960) and Appelt and Schalscha (1970) are among those who have also observed accumulation of recently fixed phosphate as aluminium phosphate.

Phosphorus Fixed as Iron Phosphate: A substantial proportion of the added phosphate was fixed as iron phosphate, the amounts fixed in this way being about two-thirds of the amounts fixed as aluminium phosphate.

Phosphorus Fixed as Calcium Phosphate: Comparatively small amounts of phosphate were fixed as calcium phosphate in all the samples compared to those amounts fixed as aluminium or iron phosphates. Correspondingly small increases occurred between the three and thirty day periods. There is, therefore, little doubt that fixation of applied water soluble phosphate as calcium phosphate in these soils is far less important than that due to aluminium and iron phosphate formation.

Chang and Chu (1961) found in their experiments that soluble phosphate added to soils kept at field moisture capacity for three days was mainly fixed as aluminium phosphate, followed by iron phosphate and calcium phosphate, as was observed in the present study. However, they found that keeping the same soils under the same conditions for 100 days, caused the amount of iron phosphate to increase while those of aluminium and calcium phosphate decreased.

Hinga (1973), in his study of phosphate sorption capacity in relation to properties of various soils in Kenya, obtained correlations between P-sorption and various soil properties. The correlation coefficients decreased in the order: Al_2O_3, $Al_2O_3 + Fe_2O_3$, CECv (C.E.C. due to variable charge), Fe_2O_3, organic carbon content and AEC (anion exchange capacity).

The results of the present study, besides those of others including Chang and Chu (1961) and Hinga (1973), suggest that fixation of added soluble phosphate by the various cations would first occur on the surface of the solid phases with which the phosphate comes in contact, and that the relative amounts and kinds of phosphates formed would depend on the specific surface area of the solid phases associated with aluminium, iron and calcium.

These conclusions are supported by the surface activity studies of inorganic soil phosphorus in the present investigation.

4.5.1 Per cent Recovery of the Added Phosphate

The balance of phosphate not accounted for by that recovered as water soluble (saloid-bound), aluminium phosphate, iron phosphate and calcium phosphate might have been in forms other than these fractions. In view of the very long time required for occlusion of phosphorus to occur it is unlikely that the unrecovered amounts had gone into the occluded form; the likely possibility is that it might have been adsorbed on the surface of clay minerals

TABLE XVIa

FIXATION OF ADDED 200 PPM OF POTASSIUM DIHYDROGEN PHOSPHATE, KH_2PO_4, IN SOILS AT FIELD MOISTURE CAPACITY, 3 AND 30 DAYS RESPECTIVELY AFTER TREATMENT

PLOT SAMPLES

Plot No. & sampling depth (cm)	Net increase of phosphorus in each form (ppm)					% recovery
	P soluble in N NH_4Cl	Al - PO_4	Fe-PO_4	Ca-PO_4	Total P recovered	
			THREE DAYS			
11 (1) 0 - 15	21	74	53	9	157	78.5
27 (1) 0 - 15	18	78	54	11	161	80.5
			THIRTY DAYS			
11 (1) 0 - 15	8	80	61	12	161	80.5
27 (1) 0 - 15	9	85	59	13	166	83.0

Plot No & sampling depth (cm)

11 (1) 0 - 15 : Total P fixed in 3 days = 179 PPM

11 (1) 0 - 15 : Total P fixed in 30 days = 192 PPM

27 (1) 0 - 15 : Total P fixed in 3 days = 182 PPM

27 (1) 0 - 15 : Total P fixed in 30 days = 191 PPM

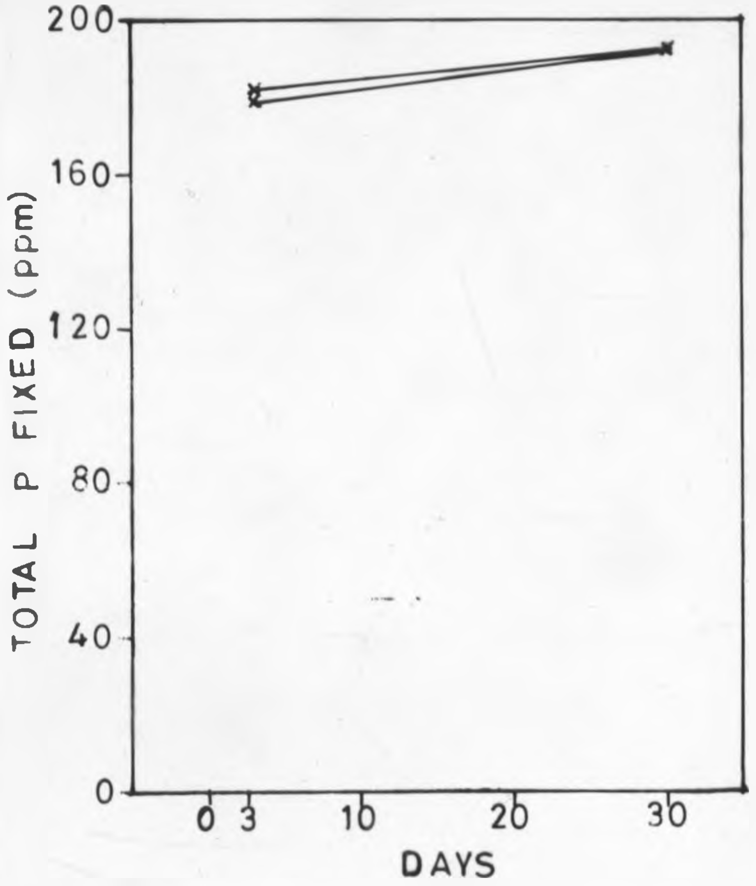


Fig. 2a. FIXATION PATTERN FOR KH_2PO_4, COFFEE PLOT SAMPLES.

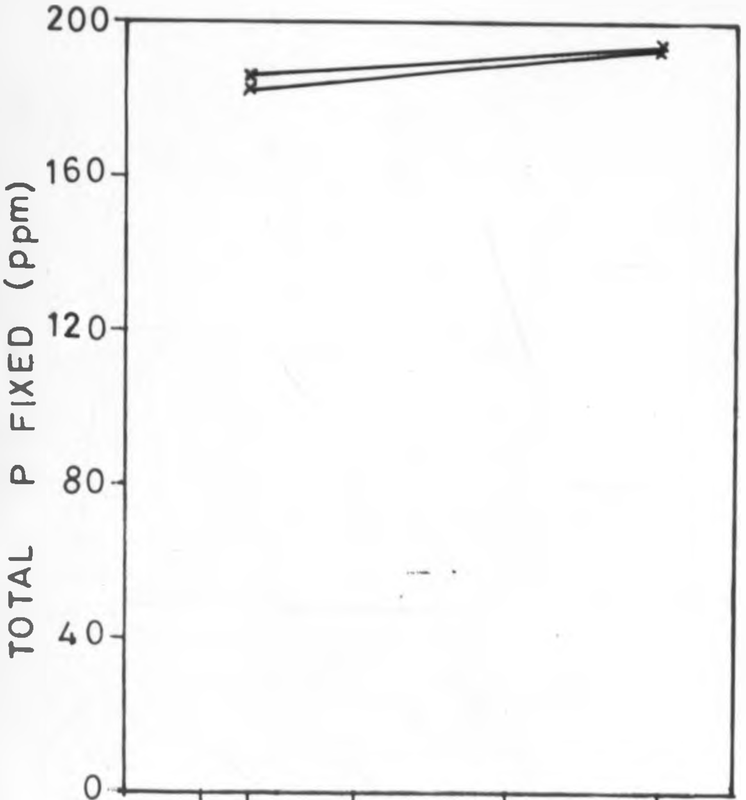


Fig. 2b. FIXATION PATTERN FOR KH_2PO_4, PROFILE SAMPLES

TABLE XVI b

FIXATION OF ADDED 200 PPM OF POTASSIUM DIHYDROGEN PHOSPHATE, KH_2PO_4, IN SOILS AT FIELD MOISTURE CAPACITY, 3 AND 30 DAYS RESPECTIVELY AFTER TREATMENT

SOIL PROFILE SAMPLES

Sampling depth (cm)	Net increase of phosphorus in each form (ppm)					
	P soluble in N NH_4Cl	Al-PO_4	Fe-PO_4	Ca-PO_4	Total P recovered	% recovery
			THREE DAYS			
0 - 8	17	71	50	14	152	76.0
8 - 15	14	74	54	15	157	78.5
			THIRTY DAYS			
0 - 8	7	76	53	15	151	75.5
8 - 15	6	77	61	16	160	80.0

Soil profile sampling depth (cm)

0 - 8 cm : Total P fixed in 3 days = 183 PPM
0 - 8 cm : Total P fixed in 30 days = 193 PPM
8 - 15 cm: Total P fixed in 3 days = 186 PPM
8 - 15 cm: Total P. fixed in 30 days = 194 PPM

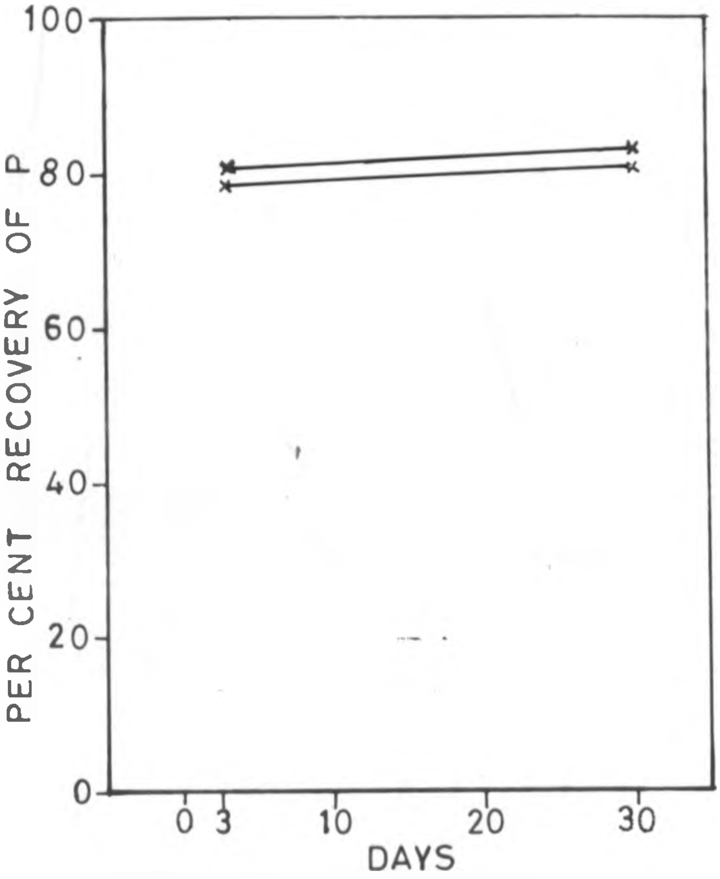


Fig. 2c. RECOVERY PATTERN FOR KH_2PO_4, COFFEE PLOT SAMPLES.

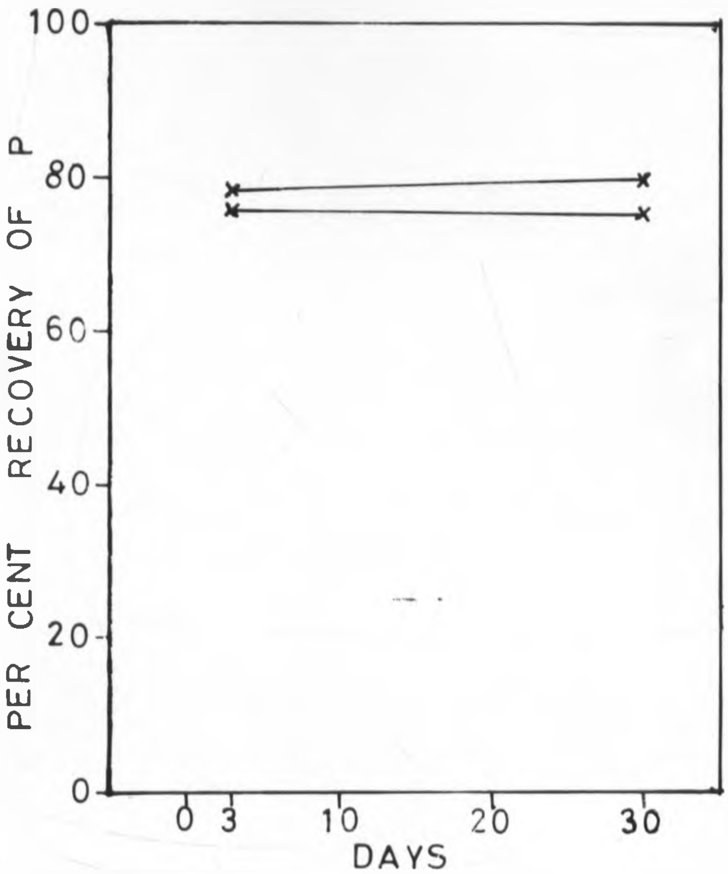


Fig. 2d. RECOVERY PATTERN FOR KH_2PO_4, PROFILE SAMPLES

and hydrous iron oxides. Yuan et al. (1960) obtained a recovery of 86-97 per cent of the phosphate added to some acid soils of Florida.

The higher per cent recovery for thirty days compared to that for three days is possibly due to phosphate which had been more strongly adsorbed in other ways (such as on the surface of clay minerals and hydrous iron oxides) going to recoverable forms, such as aluminium and iron phosphate, during the period of the experiment.

4.6 Surface Activity of Inorganic Soil Phosphorus Fractions

4.6.1 Laboratory studies on soils previously characterised for P-fractions by chemical analysis.

The surface activity of aluminium, iron and calcium phosphates and their percentages of total of the fractions are shown in tables XVIIa and XVIIc. According to Chu and Chang (1966) the occluded phosphate does not take part in the exchange reaction with the solution phase phosphorus since the former is coated by iron oxide; hence this fraction was not included in these studies.

Tables XVIIb and XVIId show the surface phosphorus and specific surface activities of the various active inorganic phosphates in the soil. These were calculated as shown under section 3.2.6. The tables present some interesting features with regard to the nature and distribution of the inorganic phosphates. In both the plot samples and the

TABLE XVIIa

SURFACE ACTIVITY OF Al-, Fe-, AND Ca- PHOSPHATES IN SOILS DETERMINED IN THE SUCCESSIVE EXTRACTS OF NH_4F, NaOH, AND H_2SO_4, THE SOIL BEING EQUILIBRATED WITH ^{32}P IN SOLUTION BEFORE PHOSPHORUS FRACTIONATION

PLOT SAMPLES

ACTIVITY OF ^{32}P SOLUTION USED = 1621 COUNTS/SEC.

Plot No.	Sampling depth (cm)	Al - P c/sec.	Fe - P c/sec.	Ca - P c/sec.	Surface activity of fraction as % of total of fractions		
					Al - P	Fe - P	Ca - P
11 (1)	0 - 15	372.8	827.8	105.3	28.5	63.4	8.1
11 (1)	15 - 30	362.8	888.8	104.5	26.8	65.5	7.7
27 (1)	0 - 15	312.3	861.0	95.0	24.6	67.9	7.5
27 (1)	15 - 30	314.5	948.8	109.0	22.9	69.1	8.0
14	0 - 15	347.0	983.3	108.5	24.1	68.3	7.6
14	15 - 30	245.8	911.3	86.0	19.8	73.3	6.9

TABLE XVIIb

SURFACE PHOSPHORUS AND SPECIFIC SURFACE ACTIVITIES OF THE VARIOUS INORGANIC PHOSPHATES IN SOILS

PLOT SAMPLES

Plot No.	Sampling depth (cm)	Surface phosphorus of fractions (ppm)			Specific surface activity of P fractions (%)		
		Al - P	Fe - P	Ca - P	Al - P	Fe - P	Ca - P
11 (1)	0-15	9.7	21.6	2.7	60.6	33.8	15.0
11 (1)	15-30	8.2	20.1	2.4	68.3	71.8	24.0
27 (1)	0-15	7.7	21.2	2.3	38.5	42.4	17.7
27 (1)	15-30	7.1	21.5	2.5	54.6	67.2	35.7
14	0-15	6.3	17.8	2.0	25.2	16.3	10.0
14	15-30	5.6	20.9	2.0	26.7	25.2	11.8

TABLE XVIIc

SURFACE ACTIVITY OF Al-, Fe-, AND Ca- PHOSPHATES IN SOILS DETERMINED IN THE SUCCESSIVE EXTRACTS OF NH_4F, NaOH, AND H_2SO_4, THE SOIL BEING EQUILIBRATED WITH ^{32}P IN SOLUTION

BEFORE PHOSPHORUS FRACTIONATION

SOIL PROFILE SAMPLES

ACTIVITY OF ^{32}P SOLUTION USED = 3301 C/SEC

Sampling depth (cm)	Al - P c/sec.	Fe - P c/sec.	Ca - P c/sec.	Surface activity of fraction as % of total of fractions		
				Al-P	Fe - P	Ca - P
0 - 8	603.3	1696.0	212.3	24.0	67.5	8.5
8 - 15	613.3	1784.8	162.0	24.0	69.7	6.3
15 - 30	484.0	2122.3	165.5	17.5	76.6	7.9
30 - 50	439.0	2020.3	137.0	16.9	77.8	5.3
50 - 90	346.3	1712.0	97.0	16.1	79.4	4.5
90 - 140	349.0	2026.3	236.0	13.4	77.6	9.0
140 - 190	261.0	2066.0	269.3	10.1	79.6	10.3
190 - 240	314.8	1241.5	185.3	18.1	71.3	10.6
240 - 290	451.8	1799.8	198.3	18.4	73.5	8.1
290 - 340	1204.0	1141.8	271.8	46.0	43.6	10.4

TABLE XVIId

SURFACE PHOSPHORUS AND SPECIFIC SURFACE ACTIVITIES OF THE VARIOUS INORGANIC PHOSPHATES IN SOILS

Sampling depth (cm) of the soil profile	Surface phosphorus of fractions (ppm)			Specific surface activity of P fractions (%)		
	Al - P	Fe - P	Ca - P	Al - P	Fe - P	Ca - P
0 - 8	3.9	11.0	1.4	39.0	26.2	10.8
8 - 15	4.3	12.5	1.1	61.4	34.7	13.8
15 - 30	3.3	14.4	1.1	30.0	49.7	10.0
30 - 50	2.9	13.6	0.9	26.4	43.9	9.0
50 - 90	2.3	11.4	0.6	23.0	16.1	6.7
90 - 140	4.6	26.9	3.1	38.3	34.5	18.2
140 - 190	5.4	42.8	5.6	38.6	59.4	20.7
190 - 240	2.2	8.5	1.3	18.3	12.9	14.4
240 - 290	3.6	14.2	1.6	32.7	50.0	20.0
290 - 340	8.4	7.9	1.9	70.0	26.3	14.6

soil profile, the activity of the surface phosphate fractions decreases in the order: iron phosphate, aluminium phosphate and calcium phosphate, indicating a corresponding decrease in the amounts of surface phosphorus of the fractions respectively. At the 290-340 cm horizon of the deep profile, however, activity of surface aluminium phosphate is higher than that of iron phosphate and much higher than that of calcium phosphate; this indicates the presence of more surface phosphate in the form of aluminium phosphate compared to the other fractions.

Surface aluminium and iron phosphates are much higher than surface calcium phosphates in all the samples except in the 140-190 cm horizon of the profile where surface aluminium phosphate is slightly less than surface calcium phosphate. This may be explained by the fact that in this horizon there is much more total calcium phosphate than total aluminium phosphate.

The second feature to note is that the specific surface activity (that is, the surface phosphate of a specific fraction as a per cent of that fraction) of aluminium and iron phosphates is higher than that of calcium phosphate. In the plot samples, the means of the specific surface activity of aluminium phosphate, iron phosphate and calcium phosphate decrease in the order: 45.7, 42.8 and 19.0 per cent. In the soil profile the values also decrease in that order, being 37.8, 35.4 and 13.8 per cent. This phenomenon has been observed by others, including Chu and Chang (1966), Rotini and El-Nennah (1971-1972).

The magnitudes of the respective surface phosphate fractions and their specific surface activities may be explained by the mode of occurrence of the various phosphates in the soil. Juo and Ellis (1968) provided evidence to support the concepts that calcium phosphate in soils is of primary origin. Iron and aluminium phosphates, however, are largely of secondary origin formed in the course of geological and pedological weathering and, as they are formed, there is a tendency for them to be associated to some extent with the clay fraction because of its large surface area. Consequently greater amounts of surface aluminium and iron phosphates are usually found than surface calcium phosphate in soils.

The means of specific surface activity of aluminium, iron and calcium phosphates of the plot samples are slightly higher than the means of the soil profile horizons respectively. This may be related to the fact that the mean of the percent clay of the six sets of the plot samples is slightly higher than the mean of the per cent clay of the ten soil profile samples used in these studies, being 68.3 and 64.5 respectively.

The agricultural importance of these surface activity studies concerns the evaluation of the relative availability of inorganic phosphate fractions in the soils. This can be viewed as follows: in the soils studied, regardless of pH, aluminium and iron phosphate may be more important sources of available phosphorus than calcium phosphate, owing to the high specific surface activity of the first two, and the much larger amount of surface phosphorus of the second. Calcium phosphate may not be the main source of available phosphorus, owing to its low specific activity and its low total amount.

4.6.2 Pot-culture seedling studies

The yields of dry matter of the barley seedlings after harvest are shown in table XVIIIa.

There are no significant differences between the control and the treated soils. This means that the contribution made by the very small amount of the applied phosphate fertilizer in form of potassium dihydrogen phosphate with regard to response was not significant. This is said with the assumption that the other nutrients which were added, temperature and moisture conditions were as satisfactory as intended.

A basic assumption of the tracer technique is that the radiations emanating from radioactive isotopes do not affect the normal physiological activity of plants. Marais and Fourie (1959), however, conducted experiments which showed that the presence of ^{32}P affected the dry weights and phosphorus absorption of rye and tomato plants by as much as 15 per cent, and that the radiation effect depended on the crop, its age, and the soil in which it was grown. They reported that this finding was later confirmed by the results of several other experiments which indicate that possibility of radiation effects should be considered in experiments involving radioactive isotopes.

TABLE XVIIIa

POT CULTURE SEEDLING EXPERIMENT: PLOT 14 SOIL SAMPLES USED

WEIGHTS OF DRY MATTER OF BARLEY SEEDLINGS AFTER HARVEST (TOP* AND SUB* REFER TO THE SOIL SAMPLES TAKEN FROM 0-15 CM AND 15-30 CM DEPTHS RESPECTIVELY).

Pot No.		g
I	Control Top	3.06
II	Control Sub	2.92
I	Top ^{32}P	3.24
2	Top ^{32}P	2.47
3	Top ^{32}P	2.51
6	Sub ^{32}P	2.51
7	Sub ^{32}P	2.68
8	Sub ^{32}P	2.77

* Top soil samples were replicated three times in the ^{32}P treatments (that is, 1,2,3).

* Subsoil samples were also replicated three times in the ^{32}P treatments (that is, 6,7,8).

Total uptake of phosphorus

The total uptake of phosphorus by the seedlings in the control topsoil was 4.10 mg; the corresponding uptake in the control subsoil was 3.60 mg. These amounts, when compared with the total uptake in the treated soil shown in table XVIIIb, present no significant differences from the latter. This suggests that the small amount of the applied carrier phosphate played a minor part in the total uptake by the seedlings.

Although it is appreciated that the total phosphorus uptake in the treated topsoil was of the same magnitude as that in the treated subsoil, it was observed that the total activity of the plants grown in the topsoil was about twice as much as the total activity of the plants grown in the subsoil. This indicates that the subsoil 'fixed' more phosphorus than the topsoil. Moreover, these activities were almost negligible compared to what was applied; a very large proportion of the applied phosphate was immobilized or at least failed to reach the plant. One of the obvious advantages of the use of ^{32}P in experiments such as the present one is that it is possible to determine the relative contribution of the soil and fertilizer to the nutrition of the plant if the contribution of the plant itself (particularly the seed) can be estimated accurately. The experiment showed that less than 1 per cent of the applied potassium dihydrogen phosphate went to the plants.

TABLE XVIIIb

POT CULTURE SEEDLING EXPERIMENT: RADIOACTIVITY ASSAYED IN PLANTS AFTER HARVEST AND TOTAL AMOUNT OF P ABSORBED BY THE PLANTS

Plot No.	a Total activity in plants (uptake) c/sec.	b Total activity applied c/sec.	$\frac{a}{b} \times 100$ i.e. % act. in crop	Total amount of P absorbed by plants (mg)
1 Top ^{32}P	8141.1	917489	0.89	4.14
2 Top ^{32}P	7170.9	917489	0.78	3.15
3 Top ^{32}P	6010.0	917489	0.66	3.88
6 Sub ^{32}P	3746.8	917489	0.41	3.39
7 Sub ^{32}P	3707.8	917489	0.40	3.83
8 Sub ^{32}P	4220.0	917489	0.46	3.88

Applied P per pot = 3.74 mg as KH_2PO_4

Specific activity of applied P = 917489/3.74
= 245318
counts per sec/mg.

Residual ^{32}P in the soil-P fractions

Table XVIIIc shows the distribution of residual ^{32}P in the soil after the harvest of the seedlings. Most of the applied activity in the residual soil was recovered as iron phosphate, followed by aluminium phosphate and least as calcium phosphate in all the replicated pots. This shows the relative abundance of the various phosphate fractions in the soils. This pattern of distribution is in accord with the surface activity studies conducted earlier.

The effort made to separate as much sand from the soil as possible before the soil was taken for radiochemical assay was not completely successful because some sand always managed to pass through the sieve with the soil (< 0.5 mm). The data, therefore, do not necessarily pertain to pure soil, although the bulk of the aliquots assayed consisted of soil. Since the sand with which the soils had been diluted had been thoroughly washed and since, in any case, the soil consisted largely of clay enabling it to have a larger exposed surface area of aluminium and iron to support surface aluminium and iron phosphates than any sand could, it is reasonable to assume that the sand might have had some diluent effect on the soil as far as the radiochemical assay was concerned. Assuming that this was the case it follows that the data in table XVIIIc and columns 2,3 and 4 of table XVIIId and (d) in table XVIIIe are proportionally lower than the true figures. Hence it follows that the high percent activity unaccounted for by the total activity measured in the soil and the crop could be lower than indicated in table XVIIId, and the unexpectedly high values of (c-d) in table XVIIIe could be higher than really was the case.

TABLE XVIIIc

RESIDUAL ^{32}P IN THE SOIL-P FRACTIONS OBTAINED BY REFRACTIONATION OF SOIL USING CHANG AND JACKSON'S (1957) METHOD

	Total activity per pot, counts/sec. (not corrected for diluent effect of sand)			^{32}P in soil - P fraction as % of applied activity		
Pot No.	Al - P	Fe - P	Ca - P	Al - P	Fe - P	Ca - P
1 Top ^{32}P	161,460	365,700	65,376	17.6	39.9	7.1
2 Top ^{32}P	176,760	400,200	66,660	19.3	43.6	7.3
3 Top ^{32}P	172,740	409,800	68,220	18.8	44.7	7.4
6 Sub ^{32}P	137,136	390,900	71,700	15.0	42.6	7.8
7 Sub ^{32}P	149,580	417,900	63,156	16.3	45.6	6.9
8 Sub ^{32}P	146,556	402,900	56,856	16.0	43.9	6.2

Total activity applied per pot = 917,489 counts/sec.

TABLE XVIIId

BALANCE SHEET OF THE ^{32}P APPLIED TO THE EXPERIMENTAL POTS OF BARLEY SEEDLINGS.

DATA NOT CORRECTED FOR DILUENT EFFECT OF SAND

Pot No.	Total activity in soil after harvest of crop c/sec	Residual total activity in soil as % of applied activity	Residual % activity in soil + % activity in crop	% activity unaccounted for by activity measured in soil & crop
1 Top ^{32}P	609300	66.41	67.30	32.70
2 Top ^{32}P	642060	69.98	70.76	29.24
3 Top ^{32}P	685860	74.75	75.41	24.59
6 Sub ^{32}P	631284	68.81	69.22	30.78
7 Sub ^{32}P	615564	67.09	67.49	32.51
8 Sub ^{32}P	649668	70.81	71.27	28.73

The percent uptake of ^{32}P by the barley seedlings from each of the soil-P fractions.

Since the soils in the experimental pots had been thoroughly mixed with ^{32}P and allowed to equilibrate under fairly constant conditions before planting the seeds and, since the experiment lasted for three weeks, it can be assumed that according to McAuliffe et al. (1948) the following relationships between soil-P fractions applied.

$$\frac{\text{Al-P32 surface}}{\text{Al-P31 surface}} = \frac{\text{Fe-P32 surface}}{\text{Fe-P31 surface}} = \frac{\text{Ca-P32 surface}}{\text{Ca-P31 surface}}$$

The data concerning per cent uptake from each fraction shown in table XVIIIe were obtained on the assumption that these relationships applied. It is shown that the per cent uptake decreased in the order: iron phosphate, aluminium phosphate and calcium phosphate.

The practical significance of the results is that iron phosphate and aluminium phosphate appear to contribute more to plant growth than calcium phosphate.

TABLE XVIIIe

THE % UPTAKE OF ^{32}P BY THE BARLEY SEEDLINGS FROM EACH OF THE SOIL-P FRACTIONS. THE RESULTS ARE BASED ON TABLE XVIIIc DATA (UNCORRECTED FOR DILUENT EFFECT OF SAND)

Pot No.	c The % uptake by crop of total P applied	d % uptake from each fraction			c − d > 0, probably due to diluent effect of sand in (d)
		Al − P	Fe − P	Ca − P	c − d
1 Top ^{32}P	0.89	0.15	0.36	0.06	0.31
2 Top ^{32}P	0.78	0.15	0.34	0.06	0.23
3 Top ^{32}P	0.66	0.12	0.30	0.05	0.19
6 Sub ^{32}P	0.41	0.06	0.17	0.03	0.15
7 Sub ^{32}P	0.40	0.07	0.18	0.03	0.12
8 Sub ^{32}P	0.46	0.07	0.20	0.03	0.16

Percent of the Total Phosphorus in the Plant Derived from the Fertilizer

The data in table XVIIIf were obtained by using the suggestion of Fried and Broeshart (1967) that when an element, M, in the fertilizer is labelled with an isotope of that element, M^1(which may be either a stable isotope or a radioisotope) the fraction of M in the plant derived from the fertilizer, Fm, is found as the ratio of the specific activities of the element in the plant and the fertilizer, that is:

$$Fm = M^1(\text{plant})/M(\text{plant}) \div M^1(\text{fertilizer})/M(\text{fertilizer})$$

where M is the amount of a given unlabelled nutrient ion; M^1, amount of a given labelled nutrient ion; and Fm, the fraction of the nutrient ion in the plant derived from the fertilizer.

It appears therefore that a very small amount of phosphorus in the plants was derived from the applied potassium dihydrogen phosphate; a large percent of the phosphorus in the plants came either from the seeds or the soil or from both. It was not possible to make a justifiable distinction between the contribution made by the seeds and that made by the soil in supplying the phosphorus because it was impracticable to ascertain the amounts derived from the seeds which did not germinate and subsequently decayed. Between 20 and 40 percent of the seeds failed to germinate. The experiment, however, is useful in permitting an evaluation of the fertilizer source in relation to the soil (and the seed). Seeds with a high percent germination can enable one to evaluate the fertilizer source in relation to the soil if the contribution of phosphorus by such seeds is estimated fairly accurately.

TABLE XVIII f

PER CENT OF TOTAL PHOSPHORUS IN BARLEY SEEDLINGS DERIVED FROM APPLIED POTASSIUM DIHYDROGEN PHOSPHATE (KH_2PO_4) FERTILIZER

Plot 14 samples (Top = 0-15 cm) Sub = 15-30 cm) Pot No.	Specific activity of fertilizer in plant (A) Counts per sec/mg	Specific activity of applied fertilizer (B) counts per sec/mg	Fraction of P in plant derived from fertilizer $(\frac{A}{B})$	% P in plant derived from fertilizer $(\frac{A}{B}) \times 100$
1 Top ^{32}P	1966.4	245318	0.0080	0.80
2 Top ^{32}P	2276.5	245318	0.0092	0.92
3 Top ^{32}P	1549.0	245318	0.0063	0.63
6 Sub ^{32}P	1105.3	245318	0.0045	0.45
7 Sub ^{32}P	968.1	245318	0.0039	0.39
8 Sub ^{32}P	1087.6	245318	0.0044	0.44

TABLE XVIIIg

SELF-ABSCRPTION CORRECTION DATA FOR RADIOACTIVITY COUNTS OF BARLEY SEEDLINGS

Dry weight of barley counted	Observed activity	Observed activity after dead time correction	Observed activity after dead time and decay corrections	Apparent specific activity	Apparent sp. activity as % of normal	Normalized total activity
g	c/100 sec.	c/100 sec.	c/100 sec.	c/100 sec./mg	%	c/100 sec.
0.10	3058	3074	22479	224.79	99.6	22569
0.20	6108	6171	45126	225.63	100	45126
0.40	11270	11486	83993	209.98	93.1	90218
0.60	15831	16261	118910	198.18	87.8	135433
0.80	20163	20866	152585	190.73	84.5	180574
1.0	24492	25536	186735	186.74	82.8	225525

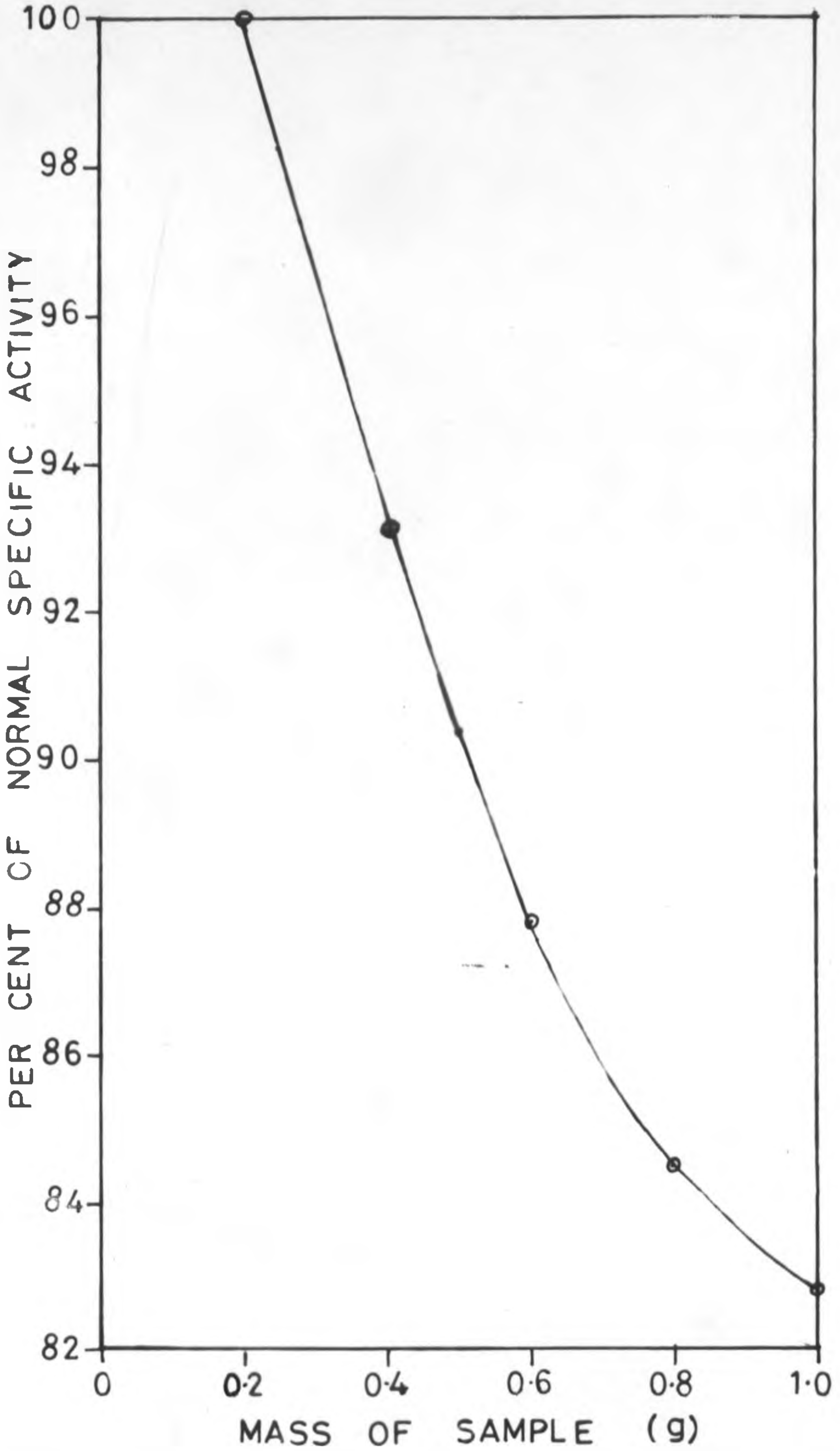


Fig. 3 — SELF-ABSORPTION CURVE FOR BARLEY SAMPLES OF CONSTANT SPECIFIC ACTIVITY.

Experiment with coffee seedlings

The coffee seedlings (which had been pregerminated in sand) were unable to develop a root system sufficient to exploit thoroughly the pot soils during the predetermined time of the experiment. This predetermined time was based on the half-life (which is defined as the time required for the activity of a radionuclide to decrease by one-half, that is, for half of the atoms present to disintegrate) and on the radioactivity of the ^{32}P. As a result of the insufficiently developed root system the uptake of the phosphorus was negligible. The aim of the experiment was the same as that with barley seedlings. It appears questionable whether it is possible, using the same procedure, to achieve results similar to those obtained with barley seedlings. An attempt to do so would necessarily require the application of a very high level of radioactivity to compensate for the rather short half-life of ^{32}P (14.3 days) in relation to the slow growth of coffee seedlings. The obvious disadvantages of this are the hazards involved in handling, and possible injury to plants. In view of these considerations the use of ^{32}P with coffee seedlings may have to involve a different experimental approach.

CHAPTER V

SUMMARY AND CONCLUSIONS

The decrease in total phosphorus from 284 ppm at the surface of the soil profile to 230 ppm in the 30-50 cm horizon was largely accounted for by a decrease in organic phosphorus. The concentration of total occluded phosphate, however, contributed predominantly to the downward trend of increase in total phosphorus. The distribution of total phosphorus in the plots was found to be related to fertilizer, mulch, and cattle manure applications and also to sampling depths. In the two sampling depths, 0-15 and 15-30 cm, ranges of total phosphorus increased as follows:- controls, 285-430 ppm; 4P and 19P, which received phosphate fertilizers, 428-974 ppm; 9CP and 31CP, which received cattle manure and phosphate fertilizers, 694-1143 ppm. The effect of mulch on total phosphorus content of the soil in plots 14 PM and 29PM which received phosphate and mulch was somewhat similar to that of cattle manure. The apparent relative increase of total P was found to be greater for 0-15 than 15-30 cm. The differences appear to reflect the phosphate fertilizers, cattle manure, and mulch added to the P, CP and PM plots over the years. Limited mobility of phosphate ions in the soil may account for the highly significant difference between the amounts of total phosphorus in the two sampling depths in the plots.

In the 0-30 cm layer of the soil profile studied the mean (in ppm) of the various inorganic phosphate fractions were: Ca-PO_4, 10.6; Al-PO_4, 9.3; Fe-PO_4, 35.6; occluded - PO_4, 96.3. Although the amount of aluminium phosphate is slightly less than that of calcium phosphate, these figures tend to suggest the degree of chemical weathering of the soil. In the 0-30 cm layer of the control plots, the means (in ppm) of the various inorganic phosphate fractions were: Ca-PO_4, 12.0; Al-PO_4, 15.3; Fe-PO_4, 43.5; occluded - PO_4, 108.8. This distribution tends to measure the degree of chemical weathering of the soil, the chemical weathering sequence being calcium phosphate, aluminium phosphate, iron phosphate, and occluded phosphate. The occluded phosphate is the most weathering-resistant form and accumulates during a long time. Thus the formation and transformation of the various phosphate species following the order of calcium, aluminium, iron and occluded phosphate, corresponds to increasing stages in a weathering sequence due to their different stabilities.

It was noted in the present study that the high percentage of the total P which is occluded reinforced the general view that analysis of total P alone in such soils has little value, and perhaps none in predicting phosphorus availability.

Application of phosphate fertilizer and mulch or cattle manure greatly increased the accumulation of calcium phosphate and aluminium phosphate when compared to the levels of these two fractions in the untreated plots. Although it was apparent that iron phosphate was also increased by the fertilizer treatments, it was noticeable that the rates of increase were lower than those of calcium and aluminium phosphates. In the PM plots, however, calcium phosphate was found to be much higher than iron and aluminium phosphates in the 0-15 cm but not in the 15-30 cm sampling layers. It was suggested that mulch, besides phosphate fertilizers, might account for this difference through its contribution of phosphate. Fertilizer treatments or mulching or both did not seem to have any noticeable effect on the relatively insoluble (occluded) form of phosphate indicating that it is relatively unimportant in problems of phosphate absorption.

There were highly significant differences between the amounts of iron phosphate in the 0-15 and 15-30 cm sampling horizons of the plots; the same applied for calcium phosphate in the two horizons. These differences and the significant differences between the concentrations of aluminium phosphate in the two sampling horizons are probably due to limited mobility of phosphate ions in the soil.

The percentage of organic phosphorus in the profile decreased progressively with depth, the maximum being 44.7 per cent at the surface horizon and the minimum being less than 2.8 per cent below the 390-440 cm horizon; the decline was attributed to decreasing amounts of organic matter which followed the same trend. This decline of organic phosphorus with depth of a profile has been observed by others. The low percentages (less than 50%) of organic phosphorus in the treated plots was explained by sharp increases of inorganic phosphorus fractions caused by application of the fertilizers.

Significant correlations were found between available phosphorus determined by the $NaHCO_3$ method of Olsen and inorganic phosphorus fractions. The correlation coefficient between iron phosphate and available phosphorus suggested that iron phosphate was the main contributor to available phosphorus in this soil. One of the current methods of estimating the available phosphorus status of soils at the Coffee Research Station, Ruiru, involves extraction of phosphorus with 0.1N HCl-0.025N H_2SO_4 mixture; this extractant is likely to get out mostly calcium phosphate which was found to be the least important form in the soils of the present study. In view of this, it is suggested that the $NaHCO_3$ extractant is better than the 0.1N HCl-0.025N H_2SO_4 mixture as far as estimation of available phosphorus in these soils is concerned.

The water soluble phosphorus, KH_2PO_4, applied to some soil samples was mostly fixed as aluminium phosphate. The amounts fixed in this form and also as iron phosphate increased from three days to thirty days. It was noted that other workers have also observed accumulation of recently fixed phosphate as aluminium phosphate. The amounts fixed as iron phosphate were about two-thirds of the amounts fixed as aluminium phosphate. Comparatively small amounts of phosphate were fixed as calcium phosphate. There was, therefore, little doubt that fixation of applied water soluble phosphate as calcium phosphate in these soils is far less important than that due to aluminium and iron phosphate formation.

The results of the present study, besides those of other investigators, suggest that fixation of added soluble phosphate by the various cations would first occur on the surface of the solid phases with which the phosphate comes in contact, and that the relative amounts and kinds of phosphate formed would depend on the specific surface area of the solid phases associated with aluminium, iron and calcium.

These conclusions were supported by the surface activity studies of inorganic soil phosphorus in the present investigation.

A recovery of 75.5 - 83.0 per cent of the water soluble phosphate added to the soils was obtained after a period of 30 days. The balance of phosphate not accounted for by that recovered as water soluble, aluminium phosphate, iron phosphate and calcium phosphate might have been more strongly adsorbed on the surface of clay minerals and hydrous iron oxides.

In both the plot samples and the soil profile, the activity of the surface phosphate fractions decreased in the order: iron phosphate, aluminium phosphate and calcium phosphate, indicating a corresponding decrease in the amounts of surface phosphorus of the fractions respectively. Surface aluminium and iron phosphates were found to be much higher than surface calcium phosphate in all the samples except in the 140-190 cm horizon of the profile where surface aluminium phosphate was slightly less than surface calcium phosphate.

It was also observed that the specific surface activity of aluminium and iron phosphates was higher than that of calcium phosphate. The means of the specific surface activity of aluminium phosphate, iron phosphate and calcium phosphate decreased in that order.

The magnitudes of the respective surface phosphate fractions and their specific surface activities may be explained by the mode of occurrence of the various phosphates in the soil. Formation of iron and aluminium phosphates mainly in the course of geological and pedological weathering tends to associate these fractions to some extent with the clay fraction because of its large surface area. Calcium phosphate in soils is considered to be of primary origin. Consequently greater amounts of surface aluminium and iron phosphates are usually found than surface calcium phosphate in soils.

The agricultural importance of these surface activity studies concerns the evaluation of the relative availability of inorganic phosphate fractions in the soils. In the soils studied, regardless of pH, aluminium and iron phosphate may be more important sources of available phosphorus than calcium phosphate, owing to the high specific surface activity of the first two, and the much larger amounts of surface phosphorus of the second. Calcium phosphate may not be the main source of available phosphorus, owing to its low specific activity and its low total amount.

In the pot-culture seedling experiment with barley and ^{32}P, the total activity of the plants grown in the topsoil was about twice as much as the total activity of the plants grown in the subsoil. This indicated that the subsoil 'fixed' more phosphorus than the topsoil. Moreover, these activities were almost negligible compared to what was applied; a very large proportion of the applied phosphate was immobilized or at least failed to reach the plant. The experiment showed that less than 1 per cent of the applied KH_2PO_4 went to the plants. After the harvest of the seedlings, it was observed that most of the applied activity in the residual soil was recovered as iron phosphate, followed by aluminium phosphate and least as calcium phosphate. This showed the relative abundance of the various phosphate fractions in the soils. This pattern of distribution was in accord with the surface activity studies.

The per cent uptake of ^{32}P by the barley seedlings from each of the soil-P fractions showed that the uptake decreased in the order: iron phosphate, aluminium phosphate and calcium phosphate. The practical significance of these results is that iron phosphate and aluminium phosphate appear to contribute more to plant growth than calcium phosphate in the present study.

Coffee seedlings were unable to develop a root system sufficient to exploit thoroughly the ^{32}P treated pot soils during the predetermined time of the experiment. The aim of the experiment was the same as that with barley seedlings. It appeared questionable whether it would be possible, using the same procedure, to achieve results similar to those obtained with barley seedlings. An attempt to do so would necessarily require the more hazardous application of a very high level of radioactivity to compensate for the rather short half-life of ^{32}P in relation to the slow growth of coffee seedlings. In view of these considerations the use of ^{32}P with coffee seedlings may have to involve a different experimental approach.

REFERENCES

1. Abdul, B.A. (1964). Effect of lime on availability of phosphorus in Zamorano soils. Soil Sci. Soc. Amer. Proc. 28: 672-673.

2. Acquaye, D.K. (1963). Some significance of soil organic phosphorus mineralization in the phosphorus nutrition of cocoa in Ghana. Plant and Soil 19: 65-80.

3. Aguilera, N.H. and Jackson, M.L. (1953). Iron oxide removal from soils and clays. Soil Sci. Soc. Amer. Proc. 17: 359-364.

4. Ahn, P.M. (1970). West African Agriculture. Vol. I West African Soils. Oxford University Press.

5. Al-Abbas, A.H. and Barber, S.A. (1964a). A soil test for phosphorus based upon fractionation of soil phosphorus: II. Development of soil test. Soil Sci. Soc. Amer. Proc. 28: 221-224.

6. ____________ and ___________. (1964b). A soil test for phosphorus based upon the fractionation of soil phosphorus: Correlation of soil phosphorus fractions with plant-available phosphorus. Soil Sci. Soc. Amer. Proc. 28: 218-221.

7. Aldrich, D.G. and Buchanan, J.R. (1954). Phosphorus content of soils and their parent rocks in Southern California. Soil Sci. 77:369-376.

8. Amer, F. (1962). Determination of ^{32}P exchangeable phosphorus in soils. IAEA/FAO Symp. Radioisotopes Soil-Plant Nutrition Studies, IAEA, Vienna, 43-58.

9. ________ et al. (1955). Characterization of soil phosphorus by anion exchange resin adsorption and ^{32}P equilibration. Plant and Soil 4: 391-408.

10. Appelt, H. and Schalscha, E.B. (1970). Effect of added phosphate on the inorganic phosphorus fractions of soils derived from volcanic ash. Soil Sci. Soc. Amer. Proc. 34: 599-602.

11. Arambarri, P. and Talibudeen, O. (1959a). Factors influencing the isotopically exchangeable phosphate in soils. Part I. The effect of low concentrations of organic anions. Plant and Soil 11: 343-354.

12. ____________ and ____________ (1959b). Factors influencing the isotopically exchangeable phosphate in soils. Part II. The effect of base saturation with sodium and calcium in non-calcareous soils. Plant and Soil 11: 355-363.

13. ____________ and ____________ (1959c). Factors influencing isotopically exchangeable phosphate in soils. Part III. The effect of temperature in some calcareous soils. Plant and Soil 11: 364-376.

14. Basak, M.N. and Bhattacharya, R. (1962). Phosphate transformations in rice soil. Soil Sci. 94: 258-262.

15. Bates, J.A.R. and Baker, T.C.N. (1960). Studies on a Nigerian forest soil: II. Distribution of phosphorus in the profile and in various soil fractions of a Nigerian soil. J. of Soil Sci. 11: 257-265.

16. Bhangoo, M.S. and Smith, F.W. (1957). Fractionation of phosphorus in Kansas soils and its significance in response of wheat to phosphate fertilizers. Agron. J. 49: 354-358.

17. Birch, H.F. (1949). The estimation of adsorbed and acid soluble phosphates in East African soils. In: Proceedings of the first commonwealth conference on tropical and subtropical soils, 1949. Comm. Bur. of Soil Sci., Harpenden, England. Tech. Comm., No. 46, pp. 225-230.

18. __________ (1958). The effect of soil drying on humus decomposition and nitrogen availability. Plant and Soil 10: 9-31.

19. __________ (1959). Further observations on humus decomposition and nitrification. Plant and Soil 11: 262-286.

20. __________ (1960). Nitrification in soils after different periods of dryness. Plant and Soil 12: 81-96.

21. Black, C.A. (1953). Soil and fertilizer phosphorus in crop nutrition.Agronomy IV: 131. Academic Press, New York.

22. __________ (ed.) et al. (1965). Methods of Soil Analysis, Part 2. American Soc. of Agron., Madison, Wisconsin, U.S.A.

23. Bray, R.H. and Dickman, S.R. (1941). Adsorbed phosphates in soils and their relation to crop responses. Soil Sci. Soc. Amer. Proc. 6: 312-320.

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

25. Buehrer, T.F. (1932). The physico-chemical relationships of soil phosphates. Ariz. Agric. Expt. St. Tech. Bull. No. 42, pp. 154-212.

26. Burd, J.S. (1948). Chemistry of the phosphate ions in soil systems. Soil Sci. 65: 227-247.

27. Chai, M.C. and Caldwell, A.C. (1959). Forms of phosphorus and fixation in soils. Soil Sci. Soc. Amer. Proc. 23: 458-460.

28. Chang, S.C. and Chu, W.K. (1961). The fate of soluble phosphate applied to the soil. J. of Soil Sci. 12: 286-293.

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

30. __________ and ____________ (1958). Soil phosphorus fractions in some representative soils. J. of Soil Sci. 9: 109-119.

31. __________ and Juo, A.S.R. (1963). Available phosphorus in relation to forms of phosphorus in soils. Soil Sci. 95: 91-96.

32. Chenery, E.M. (1955). Aluminium in the tea bush, a preliminary study. Plant and Soil 6: 174-200.

33. Chirikov, F.V. and Volkova, V.V. (1941). The availability to plants of the phosphoric acid of different forms of soil phosphate. Soils and Fertilizers 8: 78-79 (1945).

34. Chu, W.K. and Chang, S.C. (1966). Surface activity of inorganic soil phosphorus. Soil Sci. 101: 459-464.

35. Cole, C.V. and Jackson, M.L. (1951). Solubility equilibrium constant of dihydroxy aluminium dihydrogen phosphate relating to a mechanism of phosphate fixation in soils. Soil Sci. Soc. Amer. Proc. 15: 84-89.

36. __________ et al. (1953). The nature of phosphate sorption by calcium carbonate. Soil Sci. Soc. Amer. Proc. 17: 352-356.

37. Coleman, N.T. et al. (1960). Phosphate-sorption reactions that involve exchangeable aluminium. Soil Sci. 90: 1-7.

38. Coleman, R. (1944). Phosphorus fixation by the coarse and fine clay fractions of kaolinite and montmorillonite clays. Soil Sci. 58: 71-77.

39. __________ (1945). The mechanism of phosphorus fixation by montmorillonitic and kaolinitic clays. Soil Sci. Soc. Amer. Proc. 9: 72-78.

40. Dahnke, W.C. et al. (1964). Phosphorus fractionation in selected soil profiles of El Salvador as related to their development. Soil Sci. 98: 33-38.

41. Dalton, J.D. et al. (1952). Effect of organic matter on phosphate availability. Soil Sci. 73: 173-181.

42. Davis, L.E. (1935). Sorption of phosphates by non-calcareous Hawaiian soils. Soil Sci. 40: 129-158.

43. Dean, L.A. (1938). An attempted fractionation of soil phosphorus. J. of Agric. Sci. 28: 234-246.

44. Dean, L.A. (1949). Fixation of soil phosphorus. In A.G. Norman (ed.), Adv. in Agron. Vol. I, pp. 391-411. Academic Press Inc., N.Y.

45. Dormaar, J.F. and Webster, G.R. (1963). Status of organic phosphorus in some Alberta soils. Canadian J. of Soil Sci. 43: 27-34.

46. Doughty, J.L. (1930). Phosphate fixation by a peat soil. Soil Sci. 29: 23-35.

47. ____________ (1935). Phosphate fixation in soils, particularly as influenced by organic matter. Soil Sci. 40: 191-202.

48. Dyal, R.S. (1953). Mica leptyls and wavellite content of clay fraction from Gainesville loamy fine sand of Florida. Soil Sci. Soc. Amer. Proc. 17: 55-58.

49. Edwards, D.C. (1951). The vegetation in relation to soil and water conservation in East Africa. In: Management and Conservation of vegetation in Africa, a symp., 1951. Comm. Bur. of Pastures and Field Crops, Penglais, Aberystwyth, Wales. Bull. No. 41, pp. 28-43.

50. Eid, M.T., Black, C.A. and Kempthorne, O. (1951). Importance of soil organic and inorganic phosphorus to plant growth at low and high soil temperatures. Soil Sci. 71: 361-370.

51. Ellis, R.J. and Truog, E. (1955). Phosphate fixation by montmorillonite. Soil Sci. Soc. Amer. Proc. 19: 451-454.

52. Ensminger, L.E. (1949). The relationship between water lost and PO_4 adsorbed on phosphating clay minerals and soil colloids. Soil Sci. Soc. Amer. Proc. 13: 170-174.

53. Fassbender, H.W. (1969). Phosphorus fixation in tropical soils. Agric. Digest 18: 20-28.

54. Fife, C.V. (1959a). An evaluation of ammonium fluoride as a selective extractant for aluminium-bound soil phosphate: I. Preliminary studies on non-soil systems. Soil Sci. 87: 13-21.

55. ________ (1959b). An evaluation of ammonium fluoride as a selective extractant for aluminium-bound soil phosphate: II. Preliminary studies on soils. Soil Sci. 87: 83-88.

56. ________ (1962). An evaluation of ammonium fluoride as a selective extractant for aluminium soil phosphate III. Detailed studies on selected soils. Soil Sci. 93: 113-123.

57. Fisher, R.A. and Thomas, R.P. (1935). The determination of the forms of inorganic phosphorus in soils. Agron. J. 27: 863-873.

58. Ford, M.C. (1933). The nature of phosphate fixation in soils. Agron. J. 25: 134-144.

59. Fried, M. (1957). Measurement of plant nutrient supply of soils by radioactive isotopes. Atomic Energy and Agriculture, American Association for the Advancement of Science, 1-18.

60. ________ and Broeshart, H. (1967). The Soil-Plant System in Relation to Inorganic Nutrition, Academic Press, New York, 150-219.

61. Fried, M. and Shapiro, R.E. (1956). Phosphate supply pattern of various soils. Soil Sci. Soc. Amer. Proc. 20: 471-475.

62. Gethin Jones, G.H. (1949). Colonial soil types: systematic soil classification and nomenclature. In: Proceedings of the first commonwealth conference on tropical and sub-tropical soils, 1949. Comm. Bur. Soil Sci., Harpenden, England. Tech. Comm. No. 46, p. 92.

63. ________________ (1953). Detailed soil survey of the Coffee Research Station, Ruiru. In: The soils of the Nairobi - Thika - Yatta - Machakos area, Dept. of Agric., Nairobi, by Scott, R.M. (1963) pp. 54-60.

64. Ghani, M.O. (1943a). Fractionation of soil phosphorus. I. Method of extraction. Indian J. of Agric. Sci. 13: 29-45.

65. __________ (1943b). The use of 8-hydroxyquinoline as a means of blocking active iron and aluminium in the determination of available phosphoric acid of soils by dilute acid extractions. Indian J. of Agric. Sci. 13: 562-565.

66. __________ and Aleem, S.A. (1943a). Studies on the distribution of different forms of phosphorus in some Indian soils. I. Surface distribution. Indian J. of Agric. Sci. 13: 283-288.

67. __________ and __________ (1943b). Studies on the distribution of different forms of phosphorus in Indian soils. II. Vertical distribution. Indian J. of Agric. Sci. 13: 377-381.

68. Ghani, M.O. and Islam, M.A. (1946). Phosphate fixation in acid soils and its mechanism. Soil Sci. 62: 293-306.

69. Glen, R.C. et al. (1959). Flow sheet for soil phosphate fractionation. Agron. Abstracts, pp.9.

70. Godfrey, C.L. and Riecken, F.F. (1954). Distribution of phosphorus in some genetically related loess-derived soils. Soil Sci. Soc. Amer. Proc. 18: 80-84.

71. Hamilton, H.A. and Lessard, J.R. (1960). Phosphorus fractions in a soil sampled at different depths and the effect of lime and fertilizer on oats and clover in a greenhouse test. Canadian J. of Soil Sci. 40: 71-79.

72. Haseman, J.R. et al. (1950a). Mineralogical character of some iron and aluminium phosphates containing potassium and ammonium. Soil Sci. Soc. Amer. Proc. 15: 76-84.

73. ____________ et al. (1950b). Some reactions of phosphate with clays and hydrous oxides of iron and aluminium. Soil Sci. 70: 257-271.

74. Hemwall, J.B. (1957). The fixation of Phosphorus in soils. In A.G. Norman (ed.), Adv. in Agron., Vol. IX, pp. 95-112. Academic Press Inc., N.Y.

75. Hesse, P.R. (1962). Phosphorus fixation in mangrove swamps. Nature 193: 295-296.

76. __________ (1963). Phosphorus relationships in a mangrove swamp mud with particular reference to aluminium toxicity. Plant and Soil 19: 205-218.

77. Hinga, G. (1973). Phosphate sorption capacity in relation to properties of several types of Kenya soil. E. Afr. Agric. and For. J. 38: 400-404.

78. Hsu, P.H. (1964). Adsorption of phosphate by aluminium and iron in soils. Soil Sci. Soc. Amer. Proc. 28: 474-478.

79. ________ and Jackson, M.L. (1960). Inorganic phosphate transformations by chemical weathering in soils as influenced by pH. Soil Sci. 90: 16-24.

80. Huxley, P.A., Turk, A. and Mitchell, H.W. (1969). Confidence limits of expected rainfall in coffee areas in Kenya. Kenya Coffee 34: 57.

81. Islam, M.A. and Choudhury, A.A. (1960). Distribution of iron, manganese and phosphorus in the paddy soil profile. J. of Agric. Sci. 54: 318-320.

82. __________ and Elahi, M.A. (1954). Reversion of ferric iron to ferrous iron under waterlogged conditions and its relation to available phosphorus. J. of Agric. Sci. 45: 1-2.

83. Jackson, M.L. (1958). Soil Chemical Analysis. Prentice Hall, Inc., Englewood Cliffs, N.J.

84. ____________ (1964). Chemical composition of soils. In F.E. Bear (ed.) Chemistry of the Soil, Chap. 2, Amer. Chem. Soc. Mon. No. 160. Reinhold Publ. Corp., N.Y.

85. John,M.K. (1972). Extractable phosphorus related to forms of phosphorus and other soil properties. J. Sci. Fd. Agric. 23: 1425-1433.

86. Jones, P.A., Robinson, J.B.D. and Wallis, J.A.N. (1960a). Fertilizers, manure and mulch in Kenya coffee growing. Empire J. Expt. Agric.; 28: 335; Kenya Coffee (1961); 26: 441-459.

87. ___________, _______________, and ____________ (1960b). Fertilizers, manure and mulch in Kenya coffee growing. Empire J. Expt. Agric.; 28: 335-352.

88. Joos, L.L. and Black, C.A. (1950). Availability of phosphate rock as affected by particle size and contact with bentonite and soil of different pH values. Soil Sci. Soc. Amer. Proc. 15: 69-75.

89. Juo, A.S.R. and Ellis, B.G. (1968). Particle size distribution of aluminium, iron and calcium phosphate in soil profiles. Soil Sci. 106: 374.

90. Kaila, A. (1950). On the dependence of the amount of organic phosphorus on the carbon content of soil. 4th Intern. Congr. Soil Sci., Amsterdam, Netherlands. I: 191.

91. Kanwar, J.S. (1956). Phosphate retention in some Australian soils. Soil Sci. 82: 43-50.

92. Kardos, L.T. (1964). Soil fixation of plant nutrients. In F.E. Bear (ed.) Chemistry of the Soil, Chap. 9, Amer. Chem. Soc. Mon. No. 160. Reinhold Publ. Corp.,N.Y.

93. Karim, A. and Khan, D.H. (1955). Relationship between pH and different forms of phosphorus in some soils in East Pakistan. Soil Sci. 80: 229-233.

94. Kelly, J.B. and Midgley, A.R. (1943). Phosphate fixation - an exchange of phosphate and hydroxyl ions. Soil Sci. 55: 167-176.

95. Kittrick, J.A. and Jackson, M.L. (1954). Electron microscope observations of the formation of aluminium phosphate crystals with kaolinite as the source of aluminium. Science 120: 508-509.

96. ____________ and ____________ (1955). Rate of phosphate reaction with soil minerals and electron microscope observations on the reaction mechanism. Soil Sci. Soc. Amer. Proc. 19: 292-295.

97. ____________ and ____________ (1956). Electron microscope observations of the reaction of phosphate with minerals leading to a unified theory of phosphate fixation in soils. J. of Soil Sci. 7: 81-89.

98. Kurtz, T., DeTurk, E.E. and Bray, R.H. (1946). Phosphate adsorption by Illinois soils. Soil Sci. 61: 111-124.

99. Legg, J.O. and Black, C.A. (1955). Determination of organic phosphorus in soils. II. Ignition method. Soil Sci. Soc. Amer. Proc. 19: 139-142.

100. Le Mare, P.H. (1968). Experiments on the effects of phosphate applied to a Buganda soil. II. A chemical study of the soil phosphate, the fate of fertilizer phosphate, and relationship with iron and aluminium. J. Agric. Sci. Camb. 70: 281-285.

101. Lindsay, W.L. and Moreno, E.C. (1960). Phosphate phase equilibria in soils. Soil Sci. Soc. Amer. Proc. 24: 177-182.

102. ____________ and Stephenson, H.F. (1959). Nature of the reactions of monocalcium phosphate monohydrate in soils: IV. Repeated reactions with metastable triple-point solution. Soil Sci. Soc. Amer. Proc. 23: 440-445.

103. Lindsay, W.L. et al. (1959). Solubility criteria for the existence of variscite in soils. Soil Sci. Soc. Amer. Proc. 23: 357-360.

104. Low, P.F. and Black, C.A. (1948). Phosphate-induced decomposition of kaolinite. Soil Sci. Soc. Amer. Proc. 12: 180-184.

105. ________ and __________ (1950). Reactions of phosphate with kaolinite. Soil Sci. 70: 273-290.

106. Marais, P.G. and Fourie, S. (1959). Radiation effect on the growth and phosphorus uptake of plants grown in soil treated with ^{32}P. S. Afr. J. Agric. Sci. 2: 3-18.

107. McAuliffe, C.D. et al. (1948). Exchange reaction between phosphate and soils: Hydroxylic surface of soil minerals. Soil Sci. Soc. Amer. Proc. 12: 119-123.

108. Mehlich, A. (1968). Coffee soils in Kenya and their characteristics in relation to the mineral nutrition of Arabica coffee. Annual Report Coffee Research Station, Ruiru, 1966/67, 5-17.

109. Midgley, A.R. (1940). Phosphate fixation in soils. A critical review. Soil Sci. Soc. Amer. Proc. 5: 24-30.

110. Millar, C.E. (1955). Soil Fertility. John Wiley & Sons, Inc., New York.

111. Mortensen, J.L. and Himes, F.L. (1964). Soil Organic matter. In F.E. Bear (ed.) Chemistry of the Soil, Chap. 5, Amer. Chem. Soc. Mon. No. 160. Reinhold Publ. Corp. N.Y.

112. Murphy, H.F. (1939). The role of kaolinite in phosphate fixation. Hilgardia 12: 343-382.

113. Nutman, F.J. (1933). The root system of Coffee Arabica L. Part I. Root systems in typical soils of British East Africa. Part II. The effect of some soil conditions in modifying the 'normal' root system. Empire J. Expt. Agric. 1(3-4); 271-84 and 285-96.

114. Nye, P.H. and Bertheux, M.H. (1957). The distribution of phosphorus in forest and savannah soils of the Gold Coast (Ghana) and its agricultural significance. J. of Agric. Sci. 49: 141-159.

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

116. ___________ et al. (1954). Estimation of available phosphorus in soils by extraction with sodium bicarbonate. U.S. Dept. of Agric. Circular 939.

117. Paul, H. (1954). Phosphorus status in peat soils (pegasse) in British Guiana. Soil Sci. 77: 87-93.

118. Pearson, R.W. and Simonson, R.W. (1939). Organic phosphorus in seven Iowa soil profiles: Distribution and amounts as compared to organic carbon and nitrogen. Soil Sci. Soc. Amer. Proc. 4: 162-167.

119. _____________ et al. (1940). The vertical distribution of total and dilute acid-soluble phosphorus in twelve Iowa soil profiles. Agron. J. 32: 683-696.

120. Pereira, H.C. (1957). Field measurements of water use for irrigation control in Kenya coffee. J. of Agric. Sci. 49: 459-466.

121. ____________ and Jones, P.A. (1954). Field responses by Kenya coffee to fertilizers, manures, and mulches. Empire J. Expt. Agric. 22: 23-36.

122. Petersen, G.W. and Corey, R.B. (1966). A modified Chang and Jackson procedure for routine fractionation of inorganic soil phosphates. Soil Sci. Soc. Amer. Proc. 30: 563-565.

123. Pratt, P.F. and Garber, M.J. (1964). Correlations of phosphorus availability by chemical tests with inorganic phosphorus fractions. Soil Sci. Soc. Amer. Proc. 28: 23-26.

124. Rennie, D.A. and McKercher, R.B. (1959). Adsorption of phosphorus by four Saskatchewan soils. Canadian J. of Soil Sci. 39: 64-75.

125. Robinson, J.B.D. (1957). The critical relationship between soil moisture content in the region of wilting point and the mineralization of natural soil nitrogen. J. of Agric. Sci. 49: 100-105.

126. ______________ and Hosegood, P.H. (1965). Effects of organic mulch on the fertility of a latosolic coffee soil in Kenya. Expt. Agric. I: 67-80.

127. Rotini, O.T. and El-Nennah, M. (1971-1972). Evaluation of the relative availability of inorganic phosphorus fractions in some Italian soils using isotopic exchange and solubility criteria. Agrochimica 16: 23-30.

128. Russell, E.J. (1932). Soil Conditions and Plant Growth, p. 477. London.

129. Russell, E.W. (1961). Soil Conditions and Plant Growth, Longmans, Green and Co. Ltd., London.

130. Russell, G.C. and Low, P.F. (1954). Reaction of phosphate with kaolinite in dilute solution. Soil Sci. Soc. Amer. Proc. 18: 22-25.

131. Russell, R.S. et al. (1954). Isotopic equilibria between phosphates in soil and their significance in the assessment of fertility by tracer methods. J. of Soil Sci. 5: 85-105.

132. Sauchelli, V. (1965). Phosphates in Agriculture. Reinhold Publ. Corp. New York.

133. Saunder, D.H. (1956). Determination of available phosphorus in tropical soils by extraction with sodium hydroxide. Soil Sci. 82: 457-463.

134. Seatz, L.F. (1954). Phosphate activity measurements in soils. Soil Sci. 77: 43-52.

135. Shapiro, R.E. (1958a). Effect of flooding on availability of phosphorus and nitrogen. Soil Sci. 85: 190-197.

136. ____________ (1958b). Effect of organic matter and flooding on availability of soil and synthetic phosphates. Soil Sci. 85: 267-272.

137. Sperber, J.I. (1958). Release of phosphorus from soil minerals by hydrogen sulfide. Nature 181: 934.

138. Stelly, M. and Pierre, W.H. (1943). Forms of inorganic phosphorus in the C horizons of some Iowa soils. Soil Sci. Soc. Amer. Proc. 7: 139-147.

139. Stevenson, F.J. (1959). Carbon nitrogen relationships in soil. Soil Sci. 88: 201-208.

140. Stout, P.R. (1939). Alterations in the crystal structure of clay minerals as a result of phosphorus fixation. Soil Sci. Soc. Amer. Proc. 4: 177-182.

141. Struthers, P.H. and Sieling, D.H. (1950). Effect of organic anions on phosphate precipitation by iron and aluminium as influenced by pH. Soil Sci. 69: 205-213.

142. Talibudeen, O. (1957). Isotopically exchangeable phosphorus in soils. II. Factors influencing the estimation of 'labile' phosphorus. J. of Soil Sci. 8: 86-96.

143. _____________ (1958). Isotopically exchangeable phosphorus in soils. III. The fractionation of soil phosphorus. J. of Soil Sci. 9: 120-129.

144. Tamimi, Y.N. et al. (1964). Reactions of ammonium phosphate with gibbsite and with montmorillonitic and kaolinitic soils. Soil Sci. 98: 249-255.

145. Taylor, D. (1957). The measurement of Radio isotopes. Methuen & Co. Ltd., London.

146. Tisdale, S.L. and Nelson, W.L. (1956). Soil fertility and fertilizers. The Macmillan Company, New York.

147. Toth, S.J. (1937). Anion adsorption by soil colloids in relation to changes in free iron oxides. Soil Sci. 44: 299-314.

148. Tripathi, B.R. et al. (1970). Native inorganic phosphorus forms and their relation to some chemical indices of phosphate availability for soils of Agra district, India. Soil Sci. 109: 93-101.

149. Truog, E. (1930). The determination of the readily available phosphorus of soils. Agron. J. 22: 874-882.

150. Turner, R.C. and Rice, H.M. (1954). Role of fluoride ion in release of phosphate adsorbed by Al and Fe hydroxide. Soil Sci. 74: 141-148.

151. Volk, V.V. and McLean, E.O. (1963). The fate of applied phosphorus in four Ohio soils. Soil Sci. Soc. Amer. Proc. 27: 53-58.

152. Wada, K. (1959). Reaction of phosphate with allophane and halloysite. Soil Sci. 87: 325-330.

153. Walker, T.W. and Adams, A.F.R. (1958). Studies on soil organic matter: I. Influence of phosphorus content of parent materials on accumulation of carbon, nitrogen, sulphur and organic phosphorus in grassland soils. Soil Sci. 85: 307-318.

154. Wang, C.H. and Willis, D.L. (1956). Radiotracer Methodology in Biological Science. Prentice-Hall, Inc., Englewood Cliffs, New Jersey.

155. Weir, C.C. (1962). Evaluation of chemical soil tests for measuring available phosphorus on some Jamaican soils. Tropical Agric. 39: 67-72.

156. __________ (1972). Phosphate studies on the Jamaican bauxite soils. Trop. Agric. (Trinidad) Vol. 49 No. 1, Jan. 1972.

157. Wiklander, L. (1950). Kinetics of phosphate exchange in soils. Annals of the Royal agr. College Sweden, 17: 407-424.

158. Wild, A. (1950). The retention of phosphate by soil: A review. J. of Soil Sci. 1: 221-238.

159. Williams, C.H. (1950a). Studies on soil phosphorus: I. A method for the partial fractionation of soil phosphorus. J. of Agric. Sci. 40: 233-242.

160. ______________ (1950b). Studies on soil phosphorus: II. The nature of native and residual phosphorus in some South Australian soils. J. of Agric. Sci. 40: 243-256.

161. ______________ (1950c). Studies on soil phosphorus: III. Phosphorus fractionation as a fertility index in South Australian soils. J. of Agric. Sci. 40: 257-262.

162. Williams, E.G. and Saunders, W.M.H. (1956). Distribution of phosphorus in profiles and particle-size fractions of some Scottish soils. J. of Soil Sci. 7: 90-108.

163. Williams, J.D.H. et al. (1967). Fractionation of soil inorganic phosphate by a modification of Chang and Jackson's procedure. Soil Sci. Soc. Amer. Proc. 31: 736-739.

164. Williams, L.A.J. (1969). The Volcanics of the Gregory Rift Valley, East Africa. Paper read at the International Symposium "Volcanoes and Their Roots," Oxford, England, Sept. 1969.

165. Williams, R. (1937). The solubility of soil phosphorus and other phosphorus compounds in sodium hydroxide solutions. J. of Agric. Sci. 27: 259-270.

166. Wright, B.C. and Peech, M. (1960). Characterization of phosphate reaction products in acid soils by the application of solubility criteria. Soil Sci. 90: 32-43.

167. Yuan, T.L. et al. (1960). Forms of newly fixed phosphorus in three acid sandy soils. Soil Sci. Soc. Amer. Proc. 24: 447-450.

APPENDIX

APPENDIX TO CHAPTER I

APPENDIX Ia

Some characteristics of Kikuyu Red Loam at the Coffee Research Station, Ruiru.

Data from Scott, R.M. (1963)

The soils of the Nairobi-Thika-Yatta-Machakos area.

Department of Agriculture, Nairobi. 60 pp.

Depth cm	Organic Matter %	Mechanical analysis %			Exchangeable bases* m.e./100 g soil			pH**
		Sand	Silt	Clay	Ca	Mg	K	
0-25	4.5	13.4	13.5	68.6	7.9	2.4	2.63	6.6
25-64	2.2	13.2	11.6	73.0	5.8	3.0	0.92	6.5
64-104	1.2	11.2	9.3	78.3	0.9	2.4	0.41	5.3
104-132	1.0	7.1	9.5	82.4	0.4	1.4	0.40	5.5
132-183	0.4	11.4	10.1	78.1	0.3	1.7	0.46	5.5
183-234	0.6	12.4	8.9	78.1	0.8	1.6	0.75	5.6

*1 soil: 10 neutral N- ammonium acetate

**1 soil: 5 water, glass electrode.

APPENDIX Ib (i)

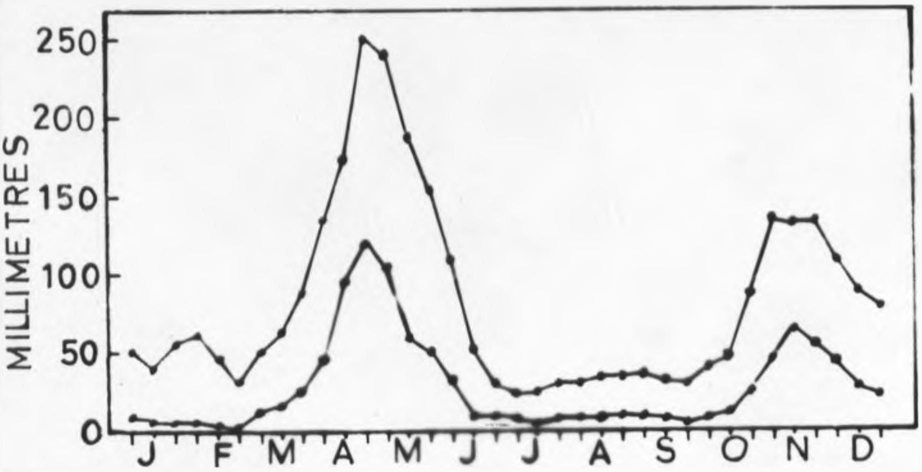
Rainfall and temperature data for
Jacaranda - Annual Means, 1945-72.

Data from 'Guide to the Coffee Research Station, Ruiru, 1974.'

MONTH	RAIN	TEMP. °C.	
	mm	max.	min.
January	50.1	26.3	12.0
February	41.8	27.7	13.0
March	98.8	27.2	13.6
April	237.9	25.0	14.7
May	187.9	24.0	13.7
June	46.1	23.2	12.1
July	24.0	22,0	11.6
August	30.4	22.5	11.6
September	31.2	25.1	12.0
October	71.0	26.1	13.4
November	148.8	24.1	14.0
December	80.1	24.7	12.9
TOTAL	1,048.1		
MEAN	87.3	24.8	12.9

APPENDIX Ib (ii)

1:1 CONFIDENCE LIMITS OF 2X10—DAY MOVING TOTALS OF RAINFALL AT COFFEE RESEARCH STATION, RUIRU, 1945—1967.



APPENDIX – Fig. I-1 AVERAGE RAINFALL DATA FOR THE COFFEE RESEARCH STATION, RUIRU.
Data from Huxley et al. (1969)

APPENDIX Ic

PROFILE MORPHOLOGY

A site for a soil profile, a pit measuring 3 ft. by 6 ft. and 20 ft. deep, was selected on the basis that it had not been cultivated for a considerable period and had a low degree of erosion; the site is well drained. Two sets of samples were taken; one of these for description and the second set for analysis.

Depth cm	Description
0 - 8	Dusky red (10 R 3/4, moist) humous clay; moderate medium and fine crumb structure; slightly sticky, slightly plastic, very friable moist, slightly hard dry; noncalcareous; many fine and medium interstitial pores; abundant fine and very fine roots; merging smooth boundary; pH 5.5.
8-15	Similar to horizon above but less humus; dark reddish brown (2.5 YR 2/4, moist) clay; very friable moist, slightly hard dry; diffuse, smooth boundary; pH 5.5.
15-30	Dark reddish brown (2.5 YR 2/4, moist) clay; moderate fine and medium subangular blocky structure breaking to strong fine and very fine granules; slightly sticky, slightly plastic; friable moist; slightly hard to hard dry; noncalcareous: many fine interstitial pores; few fine and medium roots; diffuse, smooth boundary; pH 5.0.

Depth, cm	Description
30 - 50	Dark red (2.5 YR 3/6, moist) clay; strong medium subangular blocky structure breaking to strong very fine angular blocks; slightly sticky, slightly plastic; friable moist; hard dry; noncalcareous; many fine interstitial pores; very few fine roots; diffuse boundary; pH 4.9.
50 - 90	Very similar to horizon above except for the colour which is dark reddish brown (2.5 YR 3/4, moist); diffuse boundary; pH 5.0.
90 - 140	Dark red (2.5 YR 3/6, moist) clay; strong medium subangular blocky structure breaking to moderate very fine angular blocks; sticky, slightly plastic; friable moist; hard dry; noncalcareous; many fine interstitial pores; very few fine roots; diffuse boundary; pH 5.2.
140 - 190	Very similar to horizon above, dark red (2.5 YR 3/6, moist) except for the pH which is 5.8; diffuse boundary.
190 - 240	Dark reddish brown (2.5 YR 3/4, moist) clay; strong coarse subangular blocky structure breaking to strong fine and medium angular blocks; sticky, slightly plastic; friable to firm moist; very hard dry; noncalcareous; many fine interstitial pores; few medium roots; diffuse boundary; pH 6.2.

Depth, cm	Description
240 - 290	Very similar to horizon above, dark reddish brown (2.5 YR 3/4, moist) clay; pH 6.9.
290 - 340	Similar to horizon above, dark reddish brown (2.5 YR 3/4, moist) clay; pH 7.7.
340 - 390	Similar to horizon above, dark red (2.5 YR 3/6, moist) clay; pH 7.8.
390 - 620	Similar to horizon above, but dark reddish brown (2.5 YR 3/4, moist) clay; sporadic weathered ironstones; pH ranges between 7.8 and 8.0.