

THE DISTRIBUTION OF PHOSPHORUS AND FATE
OF APPLIED PHOSPHATES IN SOME SOILS
OF MID-WESTERN NIGERIA

By

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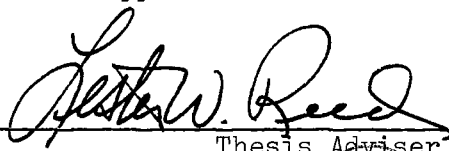
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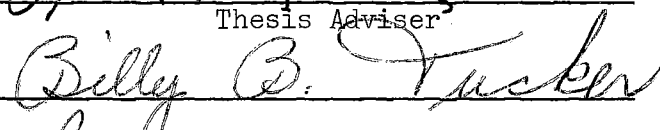
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CHAPTER I

INTRODUCTION

The present agriculturally important soils of Mid-Western Nigeria have often been broadly referred to as soils of the Benin series. It is recognized that these soils are acid and infertile. The International Bank Mission to Nigeria (101)¹ recommended that high priority be given to investigating the deficiencies of these soils and finding economic means of overcoming them.

No detailed and widespread chemical study of these soils has been made. At best the studies done have been restricted to commercial plantations where fertility tests were made solely for the purposes of determining fertilizer requirements of plantation plots. On the whole, chemical data on the fertility status of the soils of Mid-Western Nigeria have not been readily available.

The Mid-Western Nigerian Ministry of Agriculture and Natural Resources has continued to carry out fertilizer experiments on some of these soils to determine the responses of different crops to various fertilizer treatments of the soils. The experiments have consistently shown that, for upland rice, phosphorus fertilization alone resulted in remarkable yield increases. The Research Branch

¹Number in parenthesis refer to literature cited.

of the Ministry of Agriculture and Natural Resources, in its 1963/64 Annual Report (79) concluded that phosphate alone is the main deficient nutrient in peasant rice farms and recommended that phosphate alone and in combination with nitrogen be further tested on farmers' fields.

The introduction of the Food and Agriculture Organization Free From Hunger Campaign fertilizer trials and demonstrations brought about a more widespread fertilizer experimentation on the different soils of Mid-Western Nigeria. These experiments have shown that phosphorus is the most limiting nutrient element in the production of upland rice (38). For example, in 1963 the mean of 23 F.A.O. trial sites in Benin Province showed that phosphorus alone, applied at the rate of 20 pounds per acre increased the yield of upland rice by 24 percent while nitrogen alone applied at the same rate increased yields by seven percent. Nitrogen and phosphorus (20-20-0) together increased yield 15 percent while nitrogen, phosphorus and potassium (20-20-20) increased yield 10 percent.

With these findings on the role of phosphorus in the production of upland rice, and bearing in mind the fact that the rice crop will definitely assume a greater importance in the agricultural economy of Mid-Western Nigeria, it becomes necessary to make a thorough study of the phosphorus chemistry of the soils so as to understand more clearly the factors responsible for the responses to phosphorus fertilization. Such knowledge will be vital in determining the future fertilizer needs of the soils and in formulating a stable fertilizer policy. According to Kurtz (71), "knowledge of the chemistry of phosphorus in soils is a requirement for knowledge of its utilization by plants, and explanations of soil-plant relations will be clear only when the forms and properties of soil phosphorus are known."

Different forms of phosphorus fertilizers have been used on soils of Mid-Western Nigeria with varying degrees of success. The ammonium phosphates (mono-and di-basic), as phosphorus fertilizers, are destined to become very important in commerce. It was thus considered necessary to find out what happens to these phosphorus fertilizer compounds when added to the soils - by making a chemical investigation of their reactions with the soils. Results of this investigation will help determine how the compounds could be manipulated to be most effective.

CHAPTER II

REVIEW OF LITERATURE

Fractionation of Soil Phosphorus

The characterization of phosphorus compounds in the soil has been attempted by many workers and increasing precision and accuracy in the methods of characterization have continued to be attained.

Fisher and Thomas (42), developed a method based upon the relative rates of solution of soil phosphorus compounds in buffered acid extractants and differentiated the following groups of compounds:

- (A) Amorphous and finely divided crystalline phosphates of calcium, magnesium and manganese;
- (B) Amorphous phosphates of aluminum and iron;
- (C) Phosphates adsorbed upon hydrous oxides and those present in the form of apatite; and
- (D) By difference, phosphates present in crystalline phosphates of aluminum and iron.

In their method apatite was extracted with 0.002N sulfuric acid of pH2 while the other compounds (phosphorus present in amorphous and finely divided crystalline phosphates of calcium, magnesium and manganese, and in amorphous phosphates of iron and aluminum) were extracted with acetic acid of pH5 in which they were appreciably soluble.

Williams (112) developed a fractionation method by which he classified the phosphorus compounds of the soil, on the basis of their solubility in sodium hydroxide, as follows: (a) soluble - phosphorus in combination with sesquioxides, organic phosphorus, exchangeable phosphorus of clay complex, phosphorus of calcium compounds such as CaHPO_4 , phosphorus of water soluble compounds; (b) insoluble - phosphorus in compounds of the apatite class; (c) doubtful - phosphorus in the interior of the clay lattice, and phosphorus of titanium compounds.

Dean (30) 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.

Ghani (47) argued that the methods of extraction and determination of the fractions of soil phosphorus adopted by Dean (30) were more or less empirical in nature. He made the following modifications in which he divided soil phosphorus into five groups as follows:

1. Acetic acid - soluble. Mono-, di- and tricalcium phosphates.
2. Alkali-soluble inorganic. Iron and aluminum phosphates.
3. Alkali - soluble organic. Total organic P of the soil (nucleic acid, phytin, lecithin, etc.)
4. Sulfuric acid - soluble. Phosphates of the apatite types.
5. Insoluble

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

Ghani (48) modified his first method when it was discovered that some of the phosphate brought into solution by the acetic acid was re-adsorbed by the soil and then extracted in the sodium hydroxide extraction; he suggested the use of 8-hydroxyquinoline as a means of blocking re-adsorption or precipitation of phosphate by active iron and aluminum during the acetic acid extraction.

Williams (109), while adopting Ghani's (48) hydroxyquinoline method, made a further modification by omitting the final extraction with sulfuric acid. His procedure was as follows:

1. Acetic acid-8-hydroxyquinoline extraction: water soluble phosphates, calcium phosphates, hydroxy- and carbonate-apatite, magnesium and manganese phosphates.
2. Sodium hydroxide extraction: (a) Inorganic phosphates: adsorbed phosphate, basic iron and aluminum phosphates, titanium phosphate. (b) Organic phosphorus
3. Insoluble in either extractant: chloro and fluo-apatite, crystal lattice phosphorus.

Bhangoo and Smith (11) studied the chemical characterization of phosphorus present in various Kansas soils and grouped the forms into four categories:

- (a) phosphorus soluble in 0.1NHCl (calcium phosphate)
- (b) cold alkali soluble phosphorus (adsorbed phosphorus)
- (c) hot alkali soluble phosphorus (iron and aluminum phosphates)
- (d) organic phosphorus

A great turning point in phosphorus fractionation was reached in 1957 when Chang and Jackson (18) reported on their systematic method of phosphorus fractionation by which it was possible to fractionate soil inorganic P into discrete chemical forms as follows:

1. Aluminum phosphate extracted with neutral 0.5N NH_4F
2. Iron phosphate extracted with 0.1N NaOH
3. Calcium phosphate extracted with 0.5N NH_2SO_4
4. Reductant soluble iron phosphate (iron oxide occluded) extracted with a basic dithionite citrate solution.
5. Occluded aluminum phosphate extracted with neutral 0.5N NH_4F after the dithionite treatment.

Fife (40,41) worked with non-soil and soil systems. He showed that the most general selective delineation of aluminum-bound soil phosphate by ammonium fluoride extractant is likely to be attained at approximately pH8.5 instead of pH7 as proposed by Chang and Jackson (18).

Glenn, et al. (51), while supporting the views of Fife (40,41) on the pH of the NH_4F extractant for aluminum phosphate, also made the following modifications in the Chang and Jackson (18) procedure: extraction of the iron phosphate with 0.1N NaOH for 9 to 17 hours instead of 17 hours as originally proposed; followed by extraction of all occluded phosphate before removal of calcium phosphate as the 0.5N NH_2SO_4 used to extract calcium phosphate tends to remove some of the occluded phosphate.

Chang (16) after reviewing the criticisms of other investigators made the following modifications:

1. Extraction of aluminum phosphate with 0.5N ammonium fluoride of pH7 for one hour for paddy soils and extract on a pH8.2 for one hour for upland soils.

2. Extraction of iron phosphate with 0.1N sodium hydroxide in nine to 12 hours.

3. Extraction of calcium phosphate with 0.5N sulfuric acid in one hour -- after the extraction of occluded phosphate.

However, the original Chang and Jackson (18) procedure still gives accurate and reproducible results. Although, considerable progress has been made in the development of methods of phosphorus fractionation, perfection has not been attained; at best, the results obtained by present fractionation methods are still mere approximations of realities in the soil.

Distribution of Phosphorus in the Soil

Soil phosphorus fractionation has been the chief tool employed in the study of phosphorus distribution in the soil; improvements in fractionation techniques have thus meant better understanding of phosphorus distribution in the soil.

Dean (30) originally classified the phosphorus compounds of soils into three main groups: organic, inorganic and insoluble phosphorus. In his work in the classical plots at Rothamsted and Woburn he found that the largest fraction of the total soil phosphorus was in the insoluble fraction; this fraction was not increased by the long-continued use of phosphatic fertilizers at Rothamsted and Woburn. Before the work of Dean at Rothamsted, Marshall (75) had suggested that this insoluble phosphorus may form a part of the clay lattice. Dean (30) also found relatively large amounts of organic phosphorus in the soils studied; he discovered that the amounts of organic phosphorus were closely related to the carbon contents of the soils.

Pearson, et al. (90) studied the vertical distribution of total phosphorus in twelve Iowa soil profiles and in all the profiles studied they found that total phosphorus decreased with depth to a minimum between the lower A and upper C horizons. Below this zone, in eleven of the twelve 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 (89) studied organic phosphorus in seven Iowa soil profiles. They found that the amounts ranged from 205 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. For the soils, C:P ratio was between 100 and 200 and N:P ratio was between 8 and 16.

Ghani and Aleem (49) studied the vertical distribution of various phosphorus fractions in a number of Indian soil profiles and found total phosphorus to be at a minimum in the intermediate layers of the profiles. Iron and aluminum phosphates expressed as percentage of the total phosphorus were found to be at their maximum at the intermediate layers --- the zones of maximum root development. Organic phosphorus, organic carbon and nitrogen decreased with depth in most of the soils. On the average, C:N and C:P ratios decreased with depth whereas the N:P ratio showed a maximum in the subsurface.

Williams (110) examined the native phosphorus in a series of red-brown earth and solonized brown (mallee) soils of South Australia. Over 50 percent of the mean total phosphorus in both groups of soils was in the insoluble form and approximately 30 percent 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.

Fuller and McGeorge (46) showed calcareous Arizona soils to be well supplied with organic phosphorus, although the amount decreased rapidly to a depth of 24 inches. The organic phosphorus comprised a very small part of the total below this depth.

Aldrich and Buchanan (6) studied the phosphorus content of soils and parent rocks in southern California and concluded that the phosphorus content of the parent rock materials from which the soils were derived appeared to be the primary factor in determining the phosphorus content of soils.

Paul (88) found that more than 70 percent of the total phosphorus of peat soils (pegasse) in British Guiana is present as organic and inorganic alkali-soluble (iron and aluminum phosphate but mainly iron phosphate in these soils) forms.

Karim and Khan (65) made an investigation of the probable relationship between pH and the organic, adsorbed, and sesquioxide-bound forms of phosphorus in some soils of East Pakistan and made the following observations:

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

(ii) 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 the sesquioxide phosphorus decreased.

(iii) 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 thus suggested that the critical influence of pH 5.3 and 5.6 might be due to changes in the state of iron and aluminum with the change of pH of the medium.

Williams and Saunders (111) studied the phosphorus distribution in seven soil profiles of northeast Scotland and arrived at the following conclusions:

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

(ii) The clay and silt together contain 85 percent and more of the total soil organic phosphorus, but the sands also contain appreciable amounts.

(iii) The phosphorus content of the fractions vary widely depending on the soil, but the total phosphorus 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.

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

(v) In the topsoils the coarse sands account for 12-22 percent of the total soil inorganic phosphorus and the fine sands for 18-50 percent, giving totals of 34-62 percent in the combined sands. The tendency is for these proportions to increase with depth, and in the gleyed subsoils the values for the combined sands are of the order of 70-80 percent.

(vi) The inorganic phosphorus in the sands, particularly the fine sand, is very highly soluble in $0.2\text{NH}_2\text{SO}_4$ and appears to be largely calcium-bound.

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

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

Bhangoo and Smith (11) fractionated the phosphorus in seven Kansas surface soils and corresponding subsoils and found that iron and aluminum phosphates accounted for more than half of the total phosphorus in surface material and about two-thirds of that in subsoils. Organic phosphorus represented about one-third of the total phosphorus in surface soils and one fifth in subsoils.

Walker and Adams (106) analyzed twenty-two grassland soils of New Zealand to a depth of 21 inches for carbon, nitrogen, sulphur and organic and total phosphorus. They found that the total phosphorus content of the soils was closely related to phosphorus content of the parent materials, and that the 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 phosphorus is the only one of these four elements that must be supported by the

parent material, they concluded that, in the particular climatic zone of New Zealand, the major factor governing accumulation of organic matter is the phosphorus content of the parent material.

Nye and Bertheux (83) studied the distribution of phosphorus in forest and savannah soils of the Gold Coast (Ghana). They found that the forest soils contained much more inorganic as well as more organic phosphorus than the savannah soils, in spite of the more intense leaching and deeper weathering of the forest soils. The higher amount of organic phosphorus found in the forest soil was attributed to the increased amount of organic matter in the forest soils. The organic phosphorus content for the soils was closely correlated with the organic carbon content. The carbon:phosphorus ratio averaged 233 in forest soils and 247 in savannah soils. The nitrogen:phosphorus ratio averaged 21.6 in forest soils and 19.5 in savannah soils. The C/P and N/P ratios fell with depth in the profiles.

Nye and Bertheux also found that, in the leached forest soils, the total phosphorus was greatest in the surface horizons and decreased with depth while the savannah soils showed less clear evidence of a surface accumulation. In both the forest and savannah sites the acid-soluble phosphorus (calcium phosphate) in leached profiles fell rapidly to trace values below one foot depth. The inorganic alkali-soluble (iron and aluminum phosphates) fraction declined much more slowly with depth than the acid soluble fraction. The proportion of the total phosphorus in the insoluble form tended to increase with depth, corresponding to the declining proportions of the acid- and alkali-soluble inorganic and the organic phosphorus.

The averages for the forest and savannah soils showed that the insoluble phosphorus amounted to more than half of the total phosphorus. The amount of organic phosphorus fell with depth, but it fell more slowly than might be expected from the fall in total organic matter.

These show that earlier workers were able to identify calcium, aluminum and iron phosphates as important or active forms of soil inorganic phosphorus. There remained, however, a highly noticeable phosphate fraction which they could not characterize; this was called insoluble or residual phosphorus.

Chang and Jackson (18) developed a more illuminating classification and identification of the soil inorganic phosphorus fractions. They classified inorganic phosphates in the soil into four main groups: calcium phosphate, aluminum phosphate, iron phosphate, and the reductant soluble phosphate extractable after removal of the first three forms. Calcium phosphate exists mainly in hydroxyapatite, but dicalcium, monocalcium, and octacalcium phosphate also exist in small amounts or as transitional forms. Iron, aluminum and calcium phosphates also included adsorbed and surface-precipitated phosphates associated with the respective types of soil particles.

Reductant soluble phosphate is the fraction which earlier workers had referred to as insoluble, residual or lattice phosphorus. Chang and Jackson (18) showed that this insoluble fraction is almost completely dissolved by the dithionite-citrate reduction-chelation procedure of Aguilera and Jackson (3) for dissolving free iron oxide coatings. An iron oxide precipitate apparently is formed on the surface of iron phosphate and on the surface of aluminum-iron phosphate (barrandite-like) in the course of chemical weathering in

soils by hydrolysis of iron phosphate and other iron salts. The relative insolubility of iron oxide in the extractants for the other inorganic phosphate fractions must account for the fact that phosphate thus covered can only be dissolved after the removal of the iron oxide coating. The reductant soluble phosphate has also been referred to as occluded phosphate.

Other workers have observed that total phosphorus tends to decrease with increasing profile depth but Hamilton and Lessard (52) found 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 in the 6-12 inch layer to 538 in the 18-24 inch layer. The contribution of calcium phosphates to total phosphorus increased from 41.1 percent in the surface layer to 88.4 percent in the 18-24 inch layer. Aluminum phosphate was highest in the 0-6 inch layer and accounted for five percent 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 aluminum phosphates, formed a substantial percentage of total phosphorus in the surface soil. Organic phosphorus decreased with depth of soil profile.

Bates and Baker (9) investigated the distribution of phosphorus in the profile and in various soil fractions of a Western Nigerian soil. They found that the soil phosphorus was accumulated in the surface soil. Below two inches there was a marked fall in total phosphorus, reflecting a large decrease in the amount of organic phosphorus. Thereafter the total phosphorus was fairly constant down the profile. The concentration of phosphorus in the iron concretions was considerably higher than in the surrounding fine earth. In the gravel horizon,

12-30 inches, over 80 percent of the total phosphorus at this level was immobilized in the concretions.

Dormaar and Webster (34) studied the status of organic phosphorus in some Alberta soils and found that total organic phosphorus content decreased with increasing depth in all profiles. They concluded that, for the soils studied, organic phosphorus formed an integral part of the organic matter.

Under the leadership of Chang and Jackson (19), the distribution of inorganic phosphorus in the soil has been carried into the realm of soil weathering and genesis. They fractionated the inorganic phosphorus of soils representing some widely different major soil groups -- using the Chang and Jackson (18) fractionation procedure. They found that three horizons of one chernozem profile, a dark brown soil, and the calcareous C₁ horizon of a grey-brown podzolic soil contained 68-95 percent of their inorganic phosphorus in the form of calcium phosphate, the other forms decreasing exponentially in the sequence. The inorganic phosphorus of two latosols increased exponentially in the order calcium phosphate (one percent), aluminum phosphate (0-3 percent), iron phosphate (10-13 percent) and occluded (reductant soluble) phosphate (66-78 percent). Three samples of podzolized soils contained intermediate distributions of the four phosphates. They concluded that the distribution of soil inorganic phosphorus in soils measured the degree of chemical weathering, the chemical weathering sequence being calcium phosphate, aluminum phosphate, iron phosphate, and occluded phosphate.

This conclusion of Chang and Jackson (19) has been confirmed by other workers in different parts of the world.

Chu and Chang (21) fractionated the phosphorus of some soils of Taiwan. They found the discrete fractions distributed in a pattern influenced by soil genesis. Iron phosphate was dominant in the pattern to which highly weathered latosols belong; calcium phosphate was dominant in the pattern for calcareous soils, mudstones, alluvial soils, saline alluvial, slate alluvial and schist alluvial soils; while iron phosphate and calcium phosphate were dominant in acid sandstones and shale alluvial soils.

Hesse (57) found the distribution of phosphorus in the mud from a Sierra Leone mangrove swamp to be as follows: water-soluble phosphorus (2 ppm), aluminum phosphate (6ppm), iron phosphate (29 ppm), reductant iron phosphate (nil), calcium phosphate (25 ppm), organic phosphorus (485 ppm). Thus 87 percent of the total phosphorus is in organic combination and the remainder is almost entirely associated with iron and calcium. Hesse concluded that the absence of occluded forms of phosphorus was not surprising since the swamp muds are comparatively unweathered. Hesse (58) obtained similar results when he fractionated the phosphorus in the mangrove swamp muds collected from Warri, Nigeria.

Benavides (10) fractionated the inorganic phosphorus of some tropical soils of Colombia, South America and a profile of an Oklahoma Minco soil series (a reddish prairie soil) for purposes of comparison. The results showed that calcium phosphate was the most important fraction in the Minco soil; reductant soluble iron phosphate was not important and varied from five to seven percent of total phosphorus. On the contrary, reductant soluble iron phosphate went up to 54 percent of total phosphorus in some of the tropical soils (which were more strongly weathered than the Oklahoma soils). Ohiaeri

(84) determined the stages of weathering of some Oklahoma soil series by studying the distribution of inorganic phosphorus fractions in their profiles.

Dahnke et al. (27) made a study of the phosphorus fractions in selected soil profiles of El Salvador, Central America. They observed that, in the younger soils, a greater proportion of the total phosphorus was 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.

The above results show that, within limits, the stage of chemical weathering of a soil could be assessed from a knowledge of the distribution of the various inorganic phosphorus fractions in it.

Available Phosphorus in Soils

It is recognized that only a fraction of the phosphorus in soils is available for direct use of growing plants. Several methods have been devised for the measurement of this available phosphorus fraction. One of the earliest ones was that of Truog (102) in which the available phosphorus is extracted from soil with 0.002N sulfuric acid. This was followed by the method of Morgan (80) in which the extracting solution is 10 percent sodium acetate. Bray and Kurtz (13) later introduced their Nos. 1 and 2 methods; in the No. 1 method the extraction solution is made up of 0.03NNH₄F and 0.025NHCl; the No. 2 extraction solution is made up of 0.03NNH₄F and 0.1NHCl. Olsen et al. (86) introduced a method in which the extraction solution is 0.5MNaHCO₃. Saunder (94) suggested the use of hot 0.1NNaOH for extracting available phosphorus in tropical soils, particularly red earths, where phosphorus

is retained in strongly adsorbed forms. Recently, Al-Abbas and Barber (4,5), by correlation of soil phosphorus fractions with phosphorus uptake by millet, developed a method in which available phosphorus is extracted with a solution of 0.3N NaOH and 0.5N $\text{Na}_2\text{C}_2\text{O}_4$.

Different merits and demerits have been claimed for each of the above methods of determination of available phosphorus but a particular method becomes useful only when the results obtained with it could be correlated with crop responses to fertilizer in the field -- for the particular area concerned. Pratt and Garber (91), and Chai and Caldwell (15) have made a comparison of some of these methods. Weir (107) evaluated some of the above methods on some Jamaican soils. According to him, in the order of decreasing precision of estimating the available phosphorus of the soils, the methods are as follows: (1) 0.002N sulfuric acid method by Troug; (2) 0.1N HCl method by Bray; (3) 0.5M NaHCO_3 method of Olsen and co-workers; (4) 10 percent sodium acetate method of Morgan; and (5) 0.1N sodium hydroxide method of Saunder.

The available phosphorus forms in soils are regarded as contributed essentially by the inorganic phosphorus fraction and organic phosphorus not contributing until it is mineralized to the inorganic form. The occluded fraction of the inorganic phosphorus, by its inactive nature, is regarded as not making any important contribution to the available phosphorus in soils. Dean (30), for example, in his work on the classical plots of Rothamsted and Woburn found that occluded phosphorus (which was then termed insoluble phosphorus) in the soil was not changed by the long-continued use of phosphatic fertilizers. Calcium, aluminum and iron phosphates are thus the phosphorus fractions which are regarded as making the major contributions to available phosphorus. The solutions used in extracting available phosphorus are believed to

extract a proportionate part of each of these fractions. The amount of either calcium, aluminum or iron phosphate extracted by any solution will depend on the relative solubilities of the different fractions in the particular solution. The correlation found between chemically determined available phosphorus and any of calcium, aluminum or iron phosphate may thus largely depend on the method by which the available phosphorus was characterized.

Ochiaeri (84), working with some Oklahoma soils found a significant correlation between aluminum phosphate and Bray and Kurtz No. 1 available phosphorus but there was no significant correlation with calcium phosphate; there was no correlation with iron phosphate and organic phosphorus. The lack of significant correlation between available phosphorus and calcium phosphate has also been observed by Pratt and Garber (91) and by Chai and Caldwell (15) who argued that calcium phosphate as measured by the Chang and Jackson (18) technique is not related to phosphorus availability as indicated by the Bray and the sodium bicarbonate tests.

Benavides (10), on the other hand, working with tropical soils of Colombia, South America found significant correlations between Bray and Kurtz No. 1 available phosphorus and calcium phosphate, iron phosphate and organic phosphorus but no significant correlation with aluminum phosphate.

According to Russell (93), 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 given dressings of 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. Simple chemical extraction methods are, therefore, unsuitable for measuring the phosphate supply available to the crop and though an incubation method is more suitable, the supply depends on the concordance in time between the crop's requirements for the phosphate and its production from the organic matter. It is probable that the amount of organic phosphate mineralized can be estimated from the readily extractable and oxidizable 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.

Abdul (1) studied the effect of lime on the availability of phosphorus in the soils of El Zamorano, Honduras. He observed that highly significant yield increases were obtained when the acid soil (pH 5.5) was limed to a pH of 6.5. The highest yields were obtained on plots receiving both lime and phosphorus. According to Abdul (1) the major portion of the potentially available phosphorus in Zamorano soils is in the organic fraction; analysis of the final soil samples showed that liming liberated the phosphorus locked up in the organic form and increased the efficiency of applied phosphorus for crop use.

Dalton et al. (28), observed that organic matter added to the soil as an amendment was effective in increasing the availability of soil phosphate. The fixation products of phosphate with iron and aluminum, they stated, were relatively poor sources of phosphate for plants. The activity of the organic matter in making soil phosphate available was attributed to the ability of certain metabolic products of

microbiological decomposition to form stable complex molecules with the iron and aluminum that are responsible for phosphate fixation in acid soils.

Acquaye (2) in Ghana found that the high correlation between cocoa yield response and organic phosphorus content of the top soil in nitrogen and phosphorus treated plots could be explained by the fact that the nitrogen and phosphorus increased the mineralization of the soil organic phosphorus.

Under certain conditions, water-logging and flooding have been shown to make soil phosphorus more available to crops. Islam and Elahi (61) 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. According to them, whatever may be the mechanism of this reduction (ferric-ferrous), water-logging seems to mobilize the fixed phosphorus in the soil and make it more available to the plants; further, the addition of organic matter such as green manures will make the phosphorus more available. Islam and Choudhury (60) studied the distribution of iron, manganese and phosphorus in the paddy soil profiles of Dacca, East Pakistan. They observed 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 this was due to its movement as 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 of phosphorus to plants, but

also exert great influence on the distribution and availability to plants of other nutrients, particularly phosphorus and sulfur.

Shapiro (95) 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 lowland (Colusa) and an upland (Korean) variety of japonica rice. The flooding increased the availability of soil phosphorus, but had no apparent effect on the availability of soil nitrogen. The applied phosphorus and nitrogen were both utilized more efficiently under flooded conditions. In a later work Shapiro (96) showed 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. According to him, reduction is the more important effect of both flooding and organic matter.

Basak and Bhattacharya (7) studied phosphate transformations in rice soil in West Bengal, India. They concluded that water-logged soils tend to show an unique capacity of regenerating an increasing quantity of available phosphorus during the active period of crop life. According to them the source of its supply and the cause of its regeneration were probably embraced in the release of phosphorus from the mineralization of organic phosphorus and the reductive transformation of iron and aluminum phosphates under anaerobiosis developed due to water-logging. The amount of phosphorus 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 (97) has shown that sulfides in the soil (produced mainly by micro-organisms) may reduce ferric phosphate to ferrous sulfide and release available phosphate. Sesquioxides would greatly hinder release of phosphates by this mechanism, but in water-logged siliceous soils, low in sesquioxides but high in hydrogen sulfide, release of phosphate might be of importance.

This phenomenon by which flooding and water-logging make phosphorus more available as a result of reduction is of tremendous importance in the fertility of paddy or swamp rice soils. The reduction considerably hinders the accumulation of occluded phosphate so that the percentage of this fraction of inorganic phosphate is always low in paddy soils.

Phosphorus Fixation and its Mechanism

It has long been recognized that phosphates added to the soil soon become fixed or immobilized. This phenomenon has been of considerable interest since the extent to which a particular soil will fix added phosphates will determine the efficiency and economics of fertilizer use on the soil.

Phosphorus fixation has been defined in different ways. Davis (29) states 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 (31) defines fixed phosphorus as the soil phosphorus which has become attached to the solid phase of soils. Midgley (78) defines phosphate fixation as the conversion of soluble form and further states that "while this fixed phosphate is considered to be insoluble in water, it may or may not be available to plants." Wild (108) states 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." According to Dean (31), 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.

The mechanisms postulated as being responsible for phosphorus fixation are as varied as the definitions given for phosphorus fixation itself. Davis (29) postulated the following mechanisms: (a) 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. (b) By double decomposition, relatively insoluble soil minerals react to form insoluble phosphates. (c) Phosphates are adsorbed at the extensive soil-solution interface. (d) Phosphates are adsorbed by the soil minerals to form complex systems in one or more of the solid soil phases. Kardos (64) places the types of reactions by which phosphorus becomes fixed in three general groups: adsorption, isomorphous replacement, and double decomposition involving solubility-product relations.

From a consideration of the ionization constants of phosphoric acid (H_3PO_4), Buehrer (14) 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^{--} , and PO_4^{---} . His work shows that all phosphate reaction systems will be fundamentally influenced by the hydrogen ion activity in the systems.

Murphy (81) found that grinding greatly increased the capacity of kaolinite to retain applied phosphate, which is quite indicative of adsorption.

Low and Black (74) plotted the amount of phosphorus fixed by kaolinite against the equilibrium concentration of phosphorus in dilute solutions and found the data to fit a typical adsorption curve which could be represented by a Freundlich adsorption equation having the form $x/m = kc^{1/n}$ where x/m = amount of phosphorus adsorbed, c = amount of phosphorus remaining in solution, k and n = constants. They further found that the degree of adsorption was increased by increasing temperature and, hence, concluded that adsorption was chemical.

Kurtz, De Turk and Bray (72) found that phosphate adsorption curves for different soils were similar in shape and could be expressed by an equation of the Freundlich type.

Hemwall (56), however, states that since many precipitation reactions could be characterized by the Freundlich isotherm, it is fallacious to characterize phosphorus fixation as adsorption on the basis of compliance with the Freundlich isotherm alone.

Rennie and McKercher (92) 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 μ gP/ml. They contend that the Freundlich equation is an empirical equation which 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 (85), and Fried and Shapiro (45) had earlier 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

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

where c = the final solution concentration (equilibrium concentration) in $\mu\text{gP/ml}$,

$\frac{x}{m}$ = μgP adsorbed per gram 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 $c/x/m$ against c can be assumed to be indicative of an adsorption reaction.

Hsu (59) has also obtained results which indicate that the relationship between the phosphate fixed and the concentration of phosphate in solution follow the Langmuir adsorption isotherm. He successively extracted one of his phosphated samples ten times with 0.0015NKCl solution and found that the phosphate desorption again followed the Langmuir adsorption isotherm.

Wada (105) in studying the reaction of ammonium phosphate with allophane and halloysite 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 $(\text{NH}_4)_2\text{HPO}_4$, was suggested by Wada as a probable mechanism of the reaction.

Most of the results obtained in the study of phosphate fixation in acid soils point to the fact that fixation is primarily due to the formation of iron and aluminum phosphate compounds. Many workers (10,25,26,35,36,37,44,50,63,69,104) have shown that the ability of acid soils to fix phosphorus is directly related to their contents of iron and aluminum. Most of these workers were able to show conclusively that removal of the iron and aluminum oxides, from the soil samples studied, drastically reduced the phosphate fixing capacity of the soils. Coleman et al. (24) observed that the amounts of phosphate sorbed by sixty subsoil samples from the North Carolina Piedmont were correlated with exchangeable aluminum content. The removal of exchangeable aluminum by salt-leaching reduced phosphate sorption by soils that contained appreciable quantities of this ion.

The phosphorus fixed as iron or aluminum phosphate could be further immobilized by the formation of occluded phosphate as described by Chang and Jackson (18).

It has been shown that precipitates of definite crystalline structure are formed when phosphate reacts with iron, aluminum and other elements in the soil (43,54,55,69,70,105).

Low and Black (73) accounted for the fixation of phosphate by kaolinite by the hypothesis that kaolinite dissociates into aluminum and silicate ions and that phosphate precipitates the aluminum ion, thereby disturbing the equilibrium and causing the clay to dissolve in accordance with solubility product principles. A similar observation was made by Kittrick and Jackson (68) and by Tamimi et al. (100).

Phosphorus fixation in alkaline and calcareous soils is usually attributed to the formation of phosphate compounds of calcium. In addition, however, the iron and aluminum compounds responsible for fixation in acid soils are also responsible for some fixation in soils of higher pH. Cole et al. (22) studied the sorption of phosphate on calcium carbonate and suggested that when soluble phosphate fertilizers are added to calcareous soils, the reactions with calcium carbonate consisted of rapid monolayer sorption on calcium carbonate surfaces.

Work by Stout (99), Kelley and Midgley (67), Low and Black (74) indicate that phosphate fixation could be accounted for by the isomorphous replacement of hydroxyl and silicate ions of clay and other soil minerals by phosphate ions. Benavides (10) found that the silicate treatment of some tropical soils increased the amounts of available phosphorus although he did not consider that such a practice could be of economic importance.

There has not been very much agreement among research workers on the possible role of organic matter in phosphate fixation.

Doughty (36) studied phosphate fixation as influenced by organic matter and concluded that soil organic matter as such had only a minor role, if any, in the fixation of phosphorus in difficultly available form when soluble phosphatic fertilizers are added to the soil.

Rennie and McKercher (92), observed that organic matter appeared to be equally as important as the inorganic colloids in determining the phosphorus adsorption capacity of the soils. Benavides (10) in studying the phosphorus sorption capacity of some tropical soils of Colombia, South America, found that there was a highly significant correlation between phosphorus sorption capacity and organic carbon and that organic matter had a very important role in the retention of phosphorus.

According to Kardos (64), 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

With the increasing precision being attained in the methods of phosphorus fractionation it has become possible to trace the transformations undergone by soluble phosphates when applied to soil.

Yuan et al. (113) studied the forms of newly fixed phosphorus in three acid sandy soils of Florida and found that over 80 percent of the applied phosphorus was retained by the soils as aluminum and iron phosphates. Less than 10 percent was in the water-soluble and calcium phosphate forms. On the average, they recovered 86-97 percent of the added phosphorus -- in the water-soluble, aluminum, iron and calcium phosphate forms.

Chang and Chu (17) 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 three days and found that the added phosphate was mainly fixed as aluminum phosphate, followed by iron phosphate and calcium phosphate. After keeping under the same conditions for one

hundred days, the amount of iron phosphate increased while that of the aluminum and calcium phosphates decreased. In two latosols the amount of iron phosphate surpassed that of aluminum phosphate. Under flooded conditions for one hundred days, iron phosphate became the dominant form of phosphate fixed in all six soils.

Hesse (57) investigated the fixation of inorganic phosphorus in the mangrove swamp muds of Sierra Leone and found that, where excess soluble phosphorus was not continuously present, there occurred a loss of aluminum phosphate with time, whereas iron phosphate increased in concentration. In the presence of excess soluble phosphorus the iron and aluminum phosphates remained constant in amount after their initial increase. Hesse thus postulated that the absence of aluminum-bound phosphorus in the mangrove muds appears to be due to a transfer to iron of any phosphorus which may have been acquired by aluminum. Hesse (58) obtained similar results in a later work with mangrove swamp muds in Nigeria; in this particular work he found that the calcium phosphate initially decreased on addition of the phosphorus.

Ohiaeri (84) traced the transformations of added phosphorus in some Oklahoma soils and found that a large portion of the applied phosphate was retained as aluminum phosphate.

CHAPTER III

MATERIALS AND METHODS

Soils

The soil samples studied were collected from the Mid-West Region of Nigeria. They represent the main upland, lowland (swamp) and the Niger River flood plain alluvial soils. The soils of Mid-Western Nigeria have not been mapped into series, but the upland soils have generally been referred to as soils of the Benin series. The collection of the samples was based on a recent soil survey by the Food and Agriculture Organization (30) land use survey team. In this survey soils were not mapped into series but the principal soil "types" in the area were identified, described and mapped.

With the exception of the Niger flood plain soils which are mostly of alluvial origin all the other soils studied were developed on sedimentary rocks, mostly unconsolidated sands and sandstones which belong to the tertiary in the Eocene age.

Table I(a) shows the soils studied and the sites of collection of the samples. For ease of description the names in the last column of the table have been tentatively adopted for the soils.

Three samples of each of the soils shown in Table I (a) were collected; sampling in each case was done at 0-12 inches and from areas with no previous fertilizer application.

TABLE I(a)
SOIL SAMPLES AND SITES OF COLLECTION

Soil	Site of Collection	Descriptive Name
A. SOILS DEVELOPED ON SEDIMENTARY ROCKS, MOSTLY UNCONSOLIDATED SANDS AND SANDSTONES		
(i) Dominantly clayey upland soils (Slopes 5-20%)	Benin City	Benin Upland Soils
(ii) Steeply dissected and steeply rolling upland soils having areas with and without lateritic gravel (Slopes 5-25%)	Auchi	Auchi Upland Soils
(iii) Dominantly sandy upland soils (Slopes less than 20%)	Umutu	Umutu Upland Soils
(iv) Flat to gently rolling lowland soils with seasonal swamps along the broad drainage channels (Slopes 1-3%)	Ughelli	Ughelli Lowland Soils
(v) Soils of the seasonally water-logged Kwale plains	Ogume	Ogume Lowland Soils
B. SOILS OF THE NIGER DELTA AND RIVERINE ALLUVIUMS		
(i) Fresh water swamps and alluvial soils of the Niger Delta, and riverine flood plains	Ashaka	Ashaka Swamp Rice Soils

The description of the Benin upland soils as dominantly clayey is purely relative and not absolute. The alluvial soils of the Niger flood plain are mainly used for the growing of swamp rice (paddy) hence the descriptive name of "swamp rice soils" has been given.

More details of the soils are given in the appendix.

Climate

The Mid-West Region, which lies between 4 and 8° North of the equator has two climatic seasons, the rainy season from April to October and the dry season from November to March. Almost all of the annual precipitation occurs during the rainy season and the average annual rainfall varies from 140 inches in the extreme south (Atlantic Coast) of the region to less than 60 inches in the northern fringe. The rains are brought by southwesterly winds from across the Atlantic Ocean while the dry spell is brought by northeasterly harmattan winds from the Sahara desert. The influences of these wind systems vary with distances from their sources of origin.

In most of Mid-Western Nigeria the mean daily maximum and minimum temperature are 87°F and 72°F respectively.

Vegetation

The principal vegetation zones with which the soil samples studied are associated are shown in Table I(b). These vegetation zones have been described by Keay (66).

TABLE I(b)

SOILS AND THE PRINCIPAL VEGETATION ZONES ASSOCIATED WITH THEM

Soil	Vegetation
(i) Benin Upland Soils	Rain Forest
(ii) Auchi Upland Soils	Rain Forest/Derived Savannah (with Relict Forest)
(iii) Umutu Upland Soils	Rain Forest
(iv) Ughelli Lowland Soils	Fresh water swamp/Rain forest
(v) Ogume Lowland Soils	Derived Savannah (with relict Forest)
(vi) Ashaka Swamp Rice Soils	Freshwater Swamp Forest

In most cases, the typical vegetation associated with the different areas has been modified by local agricultural practices.

The derived savannah vegetation of the Ogume Lowland Soils deserves special mention. Keay (66) refers to the area as the Sobo plains. This derived savannah lacks many of the fire-tolerant savannah species which are typical of derived savannah on the northern edge of the Forest. Here there are large areas of grassland (dominated by *Loudetia arundinacea*) surrounded by continuous Rain Forest and with small "islands" of forest within the "sea" of grass. The plains are water-logged for most of the year and the soils have a dark-greyish color instead of the yellowish brown color of the soils of the surrounding Rain Forest.

Keay (66) suggests that the grasslands must have been caused by over-intensive farming. The general belief, however, is that the plains were previously the course of a creek of the River Niger Delta which later disappeared. The riverlike ramifications of the plains and the course which finally joins the Niger Delta tend to justify the latter belief. A profile study of the soils of the plains might show if they previously formed the bed of a river.

There is no agriculture of any kind presently practised in these plains but if scientific methods for their management could be worked out they form a potential for large-scale production of swamp rice.

General Classification of the Soils of Mid-Western Nigeria.

In the latest classification of African soils by D'Hoore (33) the upland and lowland soils of Mid-Western Nigeria are classed as Ferrallitic Soils (*sensu stricto*). The upland ferrallitic soils

have a dominant red color while the lowland ferrallitic soils have a dominant yellowish-brown color; both soils are developed on loose sandy sediments; the lowland soils are strongly leached.

On the African continent ferrallitic soils cover more than 18 percent of the total surface. Consequently, the ferrallitic soils are the most extensive group of cultivable soil units in Africa. They reflect the final stages of weathering and leaching, wherein only the least mobile and least weatherable constituents remain, and where kaolinite and even quartz may become altered.

The soils are often deep and the horizons are only slightly differentiated with diffuse or gradual transitions. There is little or no reserve of weatherable minerals. Clay minerals are predominantly of the 1:1 lattice type and are mostly associated with large quantities of hydrous iron oxides.

In D'Hoore's (33) classification, the alluvial soils of the Niger flood plain are placed under the main group of weakly developed soils. These soils have a low level of profile development, reflected in a very weak differentiation of the horizons.

Oklahoma Soils

Two surface samples of Oklahoma soils, representative of the Miles and Hartsells series, were, in addition, studied for purposes of comparison.

Descriptions of these soils appear in the appendix.

Laboratory Methods

Determination of Phosphorus:

1. Total Phosphorus was determined by perchloric acid digestion as outlined by Harper (53). The phosphorus in the digest was determined by development of the molybdenum blue color.

2. Organic Phosphorus was determined by the method of Metha et al. (77). Two grams of soil were successively extracted with concentrated HCl and 0.5N NaOH at room temperature and 0.5N NaOH at 90°C. The difference in content of inorganic and total phosphorus in the combined extracts was taken as total organic phosphorus in the soil.

3. Inorganic Phosphorus Fractions: These were determined by the method of Chang and Jackson (18).

(a) Aluminum Phosphate:

A 4-gm sample of soil was placed in a 100-ml centrifuge tube and saturated with 50 ml of 1N NH_4Cl for 30 minutes on a shaking machine. The suspension was centrifuged and the supernatant solution discarded. To the ammonium-saturated soil in the centrifuge tube 50 ml. of neutral 0.5N NH_4F (pH 8.2 for upland soils) was added and the suspension extracted on a shaking machine for one hour. The suspension was centrifuged and the clear supernatant solution was decanted for the determination of phosphorus.

Since all the soils are surface soils all the NH_4F extracts were intensely colored with organic matter. The color was removed by treating the extracts with phosphorus-free activated charcoal (Darco G-60). Phosphorus was then determined colorimetrically in an aliquot of the colorless extract by Jackson's (62) method II in a chromomolybdic acid system. 0.8M boric acid was used to reduce interference from fluoride ions in the extract.

(b) Iron Phosphate:

The soil sample saved after the extraction of aluminum phosphate was washed twice with 25 ml. portions of saturated NaCl solution. It was then extracted overnight with 50 ml of 0.1N NaOH on a shaking machine. The soil suspension was centrifuged and the supernatant decanted for the determination of phosphorus.

As for aluminum phosphate, all the extracts were highly colored with organic matter; 2 ml of $2\text{NH}_2\text{SO}_4$ and a few drops of concentrated H_2SO_4 were added to flocculate the organic colloids. Any color that remained after centrifuging off the flocculated material was removed with phosphorus-free activated charcoal.

Phosphorus was determined colorimetrically in an aliquot of the colorless extract by Jackson's (62) method I in a sulfomolybdic acid system.

(c) Calcium Phosphate:

The soil sample saved after the extraction of iron phosphate was washed twice with 25 ml. portions of saturated NaCl solution. It was then extracted with 50 ml. of $0.5\text{NH}_2\text{SO}_4$ 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.

(d) Reductant Soluble (occluded) Iron Phosphate:

The soil sample saved after the extraction of calcium phosphate was washed twice with 25 ml. portions of saturated NaCl solution. It was then suspended in 40 ml. of 0.3M sodium citrate solution and then 1.0 gm. of solid sodium dithionite ($\text{Na}_2\text{S}_2\text{O}_4$) 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 100 ml, volumetric flask. The soil was washed twice with 25 ml. portions of saturated NaCl solution, the washings being combined with the extract in the 100 ml. flask.

The solution in the flask was made up to volume. A 5 ml. aliquot of this solution was oxidized with 72 percent perchloric acid instead of the 30 percent hydrogen peroxide recommended by Chang and Jackson (18). After oxidation phosphorus was determined as for iron phosphate.

(e) Occluded Aluminum Phosphate:

The soil residue saved after the extraction of occluded iron phosphate was extracted with 50 ml. of neutral normal NH_4F for one hour on a shaking machine. The suspension was centrifuged and an aliquot of the supernatant was taken for determination of phosphorus as for aluminum phosphate.

Soil Properties

Physical properties:

1. Mechanical Analysis: The particle size distribution of the soils was determined by use of the soil hydrometer (12).

Chemical properties:

1. Soil pH: This was determined by means of the Beckman Zeromatic pH meter.

2. Cation Exchange Capacity: This was determined by the neutral 1N ammonium acetate method. The adsorbed ammonium was displaced by distillation with magnesium oxide (62).

3. Exchangeable Cations: Exchangeable calcium and magnesium were determined from the ammonium acetate leachate by means of the versenate titration as outlined in the USDA Handbook No. 60 (103). Exchangeable sodium and potassium were determined from the ammonium acetate leachate by the Beckman Du-flame spectrophotometer with a photomultiplier attachment.

4. Exchangeable Aluminum: Exchangeable aluminum was extracted from the soils by means of 1N ammonium acetate solution of pH 4.8 as outlined by McLean et al. (76). The exchangeable aluminum in the extracts was determined by the aluminon method of Chenery (20).

5. Free Iron: This was determined colorimetrically from the citrate-dithionite extract obtained in the determination of occluded iron phosphate (62).

6. Available Phosphorus: The No. 1 method of Bray and Kurtz (13) was used for the determination of available phosphorus.

7. Total Nitrogen: This was determined by the Kjeldhal method (53).

8. Organic Matter: This was determined by the Schollenberger method as outlined by Harper (53). The organic matter was oxidized by chromic acid in the presence of excess H_2SO_4 , with external heat applied, the excess of standard chromic acid being back titrated with a ferrous solution. The percentage of carbon was calculated by dividing the percentage of organic matter by the conventional factor of 1.724.

Fate of Applied Water Soluble Phosphorus

A 5 ml. aliquot of a 400 ppm standardized solution of monobasic ammonium phosphate, $(\text{NH}_4\text{H}_2\text{PO}_4)$ was added to a 10 gm. 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 the thirty day period the soils were kept at approximately field capacity by periodic watering from a wash bottle and finally allowed to come to dryness by the end of thirty days; the soils were then fractionated for phosphorus.

The above procedures were repeated using dibasic ammonium phosphate, $(\text{NH}_4)_2\text{HPO}_4$.

In the phosphorus fractionation $1\text{N}\text{NH}_4\text{Cl}$, $0.5\text{N}\text{NH}_4\text{F}$, $0.1\text{N}\text{NaOH}$, $0.5\text{N}\text{H}_2\text{SO}_4$ were respectively used for the extraction of water soluble (saloid-bound), aluminum, iron and calcium phosphate fractions. Occluded phosphate was not determined.

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.

Statistical Analyses were made as outlined by Ostle (87).

CHAPTER IV

RESULTS AND DISCUSSION

Particle Size Distribution

Table II(a-g) shows the particle size distribution of the soils. The Mid-Western Nigerian soils ranged from sands through loamy sand to sandy loam. On the average, the Benin upland soils had the highest percentage of clay. For the upland soils the silt/clay ratio is very low (less than 0.5 in all cases). D'Hoore (33) gives 0.25 as the average silt/clay ratio for the ferrallitic African soils to which these soils belong. In the lowland soils, the silt and clay tend to be equally distributed; the Ashaka swamp rice soils also show this tendency.

The Oklahoma Hartsells soil is a loamy sand while Miles is a loam. The silt-clay relationship for these soils is entirely a reverse of the ones for the Nigerian soils, the silt percentage being predominant over the clay percentage. This may be due to the fact that the Oklahoma soils are not as strongly weathered as the Nigerian soils.

TABLE IIa
PARTICLE SIZE DISTRIBUTION: BENIN UPLAND SOILS

Sample No.	A175	A176	A177
Depth	0-12"	0-12"	0-12"
Particle Size Distribution %			
Sand	69	73	75
Silt	8	5	7
Clay	23	22	18
Textural Class	Sandy Loam	Sandy Loam	Sandy Loam

TABLE IIb
PARTICLE SIZE DISTRIBUTION: AUCHI UPLAND SOILS

Sample No.	A404	A405	A406
Depth	0-12"	0-12"	0-12"
Particle Size Distribution %			
Sand	87	89	90
Silt	3	3	1
Clay	10	8	9
Textural Class	Sand	Sand	Sand

TABLE IIc
 PARTICLE SIZE DISTRIBUTION: UMUTU UPLAND SOILS

Sample No.	A467	A468	A469
Depth	0-12"	0-12"	0-12"
Particle Size Distribution %			
Sand	85	87	89
Silt	4	2	2
Clay	11	11	9
Textural Class	Loamy Sand	Loamy Sand	Loamy Sand

TABLE IIId
 PARTICLE SIZE DISTRIBUTION: UGHELLI LOWLAND SOILS

Sample No.	A447	A448	A449
Depth	0-12"	0-12"	0-12"
Particle Size Distribution %			
Sand	85	65	77
Silt	7	17	12
Clay	8	18	11
Textural Class	Loamy Sand	Loamy Sand	Sandy Loam

TABLE IIe
 PARTICLE SIZE DISTRIBUTION: OGUME LOWLAND SOILS

Sample No.	A490	A491	A492
Depth	0-12"	0-12"	0-12"
Particle Size Distribution %			
Sand	82	84	79
Silt	8	10	12
Clay	10	6	9
Textural Class	Loamy Sand	Loamy Sand	Loamy Sand

TABLE IIIf
 PARTICLE SIZE DISTRIBUTION: ASHAKA SWAMP RICE SOILS

Sample No.	A464	A465	A466
Depth	0-12"	0-12"	0-12"
Particle Size Distribution %			
Sand	78	81	85
Silt	7	10	8
Clay	15	9	7
Textural Class	Loamy Sand	Loamy Sand	Loamy Sand

TABLE IIg
PARTICLE SIZE DISTRIBUTION: OKLAHOMA SOILS

Sample No.	62-S-693 (Hartsells)	62-S-715 (Miles)
Depth	0-3"	0-3"
Particle Size Distribution %		
Sand	54	50
Silt	38	29
Clay	8	21
Textural Class	Loamy Sand	Loam

Chemical Properties of the Soils

The essential chemical characteristics of the soils studied are shown in Table III(a-g).

With the exception of the Ashaka swamp rice soils (which are weakly acid), all the Nigerian soils studied are strongly acid, the pH in water ranging from 4.5 to 5.7. On the average the Ashaka soils have a pH of about 6.0. Soluble salts and bases (from the sea) carried up the Niger Delta Creek (Ase) on whose banks the Ashaka soils were collected might account for the higher pH of these soils. The Oklahoma Hartsells soil is weakly acid while Miles is approximately neutral.

For all the soils there were noticeable decreases in pH values when pH was determined in 1NKCl; this indicates presence of exchangeable aluminum.

TABLE IIIa
 CHEMICAL PROPERTIES: BENIN UPLAND SOILS

Sample No.	A175	A176	A177
Depth	0-12"	0-12"	0-12"
pH (Soil:Water 1:1)	4.50	4.50	5.60
pH (Soil:Water 1:2.5)	4.50	4.80	5.50
pH (Soil:LNKCl 1:2.5)	3.90	4.00	4.60
C.E.C.*(m.e./100 gm.)	5.85	4.75	4.85
Exchangeable Cations (m.e./100 gm.)			
Calcium	0.30	0.65	1.70
Magnesium	0.15	0.25	0.70
Potassium	0.07	0.11	0.11
Sodium	0.10	0.19	0.21
Aluminum	2.22	1.43	0.82
Hydrogen	3.01	2.12	1.31
Exchangeable Aluminum (ppm)	200.00	128.75	73.75
% Base Saturation	10.59	25.26	56.08
% Organic Matter	6.40	6.60	6.24
% Carbon	3.71	3.82	3.61
% Nitrogen	0.31	0.33	0.41
Carbon:Nitrogen Ratio	11.96	11.57	8.80
% Free Iron	1.17	1.56	1.04
Available Phosphorus (ppm)	3.10	3.50	3.50

*Cation Exchange Capacity

TABLE IIIb
 CHEMICAL PROPERTIES: AUCHI UPLAND SOILS

Sample No.	A404	A405	A406
Depth	0-12"	0-12"	0-12"
pH (Soil:Water 1:1)	4.90	4.90	5.50
pH (Soil:Water 1:2.5)	5.10	5.10	5.70
pH (Soil:1NKCl 1:2.5)	4.10	4.20	4.40
C.E.C.* (m.e./100 gm.)	3.30	2.55	2.20
Exchangeable Cations (m.e./100 gm.)			
Calcium	0.40	0.40	0.35
Magnesium	0.35	0.30	0.10
Potassium	0.08	0.05	0.05
Sodium	0.19	0.17	0.15
Aluminum	0.82	0.70	0.82
Hydrogen	1.46	0.93	0.73
Exchangeable Aluminum (ppm)	73.75	62.50	73.75
% Base Saturation	30.90	36.07	29.54
% Organic Matter	2.64	2.24	1.88
% Carbon	1.53	1.29	1.09
% Nitrogen	0.19	0.20	0.12
Carbon:Nitrogen Ratio	8.05	6.45	9.08
% Free Iron	0.42	0.39	0.19
Available Phosphorus (ppm)	3.50	4.20	2.80

*Cation Exchange Capacity

TABLE IIIc
CHEMICAL PROPERTIES: UMUTU UPLAND SOILS

Sample No.	A467	A468	A469
Depth	0-12"	0-12"	0-12"
pH (Soil:Water 1:1)	5.90	4.70	4.70
pH (Soil:Water 1:2.5)	5.90	4.90	4.90
pH (Soil:1NKCl 1:2.5)	5.10	4.20	4.00
C.E.C.* (m.e./100 gm.)	5.30	3.30	3.15
Exchangeable Cations (m.e./100 gm.)			
Calcium	2.10	0.20	0.30
Magnesium	1.80	0.20	0.15
Potassium	0.12	0.05	0.05
Sodium	0.13	0.13	0.13
Aluminum	0.83	1.08	0.65
Hydrogen	0.32	1.64	1.87
Exchangeable Aluminum (ppm)	75.00	187.50	58.75
% Base Saturation	78.30	17.57	20.00
% Organic Matter	9.60	6.80	2.92
% Carbon	5.56	3.94	1.69
% Nitrogen	0.63	0.35	0.16
Carbon:Nitrogen Ratio	8.38	11.26	10.56
% Free Iron	0.25	0.30	0.28
Available Phosphorus (ppm)	5.20	3.50	2.80

*Cation Exchange Capacity

TABLE IIIId

CHEMICAL PROPERTIES: UGHELLI LOWLAND SOILS

Sample No.	A447	A448	A449
Depth	0-12"	0-12"	0-12"
pH (Soil:Water 1:1)	4.60	4.50	4.60
pH (Soil:Water 1:2.5)	4.70	4.60	4.50
pH (Soil:LNKCl 1:2.5)	4.00	3.90	4.00
C.E.C.* (m.e./100 gm.)	5.45	4.80	9.50
Exchangeable Cations (m.e./100 gm.)			
Calcium	0.12	0.27	0.40
Magnesium	0.09	0.10	0.15
Potassium	0.18	0.20	0.20
Sodium	0.15	0.17	0.15
Aluminum	2.77	2.22	2.77
Hydrogen	2.14	1.84	5.83
Exchangeable Aluminum (ppm)	250.00	200.00	250.00
% Base Saturation	9.90	15.41	9.47
% Organic Matter	2.00	2.44	7.00
% Carbon	1.16	1.41	4.06
% Nitrogen	0.21	0.18	0.33
Carbon:Nitrogen Ratio	5.52	7.83	12.30
% Free Iron	0.15	0.02	0.02
Available Phosphorus (ppm)	3.50	5.90	7.30

*Cation Exchange Capacity

TABLE IIIe
 CHEMICAL PROPERTIES: OGUME LOWLAND SOILS

Sample No.	A490	A491	A492
Depth	0-12"	0-12"	0-12"
pH (Soil:Water 1:1)	5.70	5.70	5.50
pH (Soil:Water 1:2.5)	5.90	5.90	5.70
pH (Soil:1NKCl 1:2.5)	4.70	4.60	4.60
C.E.C.*(m.s./100 gm.)	3.55	4.05	4.85
Exchangeable Cations (m.e./100 gm.)			
Calcium	0.30	0.30	0.20
Magnesium	0.04	0.05	0.05
Potassium	0.32	0.28	0.25
Sodium	0.24	0.21	0.26
Aluminum	2.77	2.98	3.12
Hydrogen	0.00	0.32	0.97
Exchangeable Aluminum (ppm)	250.00	268.75	281.25
% Base Saturation	25.35	20.74	15.67
% Organic Matter	1.76	4.16	5.04
% Carbon	1.02	2.41	2.92
% Nitrogen	0.14	0.18	0.23
Carbon:Nitrogen Ratio	7.28	12.68	12.69
% Free Iron	0.12	0.02	0.03
Available Phosphorus (ppm)	3.10	4.20	3.50

* Cation Exchange Capacity

TABLE IIIf
 CHEMICAL PROPERTIES: ASHAKA SWAMP RICE SOILS

Sample No.	A464	A465	A466
Depth			
pH (Soil:Water 1:1)	6.10	5.80	6.00
pH (Soil:Water 1:2.5)	6.00	5.70	6.00
pH (Soil:LNKCl 1:2.5)	5.00	4.90	4.90
C.E.C.*(m.e./100 gm.)	4.25	6.05	3.65
Exchangeable Cations (m.e./100 gm.)			
Calcium	2.40	3.55	1.95
Magnesium	0.70	0.05	0.15
Potassium	0.33	0.28	0.30
Sodium	0.24	0.21	0.19
Aluminum	0.90	0.35	0.46
Hydrogen	0.00	1.63	0.60
Exchangeable Aluminum (ppm)	81.25	31.25	42.50
% Base Saturation	86.35	67.10	70.95
% Organic Matter	2.00	3.20	3.68
% Carbon	1.16	1.85	2.13
% Nitrogen	0.17	0.29	0.20
Carbon:Nitrogen Ratio	6.82	6.37	10.63
% Free Iron	0.61	0.32	0.25
Available Phosphorus (ppm)	8.80	87.50	33.50

*Cation Exchange Capacity

TABLE IIIg
 CHEMICAL PROPERTIES: OKLAHOMA SOILS

Sample No.	62-S-693 (Hartsells) 0-3"	62-S-715 (Miles) 5-13"
Depth		
pH (Soil:Water 1:1)	6.10	6.90
pH (Soil:Water 1:2.5)	6.40	7.40
pH (Soil:LNKCl 1:2.5)	5.60	6.10
C.E.C.* (m.e./100 gm.)	6.70	10.80
Exchangeable Cations (m.e./100 gm.)		
Calcium	3.60	5.00
Magnesium	2.30	6.40
Potassium	0.15	0.41
Sodium	0.13	0.15
Aluminum	0.35	0.37
Hydrogen	0.17	0.00
Exchangeable Aluminum (ppm)	31.25	33.75
% Base Saturation	92.23	110.74
% Organic Matter	2.64	1.16
% Carbon	1.53	0.67
% Nitrogen	0.13	0.13
Carbon:Nitrogen Ratio	11.76	5.15
% Free Iron	0.15	0.48
Available Phosphorus (ppm)	5.20	1.80

*Cation Exchange Capacity

Cation exchange capacity was low for all of the Nigerian soils. For most of the soils exchangeable aluminum accounted for a considerable part of the cation exchange complex; for the two groups of lowland soils (Ogume and Ughelli) it accounted for over 50 percent of the cation exchange capacity (with the exception of only one sample). In the upland soils (Benin, Auchi and Umutu) exchangeable hydrogen was mostly dominant over exchangeable aluminum. The Ashaka swamp rice soils had, on the average, the highest base saturation percentage (67-86); this might also be due to the sea salt transfer mentioned in the discussion of pH. With the exception of two samples, all the other Nigerian soils had base saturation percentages of less than 40. Where exchangeable aluminum or hydrogen was relatively high the base saturation was greatly depressed; the Ashaka soils had the least amount of exchangeable aluminum.

The dominance of exchangeable aluminum on the exchange complex has been observed for some acid soils of North Carolina by Coleman et al. (23). They also observed that well-developed upland soils had more of exchangeable hydrogen than exchangeable aluminum and other metallic cations.

The cation exchange capacities of the Oklahoma soils were not much higher than the ones for the Nigerian soils but calcium and magnesium (instead of aluminum and hydrogen) dominated the cation exchange complexes. The base saturation for Hartsells is 92 percent while that for Miles is over 100 percent; this super-saturation may be due to the presence of salts of calcium.

The percentage of free iron was highest for the Benin upland soils followed by Auchi and Umutu upland soils. The high percentage of free iron is expected since the clay minerals in these soils are known to be mostly associated with large quantities of iron oxides (33). The lowland and swamp rice soils had the lowest percentages of free iron; excessive leaching of the lowland soils might account for this difference. Percent free iron was comparatively low for the Oklahoma soils.

With the exception of the swamp rice soils, available phosphorus, determined by the No. 1 method of Bray and Kurtz was very low for all the Nigerian and Oklahoma soils studied.

The percentage of organic matter varied from about 2 to 9.6 for the Nigerian soils. The differences within and among the different soils are obviously related to the previous history of their sites of collection; the soils from high forest areas have a higher accumulation of organic matter than soils from disturbed and recently farmed sites. Since agriculture is still practised by bush burning, the very fine remains of charcoal in the soils may have affected the determination of organic matter - tending to give higher percentages of organic matter. The average percentage of organic matter of the Oklahoma soils is about 2.

Although there is some variability in the carbon:nitrogen ratio, yet the nitrogen contents of the soils are related to the organic matter contents - soils with higher organic matter contents having higher percentages of nitrogen. The carbon:nitrogen ratios are shown in Tables III(a-g) and VIII. The carbon: nitrogen ratios for all the Nigerian soils lie between 6 and 12 and fall within the range of the ratios for some West African soils reported by Nye and Bertheux (83).

For a Western Nigerian forest soil, Bates (8) observed the following carbon:nitrogen ratios down the profile: 15.7 (for worm casts), 13.6 (0-2"), 8.1 (2-7") and 7.0 (7-12"). Nye (82) has established that in the tall grass Guinea savannah areas of West Africa, the carbon:nitrogen ratio of sites that have been rested for some time is relatively high - about 15. This ratio falls when the sites have been cultivated for some years, owing presumably to further decomposition of high carbon organic compounds.

The carbon:nitrogen ratio of the Oklahoma Hartsells soil is 11.76 while that of the Miles is 5.15. Since both soils have the same percentage of nitrogen (0.13) the difference should be due to the lower organic matter and carbon content of the Miles soil. The Miles soil was sampled at 5-13 inches while Hartsells soil was sampled at 0-3 inches so that the lower organic matter content of the Miles soil is expected. Stevenson (98) observed a narrowing of the carbon:nitrogen ratio with depth. According to him this was due to a combination of two factors: (a) an increase, with depth, in the relative amount of the soil nitrogen as fixed ammonium, and (b) the presence of a relatively higher amount of nitrogen-rich constituents in the organic matter of subsoil as compared with surface soil.

Distribution of Phosphorus in the Soils

The distributions of the forms of phosphorus for the soils studied are shown in Table IV (a-g).

With the exception of one swamp rice soil which had a total phosphorus content of 320 ppm, all the Nigerian soils studied had total phosphorus contents of less than 200 ppm, the range being from

TABLE IVa
DISTRIBUTION OF FORMS OF PHOSPHORUS (ppm)
BENIN UPLAND SOILS

Sample No.	A175	A176	A177
Depth	0-12"	0-12"	0-12"
Total Phosphorus	139.00	192.00	181.00
Organic Phosphorus	58.30	72.80	87.50
Inorganic Phosphorus Fractions			
Aluminum Phosphate	2.50	3.70	5.00
Iron Phosphate	15.60	18.70	13.50
Calcium Phosphate	1.20	3.10	2.50
Occluded Aluminum Phosphate	9.40	12.50	7.50
Occluded Iron Phosphate	60.00	80.00	60.00
Added Total	147.00	190.80	176.00

TABLE IVb
DISTRIBUTION OF FORMS OF PHOSPHORUS (ppm)
AUCHI UPLAND SOILS

Sample No.	A404	A405	A406
Depth	0-12"	0-12"	0-12"
Total Phosphorus	75.00	75.00	54.00
Organic Phosphorus	32.50	32.00	29.20
Inorganic Phosphorus Fractions			
Aluminum Phosphate	3.70	3.70	2.50
Iron Phosphate	6.20	7.80	4.60
Calcium Phosphate	0.60	1.90	1.90
Occluded Aluminum Phosphate	2.50	2.50	2.50
Occluded Iron Phosphate	27.50	25.00	17.50
Added Total	73.00	72.9	58.20

TABLE IVc
 DISTRIBUTION OF FORMS OF PHOSPHORUS (ppm)
 UMUTU UPLAND SOILS

Sample No.	A467	A468	A469
Depth	0-12"	0-12"	0-12"
Total Phosphorus	128.00	80.00	75.00
Organic Phosphorus	87.00	47.00	48.00
Inorganic Phosphorus Fractions			
Aluminum Phosphate	7.50	3.70	2.50
Iron Phosphate	7.80	6.20	6.20
Calcium Phosphate	5.00	1.20	1.20
Occluded Aluminum Phosphate	2.50	2.50	2.50
Occluded Iron Phosphate	15.00	12.50	12.50
Added Total	124.80	73.10	72.90

TABLE IVd
 DISTRIBUTION OF FORMS OF PHOSPHORUS (ppm)
 UGHELLI LOWLAND SOILS

Sample No.	A447	A448	A449
Depth	0-12"	0-12"	0-12"
Total Phosphorus	43.00	64.00	139.00
Organic Phosphorus	16.40	31.30	96.00
Inorganic Phosphorus Fractions			
Aluminum Phosphate	6.20	7.50	9.40
Iron Phosphate	3.10	4.60	9.40
Calcium Phosphate	0.60	0.60	1.20
Occluded Aluminum Phosphate	3.80	2.50	2.50
Occluded Iron Phosphate	6.20	12.50	12.50
Added Total	36.30	59.00	131.00

TABLE IVe
 DISTRIBUTION OF FORMS OF PHOSPHORUS (ppm)
 OGUME LOWLAND SOILS

Sample No.	A490	A491	A492
Depth	0-12"	0-12"	0-12"
Total Phosphorus	107.00	107.00	107.00
Organic Phosphorus	65.00	68.30	83.60
Inorganic Phosphorus Fractions			
Aluminum Phosphate	7.50	8.80	8.80
Iron Phosphate	6.20	6.20	6.20
Calcium Phosphate	1.20	1.20	1.20
Occluded Aluminum Phosphate	2.50	2.50	2.50
Occluded Iron Phosphate	20.00	15.00	15.00
Added Total	102.40	102.00	117.30

TABLE IVf
 DISTRIBUTION OF FORMS OF PHOSPHORUS (ppm)
 ASHAKA SWAMP RICE SOILS

Sample No.	A464	A465	A466
Depth			
Total Phosphorus	128.00	320.00	160.00
Organic Phosphorus	46.60	75.70	58.20
Inorganic Phosphorus Fractions			
Aluminum Phosphate	11.20	93.40	36.20
Iron Phosphate	15.60	75.00	31.20
Calcium Phosphate	20.60	56.20	8.10
Occluded Aluminum Phosphate	6.20	5.60	3.10
Occluded Iron Phosphate	37.50	47.50	27.50
Added Total	137.70	353.40	164.30

TABLE IVg
DISTRIBUTION OF FORMS OF PHOSPHORUS (ppm)
OKLAHOMA SOILS

Sample No.	62-S-693 (Hartsells)	62-S-715 (Miles)
Depth	0-3"	5-13"
Total Phosphorus	120.00	130.00
Organic Phosphorus	74.00	55.60
Inorganic Phosphorus Fractions		
Aluminum Phosphate	5.00	1.20
Iron Phosphate	15.60	3.10
Calcium Phosphate	4.40	26.20
Occluded Aluminum Phosphate	2.50	6.20
Occluded Iron Phosphate	22.50	25.00
Added Total	124.00	117.30

43 to 192 ppm. The much higher total phosphorus content of 320 ppm for one of the swamp rice soils must have been due to the presence of household refuse (including fish bones) on the banks of the creek from which it was collected.

The total phosphorus in the soils is low compared with other parts of the world but not too different from values given by Nye and Bertheux (83) for some West African soils. Nye and Bertheux (83) 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 rocks and coarse gneisses, Bates and Baker (9)

got the following values for total phosphorus: 553 ppm (0-2"), 210 ppm (2-7"), 283 ppm (7-12"). For the surface horizons of some tropical soils of Colombia, South America, Benavides (10) got an average of 400 ppm for total phosphorus.

The sandstone parent material from which the upland and lowland soils of Mid-Western Nigeria are developed should be partly responsible for the low levels of total phosphorus in them. Other workers (6, 106, 111) have shown that the parent material from which soils are developed has a lot to do with the content of total phosphorus of the soils. Another factor that might be of importance in bringing about a low level of total phosphorus is the bush firing inherent in the agricultural practices of Mid-Western Nigeria; firing will definitely destroy the reserves of phosphorus in the organic matter accumulations on the surface of the soils. Although the soils studied were all sampled at 0-12", yet larger reserves of phosphorus at greater soil depths cannot be assumed since Nye and Bertheux (83) and Bates and Baker (9) have at least shown that, for some West African soils, the total phosphorus is accumulated at the surface. Ghani and Aleem (49) have also shown this to be true for some Indian forest soil profiles. This decrease of total phosphorus down the profile will be the more so for soils developed from sandstones such as the soils of Mid-Western Nigeria.

The total phosphorus contents of the two Oklahoma soils are also low (below 140 ppm in both cases) compared with values that have been obtained for other Oklahoma soils. Ohiaeri (84) reported an average of 300 ppm of total phosphorus for the surface horizons of

some Oklahoma soils. The sandy nature of the Oklahoma soils used in the present study might be responsible for their lower total phosphorus contents.

For tropical surface soils, organic phosphorus has sometimes been shown to form a much larger fraction of the total phosphorus (9, 10, 57) but the present study has not shown this to be true for all the soils studied. Table V(a-g) shows the phosphorus fractions expressed as percentages of the total phosphorus. For the Benin and Auchi upland soils the organic phosphorus is generally below 50 percent of the total phosphorus. For the Umutu upland soils, Ogume and Ughelli lowland soils, the organic phosphorus accounts for from 45 to over 70 percent of the total phosphorus. For the Ashaka swamp rice soils, organic phosphorus forms less than 40 percent of the total phosphorus. Exhaustive agricultural practices like bush firing mentioned above should be partly responsible for the low percentages of organic phosphorus in some of the upland soils. After firing, the organic matter that remains on the surface is depleted of phosphorus. According to Russell (93) the potentially plant available phosphate in a number of tropical soils is in the organic matter in the surface soil, so that if the surface is washed away by rain, or removed by any other cause (e.g. bush firing) the subsurface soil which now becomes the surface is exceedingly low in phosphate, and usually in many other elements as well.

From Table V, it will be seen that the total occluded (inactive) phosphate is the next largest fraction of total phosphorus after the

TABLE Va

FRACTIONS OF THE SOIL PHOSPHORUS AS PERCENTAGE OF THE TOTAL PHOSPHORUS
BENIN UPLAND SOILS

Sample No.	A175	A176	A177
Depth	0-12"	0-12"	0-12"
Organic Phosphorus	39.65	38.15	49.71
Aluminum Phosphate	1.70	1.93	2.84
Iron Phosphate	10.61	9.80	7.67
Calcium Phosphate	0.81	1.62	1.42
Total Occluded Phosphate	47.12	48.48	38.35
Total Phosphorus (ppm)	139.00	192.00	181.00

TABLE Vb

FRACTIONS OF THE SOIL PHOSPHORUS AS PERCENTAGE OF THE TOTAL PHOSPHORUS
AUCHI UPLAND SOILS

Sample No.	A404	A405	A406
Depth	0-12"	0-12"	0-12"
Organic Phosphorus	44.52	43.89	50.17
Aluminum Phosphate	5.06	5.07	4.29
Iron Phosphate	8.49	10.69	7.90
Calcium Phosphate	0.82	2.60	3.26
Total Occluded Phosphate	41.09	37.72	34.36
Total Phosphorus (ppm)	75.00	75.00	54.00

TABLE Vc

FRACTIONS OF THE SOIL PHOSPHORUS AS PERCENTAGE OF THE TOTAL PHOSPHORUS
UMUTU UPLAND SOILS

Sample No.	A467	A468	A469
Depth	0-12"	0-12"	0-12"
Organic Phosphorus	69.71	64.29	65.84
Aluminum Phosphate	6.04	5.06	3.42
Iron Phosphate	6.25	8.48	8.50
Calcium Phosphate	4.00	1.64	1.64
Total Occluded Phosphate	14.02	20.51	20.57
Total Phosphorus (ppm)	128.00	80.00	75.00

TABLE Vd

FRACTIONS OF THE SOIL PHOSPHORUS AS PERCENTAGE OF THE TOTAL PHOSPHORUS
UGHELLI LOWLAND SOILS

Sample No.	A447	A448	A449
Depth	0-12"	0-12"	0-12"
Organic Phosphorus	45.17	53.05	73.28
Aluminum Phosphate	17.07	12.71	7.17
Iron Phosphate	8.53	7.79	7.17
Calcium Phosphate	1.60	1.01	0.91
Total Occluded Phosphate	27.54	25.42	11.45
Total Phosphorus (ppm)	43.00	64.00	139.00

TABLE Vc

FRACTIONS OF THE SOIL PHOSPHORUS AS PERCENTAGE OF THE TOTAL PHOSPHORUS
OGUME LOWLAND SOILS

Sample No.	A490	A491	A492
Depth	0-12"	0-12"	0-12"
Organic Phosphorus	63.47	66.96	71.27
Aluminum Phosphate	7.32	8.64	7.50
Iron Phosphate	6.05	6.07	5.28
Calcium Phosphate	1.17	1.17	1.02
Total Occluded Phosphate	21.97	17.15	14.91
Total Phosphorus (ppm)	107.00	107.00	107.00

TABLE Vf

FRACTIONS OF THE SOIL PHOSPHORUS AS PERCENTAGE OF THE TOTAL PHOSPHORUS
ASHAKA SWAMP RICE SOILS

Sample No.	A464	A465	A466
Depth	0-12"	0-12"	0-12"
Organic Phosphorus	33.84	21.42	35.42
Aluminum Phosphate	8.13	26.42	22.03
Iron Phosphate	11.32	21.22	18.98
Calcium Phosphate	15.03	15.91	18.62
Total Occluded Phosphate	31.73	15.02	18.62
Total Phosphorus (ppm)	128.00	320.00	160.00

TABLE Vg

FRACTIONS OF THE SOIL PHOSPHORUS AS PERCENTAGE OF THE TOTAL PHOSPHORUS
OKLAHOMA SOILS

Sample No.	62-S-693 (Hartsells)	62-S-715 (Miles)
Depth	0-3"	0-3"
Organic Phosphorus	59.67	47.39
Aluminum Phosphate	4.03	1.02
Iron Phosphate	12.58	2.64
Calcium Phosphate	3.54	23.33
Total Occluded Phosphate	20.16	26.59
Total Phosphorus (ppm)	120.00	130.00

organic phosphorus, the swamp rice soils being an exception. In fact, in two samples of the Benin upland soils, the occluded phosphate percentage of the total phosphorus is higher than that of the organic phosphate.

Table VI shows the inorganic phosphorus fractions as percentages of the total inorganic phosphorus. With the exception of two samples, the active inorganic phosphorus fractions (aluminum, iron and calcium phosphates) form less than 50 percent of the total inorganic phosphorus for the upland and lowland soils; the rest of the inorganic phosphorus is in the inactive form of occluded phosphate. The percentages of the inorganic phosphorus formed by the occluded phosphate appear in the last column of Table VI. In the Benin upland soils 78 percent of the inorganic phosphorus is in the occluded

TABLE VI

DISTRIBUTION OF INORGANIC PHOSPHATE FRACTIONS AS A PERCENTAGE OF
TOTAL INORGANIC PHOSPHATE

Sample No.	Depth	Aluminum Phosphate	Iron Phosphate	Calcium Phosphate	Total Occluded Phosphate
<u>Benin Upland Soils</u>					
A175	0-12"	2.81	17.58	1.35	78.24
A176	0-12"	3.13	15.84	2.62	78.38
A177	0-12"	5.64	15.25	2.82	76.27
<u>Auchi Upland Soils</u>					
A404	0-12"	9.13	15.30	1.48	74.07
A405	0-12"	9.04	19.07	4.64	67.23
A406	0-12"	8.62	15.86	6.55	68.96
<u>Umutu Upland Soils</u>					
A467	0-12"	20.10	20.90	13.40	46.29
A468	0-12"	14.17	23.75	4.59	57.47
A469	0-12"	10.04	24.89	4.81	60.24
<u>Ughelli Lowland Soils</u>					
A447	0-12"	31.15	15.57	3.51	50.25
A448	0-12"	27.07	16.60	2.16	54.15
A449	0-12"	26.85	26.85	3.42	42.85
<u>Ogume Lowland Soils</u>					
A490	0-12"	20.05	16.57	3.20	60.16
A491	0-12"	26.11	18.39	3.56	51.92
A492	0-12"	26.11	18.39	3.56	51.92
<u>Ashaka Swamp Rice Soils</u>					
A464	0-12"	12.29	17.12	22.61	47.96
A465	0-12"	33.63	27.00	20.23	19.12
A466	0-12"	34.11	29.40	7.63	28.84
<u>Oklahoma Soils</u>					
62-S-693 (Hartsells)	0-3"	10.00	31.20	8.80	50.00
62-S-715 (Miles)	5-13"	1.94	5.02	42.46	50.56

form; in the Auchi upland soils 70 percent of the inorganic phosphorus is occluded; for the Umutu upland soils and the Ughelli and Ogume lowland soils the percentages of occlusion lie between 50 and 60. In the Ashaka swamp rice soils the percentage of the inorganic phosphorus in the occluded form is in marked contrast to the other soils, the range being from 19 to 47 percent. This sharp contrast in the distribution of occluded phosphate is in perfect agreement with the findings of many other workers (7, 60, 61, 95) who have shown that under conditions of flooding and water-logging (as obtain in the swamp rice soils) the occluded phosphate tends to be reduced and there is thus less tendency for its accumulation. Also, genetically, the swamp rice soils, by their alluvial origin are young and weakly developed so that they should have the least amount of occluded phosphate as postulated by Chang and Jackson (19) and confirmed for West African mangrove swamp soils by Hesse (57,58).

The occluded phosphate content of the lowland soils, although considerable, yet differ markedly from those of the upland soils especially Benin and Auchi; Umutu upland soil appears to be intermediate. The higher rainfall in the areas of the lowland soils and the resultant seasonal swamps and water-logging (which cause reduction and check accumulation of occluded phosphate) might account for this difference; the lowland soils also contain much less free iron; these soils are also younger and less weathered than the upland soils.

For the upland and lowland soils calcium phosphate forms an almost insignificant fraction of the active inorganic phosphates of calcium, iron and aluminum. For the upland soils most of the active

inorganic phosphate is in the form of iron phosphate, the distribution increasing in the sequence calcium phosphate, aluminum phosphate and iron phosphate. In the lowland soils the distribution increases in the sequence calcium phosphate, iron phosphate and aluminum phosphate, most of the active inorganic phosphorus being in the form of aluminum phosphate; this distribution pattern also indicates less weathering. In the Ashaka swamp rice soils there appears to be a balanced distribution of the three fractions of the active inorganic phosphorus; these soils are, in contrast to the other soils, relatively richly supplied with the three forms of active inorganic phosphate. The distribution of these fractions increases in the sequence calcium phosphate, iron phosphate and aluminum phosphate - as for the lowland soils.

The distributions of the inorganic phosphorus for the different soils are diagrammatically represented in Figures 1 and 2.

The agricultural significance of the distribution of inorganic phosphorus fractions in these soils of Mid-Western Nigeria is far-reaching. The soil phosphorus which is of immediate importance in the nutrition of crops comes from the inorganic fraction since the organic phosphorus cannot be used by crops until it has been mineralized. However, in the upland and lowland soils the inorganic phosphorus is not in a form in which it could be of much use to growing crops. In the Benin and Auchu upland soils almost all the inorganic phosphorus is immobilized in the occluded (inactive) form. In the Umutu upland, Ughelli and Ogume lowland soils between 50 and 60 percent of the inorganic phosphorus has been immobilized. The active inorganic phosphorus left for the nutrition of crops is thus so small that the

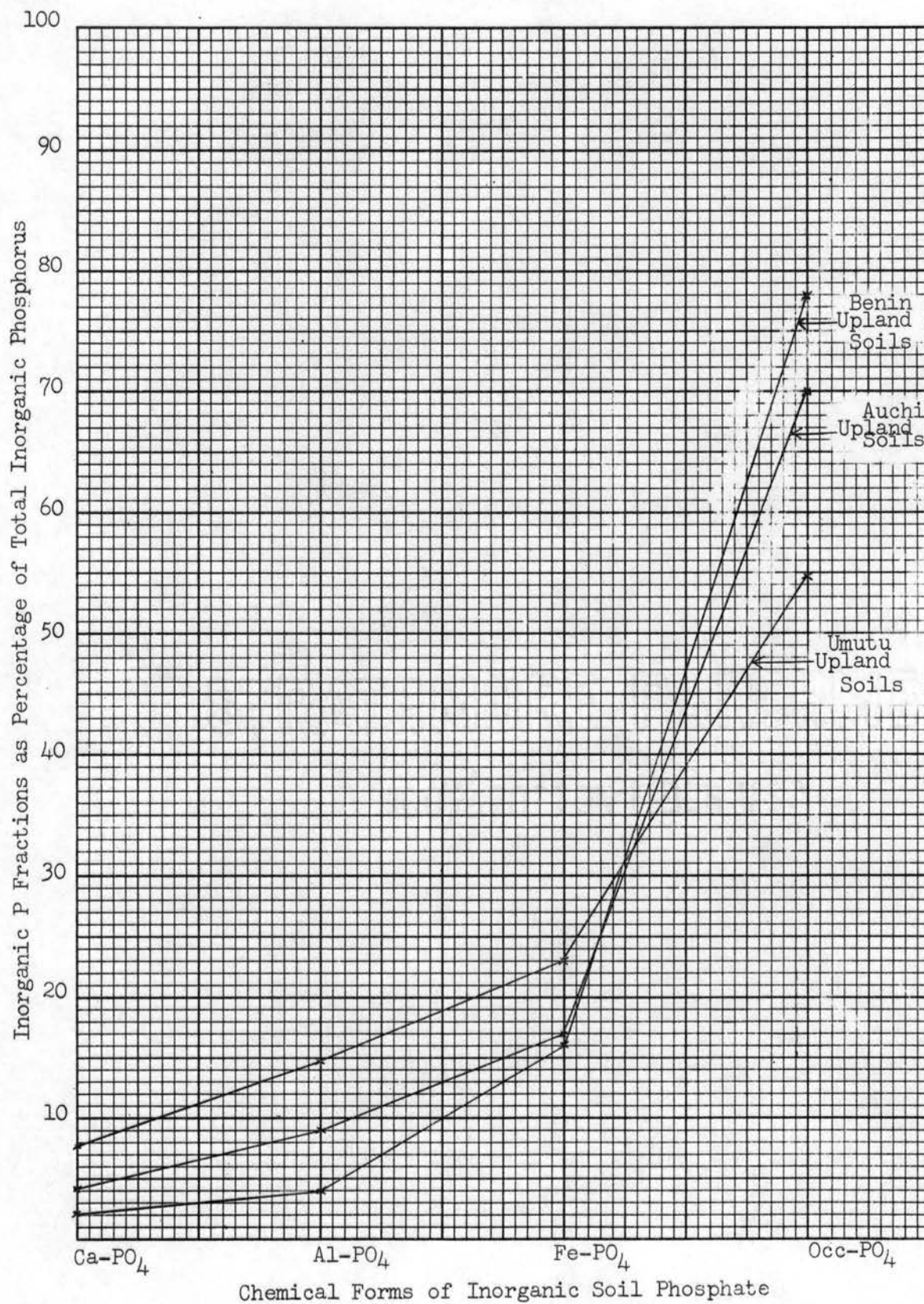


Figure 1. The percentage of the chemical forms of inorganic soil phosphate plotted as a chemical weathering sequence (Upland Soils).

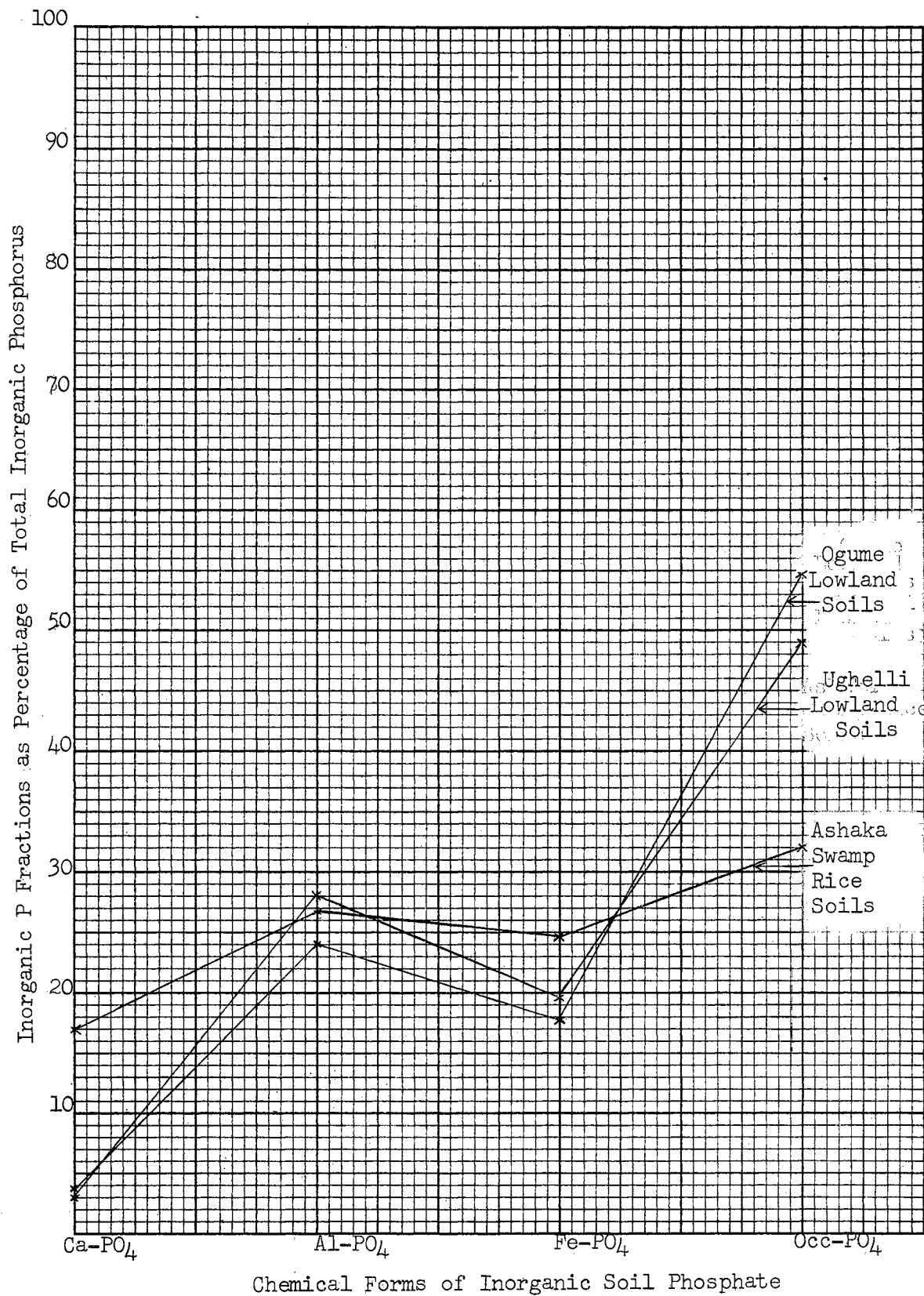


Figure 2. The percentage of the chemical forms of inorganic soil phosphate plotted as a chemical weathering sequence (Lowland and Swamp Rice Soils).

phosphorus requirements of the crops cannot be met without artificially supplementing the soil reserve of this element.

With this high level of occlusion of the inorganic phosphorus the very low levels of chemically available phosphorus for these soils are not surprising. The same reason should explain the fact that the upland soils have shown tremendous responses to phosphorus fertilization in the production of upland rice in Mid-Western Nigeria (38, 79).

Since most of the inorganic phosphorus in these soils has been immobilized, the potentially available phosphate is in the soil organic matter as organic phosphorus. Where, for economic reasons, artificial phosphorus fertilizers cannot be applied to the soils, care should therefore be taken to ensure the careful preservation of the organic matter containing the organic phosphorus. However, under the present agricultural practices in Mid-Western Nigeria the organic matter of the soil is virtually destroyed by firing before crops are planted. If this practice, for technical and economic reasons, cannot be discontinued at the present time and crop yields are to be increased and stabilized, artificial phosphorus fertilization on a large scale becomes imperative. Even where the organic matter can be preserved artificial phosphorus fertilization will still be required since the total phosphorus contents of the soils are very low.

Most of the inorganic phosphorus in the Ashaka swamp rice soils is in the active form and there is very little occlusion. Chemically available phosphorus is highest for these soils. They could thus be said to be comparatively more fertile than the upland and lowland soils. They could still benefit very well from phosphorus fertilization; the F.A.O. fertilizer trials (38) have shown responses to phosphorus fertilization.

The distribution of phosphorus in the Oklahoma soils is similar to the distribution in the lowland soils of Mid-Western Nigeria but the Miles soil has a sizeable portion of its inorganic phosphorus in the form of calcium phosphate. Occlusion of inorganic phosphorus in the two Oklahoma soils is 50 percent.

For the eighteen Nigerian soils, correlation coefficients were found between Bray No. 1 available phosphorus and the various phosphorus fractions; these are shown in Table VII. Highly significant correlations were found between available phosphorus and aluminum phosphate, iron phosphate and calcium phosphate but there were no correlations with organic phosphorus and occluded phosphate. The present findings seem to be a compromise between the findings of Benavides (10) and Ohiaeri (84) which had earlier been mentioned.

Carbon, Nitrogen and Organic Phosphorus Ratios

These ratios are shown in Table VIII. The carbon:nitrogen ratio has been discussed earlier.

There is much variability in the carbon:organic phosphorus ratio with a range of about 200 to 800. These values are high compared with ratios reported for Iowa soils by Pearson and Simonson (89). Nye and Bertheux (83) in Ghana however obtained ratios up to 500 on gneisses and granitic soils, and up to 350 for soils developed on sandstones and basic igneous rocks. The high carbon:organic phosphorus ratios for the soils of Mid-Western Nigeria obviously show that there is a serious deficiency of phosphorus in these soils.

TABLE VII
CORRELATION BETWEEN BRAY'S NO. I AVAILABLE PHOSPHORUS
AND PHOSPHORUS FRACTIONS

Fraction	Correlation Coefficient (r)	Remarks
Organic Phosphorus	0.2001	No correlation
Aluminum Phosphate	0.9983**	Significant at the 1% level
Iron Phosphate	0.9703**	Significant at the 1% level
Calcium Phosphate	0.9337**	Significant at the 1% level
Occluded Phosphate	0.2003	No correlation

TABLE VIII
CARBON, NITROGEN AND ORGANIC PHOSPHORUS RATIOS

Sample No.	Depth	C:N	C:P	N:P	C:N:P
<u>Benin Upland Soils</u>					
A175	0-12"	11.96	639.65	53.44	640:53:1
A176	0-12"	11.57	523.28	45.20	523:45:1
A177	0-12"	8.80	414.94	47.12	415:47:1
<u>Auchi Upland Soils</u>					
A404	0-12"	8.05	478.12	59.37	478:59:1
A405	0-12"	6.45	403.12	62.50	403:62:1
A406	0-12"	9.08	375.86	41.37	376:41:1
<u>Umutu Upland Soils</u>					
A467	0-12"	8.82	639.08	72.41	639:72:1
A468	0-12"	11.26	838.29	74.46	838:74:1
A469	0-12"	10.56	352.08	33.33	352:33:1
<u>Ughelli Lowland Soils</u>					
A447	0-12"	5.52	725.00	13.12	725:13:1
A448	0-12"	7.83	454.83	58.06	455:58:1
A449	0-12"	12.30	422.91	34.37	423:34:1
<u>Ogume Lowland Soils</u>					
A490	0-12"	7.28	156.92	21.53	157:21:1
A491	0-12"	12.68	354.41	27.94	354:28:1
A492	0-12"	12.69	351.80	27.71	352:28:1
<u>Ashaka Swamp Rice Soils</u>					
A464	0-12"	6.82	252.17	36.95	252:37:1
A465	0-12"	6.37	243.42	38.15	243:38:1
A466	0-12"	10.65	367.24	34.48	367:34:1
<u>Oklahoma Soils</u>					
62-S-693 (Hartsells)	0-3"	11.76	206.74	17.56	207:18:1
62-S-715 (Miles)	5-13"	5.15	121.81	23.63	122:24:1

The nitrogen:organic phosphorus ratios for the Nigerian soils lie between 30 and 70 and as observed by Pearson and Simonson (89) for Iowa soils, the variation in the nitrogen:organic phosphorus ratios is much smaller than the variation in the carbon:organic phosphorus ratio. For surface soils of Ghana, Nye and Bertheux (83) reported nitrogen:organic phosphorus ratios up to 43. As for the carbon:organic phosphorus ratio, the high nitrogen:organic phosphorus ratio of the Nigerian soils is indicative of a serious phosphorus deficiency.

The carbon:organic phosphorus and the nitrogen:organic phosphorus ratios for the Oklahoma soils are very close to corresponding ratios given for Iowa soils by Pearson and Simonson (89). The lower carbon:organic phosphorus and nitrogen:organic phosphorus ratios show that the Oklahoma soils, in relation to carbon and nitrogen, are not as phosphorus deficient as the Nigerian soils.

Fixation of Applied Water Soluble Phosphates

The patterns of fixation of added 200 ppm phosphorus in the forms of monobasic and dibasic ammonium phosphates for three and thirty days are shown in Tables IX(a-g), and X(a-g) respectively. The phosphorus fixed is taken as the difference between the total quantity added and that recovered as water soluble (saloid-bound).

Total Phosphorus Fixed: The analysis of variance for the fixation of the added phosphates by the soils of Mid-Western Nigeria is shown in Table XI. It is seen from this table that, on the whole, there is no significant difference between the total amounts of monobasic and dibasic ammonium phosphates fixed. There are, however, highly significant

TABLE IXa

FIXATION OF ADDED 200 PPM MONOBASIC AMMONIUM PHOSPHATE,
 $\text{NH}_4\text{H}_2\text{PO}_4$ FOR THREE AND THIRTY DAYS

BENIN UPLAND SOILS

Sample No.	Depth	Net Increase of Phosphorus in each Form (ppm)					
		Water Soluble (Saloid-Bound) Phosphate	Aluminum Phosphate	Iron Phosphate	Calcium Phosphate	Total (ppm) Recovered	% Recovery
<u>Three Days</u>							
A175	0-12"	21.00	88.12	43.75	1.87	154.74	77.37
A176	0-12"	35.00	90.00	39.06	2.34	166.40	83.20
A177	0-12"	50.00	87.18	20.81	1.25	159.24	79.62
<u>Thirty Days</u>							
A175	0-12"	8.75	103.75	46.88	2.50	161.88	80.94
A176	0-12"	15.00	106.25	35.93	2.50	159.68	79.84
A177	0-12"	17.50	113.75	34.87	3.12	169.24	84.62

TABLE IXb

FIXATION OF ADDED 200 PPM MONOBASIC AMMONIUM PHOSPHATE,
 $\text{NH}_4\text{H}_2\text{PO}_4$ FOR THREE AND THIRTY DAYS

AUCHI UPLAND SOILS

Sample No.	Depth	Net Increase of Phosphorus in each Form (ppm)					
		Water Soluble (Saloid-Bound) Phosphate	Aluminum Phosphate	Iron Phosphate	Calcium Phosphate	Total (ppm) Recovered	% Recovery
<u>Three Days</u>							
A404	0-12"	65.00	90.00	13.20	2.50	170.70	85.35
A405	0-12"	65.00	90.00	7.82	1.25	164.07	82.03
A406	0-12"	84.00	91.25	7.82	1.25	184.32	92.16
<u>Thirty Days</u>							
A404	0-12"	20.00	101.25	15.67	3.13	140.05	70.25
A405	0-12"	25.00	102.50	10.95	1.88	140.33	70.16
A406	0-12"	13.75	88.75	11.02	0.93	114.45	57.22

TABLE IXc

FIXATION OF ADDED 200 PPM MONOBASIC AMMONIUM PHOSPHATE,
 $\text{NH}_4\text{H}_2\text{PO}_4$ FOR THREE AND THIRTY DAYS

UMUTU UPLAND SOILS

Sample No.	Depth	Net Increase of Phosphorus in each Form (ppm)					Total (ppm) Recovered	% Recovery
		Water Soluble (Saloid Bound) Phosphate	Aluminum Phosphate	Iron Phosphate	Calcium Phosphate			
<u>Three Days</u>								
A467	0-12"	26.25	136.25	17.20	0.00	179.70	89.85	
A468	0-12"	35.50	111.92	26.56	0.00	173.98	86.99	
A469	0-12"	42.50	75.62	25.62	1.87	145.61	72.80	
<u>Thirty Days</u>								
A467	0-12"	13.12	137.50	23.45	0.00	174.07	87.03	
A468	0-12"	13.75	108.80	18.37	0.62	141.54	70.77	
A469	0-12"	30.00	97.50	28.12	1.25	156.87	78.43	

TABLE IXd

FIXATION OF ADDED 200 PPM MONOBASIC AMMONIUM PHOSPHATE,
 $\text{NH}_4\text{H}_2\text{PO}_4$ FOR THREE AND THIRTY DAYS

UGHELLI LOWLAND SOILS

Sample No.	Depth	Net Increase of Phosphorus in each Form (ppm)					Total (ppm) Recovered	% Recovery
		Water Soluble (Saloid Bound) Phosphate	Aluminum Phosphate	Iron Phosphate	Calcium Phosphate			
<u>Three Days</u>								
A447	0-12"	12.50	126.25	31.25	0.50	170.50	85.25	
A448	0-12"	23.75	122.50	17.82	0.63	164.70	82.35	
A449	0-12"	7.50	125.62	50.00	1.12	184.24	92.12	
<u>Thirty Days</u>								
A447	0-12"	7.50	123.75	40.63	0.75	172.63	86.31	
A448	0-12"	16.25	125.00	26.57	0.93	168.75	84.37	
A449	0-12"	3.75	109.38	68.75	1.38	183.26	91.63	

TABLE IXe

FIXATION OF ADDED 200 PPM MONOBASIC AMMONIUM PHOSPHATE,
 $\text{NH}_4\text{H}_2\text{PO}_4$ FOR THREE AND THIRTY DAYS

OGUME LOWLAND SOILS

Sample No.	Depth	Net Increase of Phosphorus in each Form (ppm)					Total (ppm) Recovered	% Recovery
		Water Soluble (Saloid Bound) Phosphate	Aluminum Phosphate	Iron Phosphate	Calcium Phosphate			
<u>Three Days</u>								
A490	0-12"	5.00	160.00	12.50	1.25	178.75	89.37	
A491	0-12"	5.00	176.25	6.25	0.00	187.50	93.75	
A492	0-12"	2.50	176.25	4.06	0.62	183.43	91.71	
<u>Thirty Days</u>								
A490	0-12"	1.25	147.50	18.75	1.25	168.75	84.37	
A491	0-12"	1.25	166.25	8.37	0.00	175.87	87.93	
A492	0-12"	1.25	171.25	8.37	1.25	182.12	91.06	

TABLE IXf

FIXATION OF ADDED 200 PPM MONOBASIC AMMONIUM PHOSPHATE,
 $\text{NH}_4\text{H}_2\text{PO}_4$ FOR THREE AND THIRTY DAYS

ASHAKA SWAMP RICE SOILS

Sample No.	Depth	Net Increase of Phosphorus in each Form (ppm)					Total (ppm) Recovered	% Recovery
		Water Soluble (Saloid Bound) Phosphate	Aluminum Phosphate	Iron Phosphate	Calcium Phosphate			
<u>Three Days</u>								
A464	0-12"	35.00	113.75	21.88	0.00	170.63	85.31	
A465	0-12"	82.50	100.00	21.87	0.00	204.37	102.18	
A466	0-12"	64.00	88.75	9.37	0.00	162.12	81.06	
<u>Thirty Days</u>								
A464	0-12"	13.12	118.75	21.88	0.00	153.75	76.87	
A465	0-12"	33.75	100.75	29.68	2.00	166.18	83.09	
A466	0-12"	22.50	93.75	9.37	0.00	125.62	62.81	

TABLE IXg

FIXATION OF ADDED 200 PPM MONOBASIC AMMONIUM PHOSPHATE,
 $\text{NH}_4\text{H}_2\text{PO}_4$ FOR THREE AND THIRTY DAYS

OKLAHOMA SOILS

Sample No.	Depth	Net Increase of Phosphorus in each Form (ppm)					% Recovery
		Water Soluble (Saloid Bound) Phosphate	Aluminum Phosphate	Iron Phosphate	Calcium Phosphate	Total (ppm) Recovered	
			<u>Three Days</u>				
62-S-693	0-3"	74.00	87.18	15.62	1.25	178.05	89.02
	(Hartsells)						
62-S-715	5-13"	54.00	108.12	20.30	11.25	193.67	96.83
	(Miles)						
			<u>Thirty Days</u>				
62-S-693	0-3"	30.00	103.75	21.88	0.00	155.63	77.81
	(Hartsells)						
62-S-715	5-13"	20.00	117.50	28.13	2.50	168.13	84.06
	(Miles)						

TABLE Xa

FIXATION OF ADDED 200 PPM DIBASIC AMMONIUM PHOSPHATE,
(NH₄)₂ HPO₄ FOR THREE AND THIRTY DAYS

BENIN UPLAND SOILS

Sample No.	Depth	Net Increase of Phosphorus in each Form (ppm)					% Recovery
		Water Soluble (Saloid Bound) Phosphate	Aluminum Phosphate	Iron Phosphate	Calcium Phosphate	Total (ppm) Recovered	
<u>Three Days</u>							
A175	0-12"	17.50	98.75	34.38	1.37	152.00	76.00
A176	0-12"	27.50	90.00	29.68	1.38	148.56	74.25
A177	0-12"	42.50	101.25	19.25	1.87	164.87	82.43
<u>Thirty Days</u>							
A175	0-12"	7.50	112.50	50.00	2.81	175.31	87.65
A176	0-12"	12.50	111.25	43.75	3.75	175.00	87.50
A177	0-12"	17.50	122.50	45.81	3.75	194.56	97.28

TABLE Xb

FIXATION OF ADDED 200 PPM DIBASIC AMMONIUM PHOSPHATE,
(NH₄)₂ HPO₄ FOR THREE AND THIRTY DAYS

AUCHI UPLAND SOILS

Sample No.	Depth	Net Increase of Phosphorus in each Form (ppm)					% Recovery
		Water Soluble (Saloid Bound) Phosphate	Aluminum Phosphate	Iron Phosphate	Calcium Phosphate	Total (ppm) Recovered	
<u>Three Days</u>							
A404	0-12"	47.50	105.00	9.11	0.50	162.11	81.05
A405	0-12"	57.50	101.25	6.26	0.41	164.32	82.66
A406	0-12"	50.00	95.00	7.90	0.00	152.90	76.45
<u>Thirty Days</u>							
A404	0-12"	35.00	126.25	21.92	3.13	190.05	95.02
A405	0-12"	40.00	123.75	20.32	2.50	190.32	95.16
A406	0-12"	36.25	122.50	17.27	1.25	179.77	89.88

TABLE Xc

FIXATION OF ADDED 200 PPM DIBASIC AMMONIUM PHOSPHATE,
 $(\text{NH}_4)_2 \text{HPO}_4$ FOR THREE AND THIRTY DAYS

UMUTU UPLAND SOILS

Sample No.	Depth	Net Increase of Phosphorus in each Form (ppm)					Total (ppm) Recovered	% Recovery
		Water Soluble (Saloid-Bound) Phosphate	Aluminum Phosphate	Iron Phosphate	Calcium Phosphate			
		<u>Three Days</u>						
A467	0-12"	18.75	135.00	18.76	0.00	172.51	86.25	
A468	0-12"	21.25	115.00	28.12	1.00	165.37	82.18	
A469	0-12"	42.50	93.75	39.00	0.60	175.85	87.42	
		<u>Thirty Days</u>						
A467	0-12"	15.00	147.50	28.14	0.00	190.64	95.32	
A468	0-12"	12.50	126.30	29.69	0.31	168.80	84.40	
A469	0-12"	21.25	107.50	28.12	0.00	156.87	78.43	

TABLE Xd

FIXATION OF ADDED 200 PPM DIBASIC AMMONIUM PHOSPHATE,
 $(\text{NH}_4)_2 \text{HPO}_4$ FOR THREE AND THIRTY DAYS

UGHELLI LOWLAND SOILS

Sample No.	Depth	Net Increase of Phosphorus in each Form (ppm)					Total (ppm) Recovered	% Recovery
		Water Soluble (Saloid Bound) Phosphate	Aluminum Phosphate	Iron Phosphate	Calcium Phosphate			
		<u>Three Days</u>						
A447	0-12"	10.00	131.25	31.25	0.63	173.13	86.56	
A448	0-12"	22.50	142.50	20.32	0.63	185.95	92.97	
A449	0-12"	7.50	123.13	53.13	0.62	184.38	92.19	
		<u>Thirty Days</u>						
A447	0-12"	7.50	138.75	31.25	2.50	180.00	90.00	
A448	0-12"	17.50	147.50	32.82	1.25	199.07	99.53	
A449	0-12"	1.25	128.13	71.88	1.87	203.13	101.56	

TABLE Xe

FIXATION OF ADDED 200 PPM DIBASIC AMMONIUM PHOSPHATE,
 $(\text{NH}_4)_2 \text{HPO}_4$ FOR THREE AND THIRTY DAYS

OGUME LOWLAND SOILS

Sample No.	Depth	Net Increase of Phosphorus in each Form (ppm)					Total (ppm) Recovered	% Recovery
		Water Soluble (Saloid Bound) Phosphate	Aluminum Phosphate	Iron Phosphate	Calcium Phosphate			
<u>Three Days</u>								
A490	0-12"	2.50	160.00	11.00	0.00	173.50	86.75	
A491	0-12"	2.50	166.25	6.25	0.00	175.00	87.50	
A492	0-12"	2.50	191.25	6.25	0.31	200.31	100.15	
<u>Thirty Days</u>								
A490	0-12"	1.25	162.50	25.00	0.93	189.68	94.84	
A491	0-12"	1.25	172.50	14.06	0.62	188.43	94.21	
A492	0-12"	1.25	185.00	12.50	1.25	200.00	100.00	

TABLE Xf

FIXATION OF ADDED 200 PPM DIBASIC AMMONIUM PHOSPHATE,
 $(\text{NH}_4)_2 \text{HPO}_4$ FOR THREE AND THIRTY DAYS

ASHAKA SWAMP RICE SOILS

Sample No.	Depth	Net Increase of Phosphorus in each Form (ppm)					Total (ppm) Recovered	% Recovery
		Water Soluble (Saloid Bound) Phosphate	Aluminum Phosphate	Iron Phosphate	Calcium Phosphate			
<u>Three Days</u>								
A464	0-12"	30.00	111.25	25.00	0.00	166.25	83.12	
A465	0-12"	52.50	93.75	18.75	4.37	169.37	84.68	
A466	0-12"	56.25	108.75	15.62	0.00	180.62	90.31	
<u>Thirty Days</u>								
A464	0-12"	18.75	118.75	37.50	0.00	175.00	87.50	
A465	0-12"	41.25	131.25	28.12	3.75	204.37	102.18	
A466	0-12"	28.75	96.25	18.75	0.00	143.75	71.87	

TABLE Xg

FIXATION OF ADDED 200 PPM DIBASIC AMMONIUM PHOSPHATE,
 $(\text{NH}_4)_2 \text{HPO}_4$ FOR THREE AND THIRTY DAYS

OKLAHOMA SOILS

Sample Depth No.	Net Increase of Phosphorus in each Form (ppm)					
	Water Soluble (Saloid Bound) Phosphate	Aluminum Phosphate	Iron Phosphate	Calcium Phosphate	Total (ppm) Recovered	% Recovery
		<u>Three Days</u>				
62-S-693 0-3" (Hartsells)	80.00	88.00	12.50	0.00	180.50	90.25
62-S-715 5-13" (Miles)	45.00	112.50	19.38	4.37	181.25	90.62
		<u>Thirty Days</u>				
62-S-693 0-3" (Hartsells)	46.25	105.00	31.25	2.47	189.97	94.98
62-S-715 5-13" (Miles)	30.00	113.75	37.50	6.25	188.75	94.37

TABLE XI

FIXATION OF ADDED PHOSPHATES BY THE SOILS OF MID-WESTERN NIGERIA

ANALYSIS OF VARIANCE TABLE

Source	DF	Mean Squares for Phosphorus Fixed and Percent Recovery				
		Total Phosphorus Fixed	P Fixed As Aluminum Phosphate	P Fixed As Iron Phosphate	P Fixed As Calcium Phosphate	Percent Recovery
Total	71					
Soil Types (S)	5	3,165.9882**	8,004.9834**	1,731.7675**	6.0255**	228.1637**
Type of P Added (T)	1	117.5300	1,981.0365**	145.8062	0.1624	584.1931**
S x T	5	10.2554	60.3042	12.8245	0.9497	20.7018
Days (D)	1	4,991.8366**	1,122.3532*	922.0649**	7.3600**	0.3828
T x D	1	609.6450*	315.9679	128.2134	1.1100	828.0415**
S x D	5	446.5164**	234.2400	54.7609	1.0525	81.6734
S x T x D	5	156.8539	25.5387	25.9727	0.6955	87.5673
Error	48	91.7259	167.1830	97.8256	0.8084	43.5901

**Significant at the 1% Level

*Significant at the 5% Level

differences between the total amounts of phosphorus fixed by the different soils and for three and thirty days. From Table XII(a) it is seen that the Ogume lowland soils fixed the highest amounts of phosphorus followed by the Ughelli lowland soils, Benin and Umutu upland soils. The Auchi upland and the Ashaka swamp rice soils fixed the lowest amounts of phosphorus. The Ogume and Ughelli lowland soils contain large amounts of exchangeable aluminum while the Benin upland soils contain large amounts of free iron as well as considerable amounts of exchangeable aluminum; these properties should account for the higher amounts of phosphorus fixed by these soils. It is also seen from Table XII(a) that much more phosphorus was fixed in thirty days than in three days.

From Table XI it is seen that, for the total amounts of phosphorus fixed, there is a significant interaction between type of phosphate added and number of days; there is also a highly significant interaction between soil types and number of days. The interaction between phosphate type and number of days shows that the rates of reaction of the two forms of phosphate are not the same in the soils; the phosphorus fixed in each case increases from three to thirty days but the rates of increase are different; this interaction is diagrammatically represented in Figure 3. The difference in the reaction rates of the two phosphates may be due to differences in their pH values and solubilities, dibasic ammonium phosphate being more alkaline and less soluble. The interaction between soil types and days shows that the rates at which phosphorus fixed increases from three to thirty days are not the same for all the soils; it is seen from Table XII (a), that for some soils the total amounts of phosphorus fixed for three and thirty days are about the same while they are widely different in others.

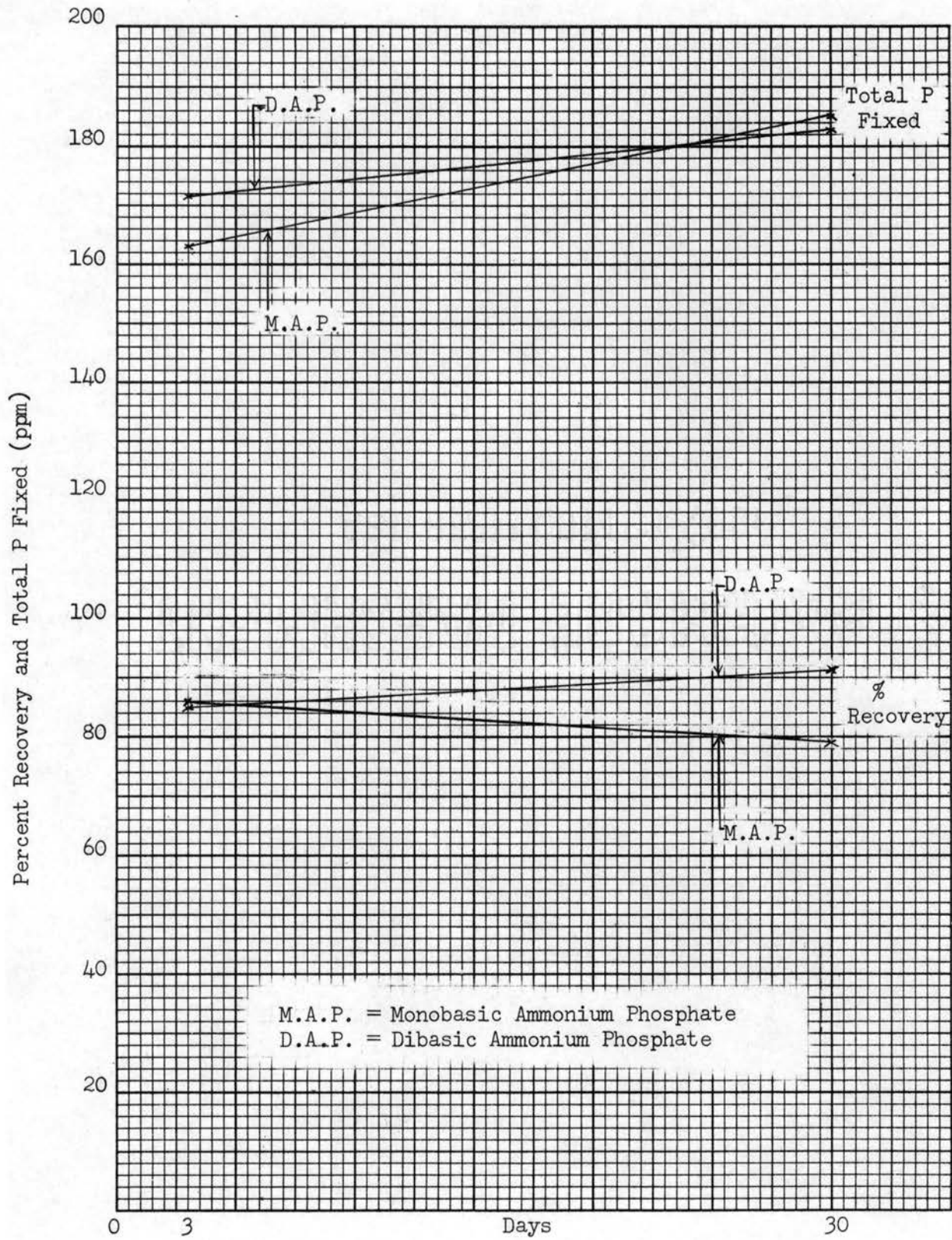


Figure 3. Fixation and Recovery Patterns for Monobasic and Dibasic Ammonium Phosphates

TABLE XIIIa

FIXATION OF 200 PPM ADDED PHOSPHATES BY THE SOILS OF MID-WESTERN NIGERIA

TABLE OF MEANS

Type of P* Added	Days	Total Phosphorus Fixed (ppm)					Average All Soils	
		Soil Types						
		Benin	Auchi	Umutu	Ashaka	Ogume	Ughelli	
1	3	164.6667	128.6667	165.2500	139.5000	195.8333	185.4167	163.2222
1	30	186.2500	180.4167	181.0433	176.8767	198.7500	190.8333	185.6950
1		175.4583	154.5417	173.1467	158.1883	197.2917	188.1250	174.4586
2	3	170.8333	148.3333	172.5000	153.7500	197.5000	186.6667	171.5972
2	30	187.5000	162.9167	183.7500	170.4167	198.7500	191.2500	182.4306
2		179.1667	155.6250	178.1250	162.0833	198.1250	188.9583	177.0139
	3	167.7500	138.5000	168.8750	146.6250	196.6667	186.0417	167.4097
	30	186.8750	171.6667	182.3967	173.6467	198.7500	191.0417	184.0628
Soil Type Averages		177.3125	155.0833	175.6358	160.1358	197.7083	188.5417	175.7363

*1 = Monobasic Ammonium Phosphate

2 = Dibasic Ammonium Phosphate

TABLE XIIIb

FIXATION OF 200 PPM ADDED PHOSPHATES BY THE SOILS OF MID-WESTERN NIGERIA

TABLE OF MEANS

Type of P* Added	Days	Phosphorus Fixed as Aluminum Phosphate (ppm)						Average All Soils
		Soil Types						
		Benin	Auchi	Umutu	Ashaka	Ogume	Ughelli	
1	3	88.4333	90.4167	107.9300	100.8333	170.8333	124.7900	113.8728
1	30	107.9167	97.5000	114.6000	104.4167	161.6667	119.3767	117.5794
1		98.1750	93.9583	111.2650	102.6250	166.2500	122.0833	115.7261
2	3	96.6667	100.4167	114.5833	104.5833	172.5000	132.2933	120.1739
2	30	115.4167	124.1667	127.1000	115.4167	173.3333	138.1267	132.2600
2		106.0417	112.2917	120.8417	110.0000	172.9167	135.2100	126.2169
	3	92.5500	95.4167	111.2567	102.7083	171.6667	128.5417	117.0233
	30	111.6667	110.8333	120.8500	109.9167	167.5000	128.7517	124.9197
Soil Type Averages		102.1083	103.1250	116.0533	106.3125	169.5833	128.6467	120.9715

*1 = Monobasic Ammonium Phosphate

*2 = Dibasic Ammonium Phosphate

TABLE XIIc

FIXATION OF 200 PPM ADDED PHOSPHATES BY THE SOILS OF MID-WESTERN NIGERIA

TABLE OF MEANS

Type of P* Added	Days	Phosphorus Fixed as Iron Phosphate (ppm)						Average All Soils
		Soil Types						
		Benin	Auchi	Umutu	Ashaka	Ogume	Ughelli	
1	3	34.5400	9.6133	23.1267	17.7067	7.6033	33.0233	20.9356
1	30	39.2267	12.5467	23.3133	20.3100	11.8300	45.3167	25.4239
1		36.8833	11.0800	23.2200	19.0083	9.7167	39.1700	23.1797
2	3	27.7700	7.7567	28.6267	19.7900	7.8333	34.9000	21.1128
2	30	46.5200	19.8367	28.6500	28.1233	17.1867	45.3167	30.9389
2		37.1450	13.7967	28.6383	23.9567	12.5100	40.1083	26.0258
	3	31.1550	8.6850	25.8767	18.7483	7.7183	33.9617	21.0242
	30	42.8733	16.1917	25.9817	24.2167	14.5083	45.3167	28.1814
Soil Types Averages		37.0142	12.4383	25.9292	21.4825	11.1133	39.6392	24.6028

*1=Monobasic Ammonium Phosphate

2=Dibasic Ammonium Phosphate

TABLE XIIId

FIXATION OF 200 PPM ADDED PHOSPHATES BY THE SOILS OF MID-WESTERN NIGERIA

TABLE OF MEANS

Type of P* Added	Days	Phosphorus Fixed as Calcium Phosphate (ppm)						Average All Soils
		Soil Types						
		Benin	Auchi	Umutu	Ashaka	Ogume	Ughelli	
1	3	1.8200	1.6667	.6233	.0000	.6233	.7500	.9139
1	30	2.7067	1.9800	.6233	.6667	.8333	1.0200	1.3050
1		2.2633	1.8233	.6233	.3333	.7283	.8850	1.1094
2	3	1.5400	.3033	.5333	1.4567	.1033	.6267	.7606
2	30	3.4367	2.2933	.1033	1.2500	.9333	1.8733	1.6483
2		2.4883	1.2983	.3183	1.3533	.5183	1.2500	1.2044
	3	1.6800	.9850	.5783	.7283	.3633	.6883	.8372
Soil Type Averages	30	3.0717	2.1367	.3633	.9583	.8833	1.4467	1.4767
		2.3758	1.5608	.4708	.8433	.6233	1.0675	1.1569

*1 = Monobasic Ammonium Phosphate

2 = Dibasic Ammonium Phosphate

TABLE XIIe
 FIXATION OF 200 PPM ADDED PHOSPHATES BY THE SOILS OF MID-WESTERN NIGERIA

TABLE OF MEANS

Type of P* Added	Days	Percent Recovery of Added Phosphates						Average All Soils
		Soil Types						
		Benin	Auchi	Umutu	Ashaka	Ogume	Ughelli	
1	3	80.0633	86.5133	83.2133	89.4967	91.6100	86.5733	86.2450
1	30	81.8000	65.8767	78.7433	74.2567	87.7867	87.4367	79.3167
1		80.9317	76.1950	80.9783	81.8767	89.6983	87.0050	82.7808
2	3	77.5600	80.0533	85.2833	86.0200	91.4667	90.5733	85.1594
2	30	90.8100	93.3533	86.0500	87.1833	96.3500	97.0300	91.7961
2		84.1850	86.7033	85.6667	86.6017	93.9083	93.8017	88.4778
	3	78.8117	83.2833	84.2483	87.7583	91.5383	88.5733	85.7022
	30	86.3050	79.6150	82.3967	80.7200	92.0683	92.2333	85.5564
Soil Type Averages		82.5583	81.4492	83.3225	84.2392	91.8033	90.4033	85.6293

*1 = Monobasic Ammonium Phosphate
 2 = Dibasic Ammonium Phosphate

For the eighteen soil samples of Mid-Western Nigeria considered together there were highly significant linear correlations between the total amounts of phosphorus fixed and exchangeable aluminum (Table XIII). This was also found by Coleman et al. (24) for soils of the North Carolina piedmont. There were no correlations between phosphorus fixed and free iron (Table XIV).

Phosphorus Fixed as Aluminum Phosphate: As shown in Tables IX and X, most of the fixed phosphorus was present as aluminum phosphate (NH_4F -soluble); this is in agreement with the highly significant correlations found between exchangeable aluminum and the total amounts of phosphorus fixed. The accumulation of recently fixed phosphate as aluminum phosphate has been observed by other workers (17, 84, 113).

There is a highly significant difference between the amounts of phosphorus fixed as aluminum phosphate by the different soils as shown in Table XI. The Ogume and Ughelli lowland soils fixed the highest amounts of phosphorus as aluminum phosphate (Table XIIb). These soils are seasonally water-logged and poorly-drained. Yuan et al. (113) have also shown poorly-drained and acid Florida soils to fix phosphorus in the same way as the Ogume and Ughelli lowland soils. This peculiar behavior of poorly-drained soils has been explained by the work of DeMumbrum (32) who found that aluminum is present in poorly-drained soils as amorphous aluminum minerals while in well-drained soils it is crystalline. The former reacts more readily with phosphorus than the latter because of its greater surface. The Ogume and Ughelli lowland soils, as shown earlier, had the highest amounts of exchangeable aluminum - of all the soils studied.

TABLE XIII

CORRELATION BETWEEN EXCHANGEABLE ALUMINUM AND AMOUNTS OF PHOSPHORUS FIXED*

Phosphorus Fixed (Form and Period of Fixation)	Correlation Coefficient (r)	Remarks
(i) Monobasic Ammonium Phosphate Fixed for 3 Days	0.8731**	Significant at the 1% Level
(ii) Monobasic Ammonium Phosphate Fixed for 30 Days	0.8593**	Significant at the 1% Level
(iii) Dibasic Ammonium Phosphate Fixed for 3 Days	0.9283**	Significant at the 1% Level
(iv) Dibasic Ammonium Phosphate Fixed for 30 Days	0.8569**	Significant at the 1% Level

*Phosphorus Fixed = Concentration Added - Concentration of Saloid-Bound Recovered.

TABLE XIV

CORRELATION BETWEEN FREE IRON AND AMOUNTS OF PHOSPHORUS FIXED*

Phosphorus Fixed (Form and Period of Fixation)	Correlation Coefficient (r)	Remarks
(i) Monobasic Ammonium Phosphate Fixed for 3 Days	-0.1483	No Correlation
(ii) Monobasic Ammonium Phosphate Fixed for 30 Days	-0.1543	No Correlation
(iii) Dibasic Ammonium Phosphate Fixed for 3 Days	-0.1991	No Correlation
(iv) Dibasic Ammonium Phosphate Fixed for 30 Days	-0.0261	No Correlation

*Phosphorus Fixed = Concentration Added - Concentration of Saloid-Bound Recovered.

There is a highly significant difference between the amounts of monobasic and dibasic ammonium phosphates fixed as aluminum phosphate as shown in Table XI. More of dibasic ammonium phosphate was fixed as aluminum phosphate (Table XIIb); it appears that the dibasic phosphate is more reactive with these soils. It is possible that the dibasic ammonium phosphate is so reactive that it decomposes the kaolinitic clays (which are dominant in these soils) and subsequently reacts with the aluminum resulting from the decomposition. Phosphate-induced decomposition of kaolinite (with the formation of more aluminum phosphate) has been reported by Low and Black (73). Tamimi et al. (100) have shown by x-ray diffraction that peaks of kaolinite in three Hawaiian soils diminished in magnitude after treatment with dibasic ammonium phosphate. They suggested that the dibasic ammonium phosphate attacked the 1:1 clays in these soils extracting aluminum and forming trankite as a reaction product.

There is a significant difference between the amounts of phosphorus fixed as aluminum phosphate for three and thirty days (Table XI), with more phosphorus being fixed as aluminum phosphate in thirty days than in three days (Table XIIb).

Phosphorus Fixed as Iron Phosphate: As shown in Tables IX and X, after aluminum phosphate, iron phosphate is the next largest form in which the fixed phosphorus recovered was present. Generally, however, the amounts of phosphorus fixed as iron phosphate were far below the amounts fixed as aluminum phosphate.

There is a highly significant difference between the amounts of phosphorus fixed as iron phosphate by the different soils as shown in Table XI. It is seen from Table XIIc that the Ughelli lowland

soils fixed the highest amounts of phosphorus as iron phosphate, followed by the Benin upland soils; the Auchi upland and the Ogume lowland soils fixed the lowest amounts of phosphorus as iron phosphate while Umutu upland and Ashaka swamp rice soils are intermediate. No correlations were found between total amounts of phosphorus fixed and free iron and a direct relationship between free iron and phosphorus fixed as iron phosphate is not obvious from the experimental data; for example, the Ughelli lowland soils which fixed the highest amounts of phosphorus as iron phosphate do not have the highest contents of free iron; the Benin upland soils which came next to the Ughelli lowland soils have the highest contents of free iron; the phosphorus fixed as iron phosphate by the Auchi upland soils is about one-third the one fixed as iron phosphate by the Ughelli lowland soils despite the fact that the Auchi upland soils contain considerably more free iron than the Ughelli lowland soils. The differences in the surface areas of the hydrous iron oxides in the different soils might account for the highly significant variations in the amounts of phosphorus fixed as iron phosphate by the different soils.

The same amounts of phosphorus were fixed as iron phosphate irrespective of the form of phosphate added (Table XI). This finding gives more strength to the reasoning that the higher amounts of dibasic ammonium phosphate fixed as aluminum phosphate is the result of its decomposition of kaolinite which results in the release of aluminum and not iron. A highly significant difference exists between the amounts of phosphorus fixed as iron phosphate for three and thirty days (Table XI); more phosphorus was fixed as iron phosphate in thirty days than in three days (Table XIIc).

Phosphorus Fixed as Calcium Phosphate: Comparatively negligible amounts of phosphorus were fixed as calcium phosphate as shown in Tables IX and X; in some cases none of the added phosphate was fixed as calcium phosphate. There were, however, highly significant differences between the amounts of phosphorus fixed as calcium phosphate by the different soils and for three and thirty days as shown in Table XI. The Benin upland soils fixed the highest amounts of phosphorus as calcium phosphate followed by the Auchi upland soils (Table XIIId); these two soils had the lowest amounts of phosphorus fixed as aluminum phosphate; it is thus possible that more of the added phosphates were left over for reaction with calcium in these soils. Although this highly significant difference in the amounts of phosphorus fixed as calcium phosphate exists yet it may not be of practical importance since the absolute amounts involved are very small.

The amounts of phosphorus fixed as calcium phosphate increased from three to thirty days (Table XIIId). As for iron phosphate, the same amounts of phosphorus were fixed as calcium phosphate irrespective of the form of phosphate added (Table XI).

Percent Recovery of the Added Phosphates: The recovery percentages are shown in the last columns of Tables IX and X. On the whole, the recovery percentages of the different soils of Mid-Western Nigeria averaged between 81 and 92 (Table XIIId). The phosphorus which could not be recovered as saloid-bound, aluminum phosphate, iron phosphate and calcium phosphate must have been fixed in forms other than these ones determined; the unrecovered phosphorus must have been strongly adsorbed on the surfaces of clay minerals and hydrous iron oxides. This strong adsorption is more likely in these soils in which 1:1 clays

and hydrous iron oxides are abundant; the soils which have the lower recovery percentages have the higher contents of free iron. It is unlikely that the unrecovered phosphorus has gone into the occluded form since occlusion of phosphorus occurs over a very long period. Yuan et al. (113) recovered 86-97 percent of the phosphate added to some acid soils of Florida.

There is a highly significant difference between the recovery percentages for the different soils as shown in Table XI. The Ogum and Ughelli lowland soils have the highest recovery percentages (Table XIIe). In these two soils the phosphorus is fixed almost exclusively as aluminum phosphate which is readily recovered in the NH_4F extractant thus accounting for the significantly higher recovery percentages. It is interesting to note that these two soils which have the highest recovery percentages also fixed the highest amounts of phosphorus. Thus, different soils might fix similar amounts of phosphorus but the percentage of the fixed phosphorus recovered as aluminum, iron and calcium phosphates might vary significantly depending on the form in which the phosphorus has been fixed.

There is a highly significant difference between the recovery percentages of the monobasic and dibasic ammonium phosphates as shown in Table XI. The dibasic ammonium phosphate has a higher recovery percentage than the monobasic ammonium phosphate (Table XIIe). The possible decomposition of kaolinite by the dibasic ammonium phosphate (resulting in the formation of more recoverable aluminum phosphate) coupled with the lower solubility of the dibasic ammonium phosphate might account for this difference. For all soils and phosphates considered together there is no significant difference between the recovery percentages for three and thirty days but there is a

highly significant interaction between the type of phosphate added and the number of days (Table XI). This interaction is diagrammatically represented in Figure 3. It shows that, for the individual phosphates, the changes in percent recovery from three to thirty days are approximately the same but in opposite directions; the main effect of one form of phosphate from three to thirty days cancels that of the other form of phosphate hence there is no overall main effect for days. Data in Figure 3 and Table XIIe show that the percent recovery of dibasic ammonium phosphate increases while that of monobasic ammonium phosphate decreases, by approximately the same amounts, from three to thirty days. The increased percent recovery for dibasic ammonium phosphate should be due to the formation of more aluminum phosphate at the end of thirty days probably as a result of further decomposition of kaolinite by the dibasic ammonium phosphate. The decreased percent recovery of the monobasic ammonium phosphate should be due to further adsorption of this compound on the surfaces of clay minerals and hydrous iron oxides. The mechanisms responsible for fixing these two forms of phosphate in the soil do not therefore appear to be exactly the same.

Fixation of Added Phosphate by the Oklahoma Soils: The patterns of fixation of the added phosphates by the Oklahoma soils are shown in Tables IXg and Xg. It is seen that the two Oklahoma soils react with the added phosphates in essentially the same manner as the Nigerian soils. The mean recovery percentages for the Oklahoma soils is 90 which is appreciably higher than the mean recovery percentages of four of the six Nigerian soils and approximately equal to those of the two remaining soils which had the highest recovery percentages.

CHAPTER V

SUMMARY AND CONCLUSIONS

With the exception of one swamp rice (paddy) soil sample which had a total phosphorus content of 320 ppm, all the soils of Mid-Western Nigeria studied had total phosphorus contents of less than 200 ppm, the range being from 43 to 192 ppm. These values are low compared with those for some other parts of the world but are similar to those of other West African soils of similar genetic origin. For all the Mid-Western Nigerian soils studied organic phosphorus ranged from 40 to 70 percent of total phosphorus. For the upland soils 60 to 78 percent of the total inorganic phosphorus was in the occluded (inactive) form; the lowland soils had 50 to 60 percent of their total inorganic phosphorus occluded while the swamp rice soils had 19 to 47 percent of their total inorganic phosphorus occluded.

Available phosphorus was with the exception of two swamp rice soils, low for all the soils. Highly significant correlations were found between available phosphorus and aluminum phosphate, iron phosphate and calcium phosphate but there were no correlations with organic phosphorus and occluded phosphate.

It is suggested that the high degree of occlusion of the inorganic phosphorus in the upland soils might account for the remarkable responses they have shown to phosphorus fertilization.

The pattern of distribution of the inorganic phosphorus fractions shows that the lowland and swamp rice soils are genetically younger and less weathered soils while the upland soils are older and much more strongly weathered.

The total phosphorus contents of the two Oklahoma soils are also below 200 ppm; these are low compared with some other Oklahoma soils. These two soils had 50 percent of their total inorganic phosphorus in the occluded form.

For the Nigerian soils, the same amounts of phosphorus were fixed irrespective of the form of ammonium phosphate added but it was possible to recover more of the fixed dibasic ammonium phosphate. For the six soils there were highly significant differences between total amounts of phosphorus fixed, phosphorus fixed as aluminum, iron and calcium phosphates and recovery percentages. In all the Nigerian soils the phosphorus fixed was present mostly as aluminum phosphate but more of the dibasic ammonium phosphate was fixed in this form. Total amounts of phosphorus fixed, phosphorus fixed as aluminum, iron and calcium phosphates increased from three to thirty days; the rates of increase of total amounts of phosphorus fixed, from three to thirty days, were not the same in all the soils.

From the three-to the thirty-day periods percent recovery did not increase for all the soils and added phosphates taken together; individually, however, the recovery percentage of the dibasic ammonium phosphate increased while that of the monobasic ammonium phosphate decreased, by the same amounts, from three to thirty days thus suggesting that the mechanisms responsible for fixing these two forms of phosphates in the soil are not exactly the same.

The dibasic and monobasic ammonium phosphates do not react with all the Nigerian soils at the same rates between the three and thirty day periods.

Highly significant correlations were found between the total amounts of phosphorus fixed and the exchangeable aluminum in the Nigerian soils.

The two Oklahoma soils fixed phosphorus in essentially the same way as the Nigerian soils but the mean recovery percentage for these two soils was appreciably higher than the recovery percentages of four of the six Nigerian soils.

This study has shown that there is a serious phosphorus deficiency in the soils of Mid-Western Nigeria and that this deficiency is due to both low contents of total phosphorus and the very low availability of the forms of phosphorus present. It has also shown that the efficiency of phosphorus fertilization will differ from soil to soil; allowances should be made for such differences in fertilizer application recommendations. There was no difference between the total amounts of monobasic and dibasic ammonium phosphates fixed but there were significant differences between their reaction rates, amounts fixed as aluminum phosphate and recovery percentages; these could result in a difference in the efficiencies of these two compounds when used as fertilizer in the soils of Mid-Western Nigeria; any such difference will have to be ascertained by field experiments with various crops on the different soils. It would appear that banding of phosphorus fertilizers in these soils will be more effective than broadcasting since phosphorus is fixed mainly as aluminum and iron phosphates; there may also be a large residual effect of the phosphorus fertilizer where phosphorus is fixed mostly as aluminum phosphate.

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APPENDIX

SOIL SAMPLE DESCRIPTIONS¹1. Benin Upland Soils

<u>Sample No.</u>	<u>Depth</u>	<u>Remarks</u>
A175	0-12"	High forest vegetation (Ogba Forest Reserve). Gentle slope towards the Ogba stream. Charcoal remains present. Sandy loam; dark reddish brown (2.5 YR 3/4 moist).
A176	0-12"	Broken high forest vegetation surrounded by farmland. Level land. Charcoal remains present. Sandy loam; dark reddish brown (2.5 YR 3/4 moist).
A177	0-12	High forest vegetation on level land. Charcoal remains present. Sandy loam; dark reddish brown (2.5 YR 3/4 moist)

General Use of the Soils:

Plantation Crops: Rubber, oil palm, cocoa, citrus, pineapples.

Field Crops: Yam, maize, cassava, rice.

¹Due acknowledgement is given to J. O. Okotie (Field Overseer-Soil Survey), M.A.N.R., Benin City for the site descriptions.

2. Auchi Upland Soils

<u>Sample No.</u>	<u>Depth</u>	<u>Remarks</u>
A404	0-12"	Broken forest vegetation on upper slope. Sand; dark reddish brown (2.5 YR 3/4 moist).
A405	0-12"	High forest vegetation on upper slope. Worm casts present. Sand; dark reddish brown (2.5 YR 3/4 moist).
A406	0-12"	Derived savannah vegetation on middle slope. Sand; dark reddish brown (2.5 YR 3/4 moist)

General Use of the Soils:

Plantation Crops: Mostly cocoa.

Field Crops: Yam, maize, cotton, cassava, rice, cowpeas.

3. Umutu Upland Soils

<u>Sample No.</u>	<u>Depth</u>	<u>Remarks</u>
A467	0-12"	High forest vegetation on level land. Worm casts and charcoal remains present. Loamy sand; dusky red (2.5 YR 3/2 moist).
A468	0-12"	Broken high forest vegetation on level land. Worm casts present. Loamy sand; dusky red (2.5 YR 3/2 moist).
A469	0-12"	Broken forest vegetation on middle slope. Worm casts present. Sand; dusky red (2.5 YR 3/2 moist).

General Use of the Soils:

Plantation Crops: Mostly Rubber and Oil Palm.

Field Crops: Yam, maize, cassava, rice.

4. Ughelli Lowland Soils

<u>Sample No.</u>	<u>Depth</u>	<u>Remarks</u>
A447	0-12"	High forest vegetation along the bank of the Ohwaro stream; lower slope. Few worm casts present. Loamy sand; dark brown (7.5 YR 3/2 moist).
A448	0-12"	High forest vegetation on lower slope. Sandy loam; dark brown (7.5 YR 3/2 moist).
A449	0-12"	Broken high forest vegetation. Worm casts present. Sandy loam; dark brown (7.5 YR 3/2 moist)

General Use of the Soil:

Plantation Crops: Mostly Rubber and Oil Palm.

Field Crops: Cassava, maize, yam.

5. Ogume Lowland Soils

<u>Sample No.</u>	<u>Depth</u>	<u>Remarks</u>
A490	0-12"	Derived savannah vegetation surrounded by high forest. Level seasonally water-logged plain land. Loamy sand; very dark grey (5 YR 3/1 moist).
A491	0-12"	Derived savannah vegetation surrounded by high forest. Level seasonally water-logged plain land. Loamy sand; very dark grey (5 YR 3/1 moist).
A492	0-12"	Derived savannah vegetation surrounded by high forest. Level seasonally water-logged plain land. Loamy sand; very dark grey (5 YR 3/1 moist).

General Use of the Soils:

None at the present time.

6. Ashaka Swamp Rice Soils

<u>Sample No.</u>	<u>Depth</u>	<u>Remarks</u>
A464	0-12"	Grassland vegetation on the bank of the Ase creek. Charcoal remains present. Loamy sand; reddish brown (5 YR 4/4 moist).
A465	0-12"	Broken forest and grassland vegetation on the bank of the Ase creek. Charcoal remains present. Loamy sand; dark reddish brown (5 YR 3/2 moist).
A466	0-12"	Grassland vegetation on the bank of the Ase creek. Charcoal remains present. Loamy sand; dark reddish brown (5 YR 3/2 moist).

General Use of the Soils:

Plantation Crops: Rubber on drier land.

Field Crops: Mostly swamp rice.

OKLAHOMA SOILS

1. Hartsells: Hartsells fine sandy loam, 1 to 3 percent slopes.
Pittsburg County, Oklahoma

Hartsells soils consist of well drained red-yellow Podzolic soils developed over Pennsylvania Age sandstone that contains thin beds of shales and clays. They are associated with Hector, but differ from them by having a more developed and deeper profile. They occur principally on the gently sloping ridge-top. Hector occurs on the steeper side slopes. They are less red than the associated Linker soils.

Soil Profile: Hartsells fine sandy loam, 1 to 3 percent slopes - Virgin. Located about 800 feet east and 350 feet south of the half mile line on the north side of Section 8 Twp. 5N, Range 13E, Pittsburg County, Oklahoma.

A₁ 0 to 3 inches. Grayish brown (10 YR 5/2) fine sandy loam; dark grayish brown (10 YR 4/2) when moist, weak fine granular structure; very friable when moist, slightly hard when dry; clear boundary; 2 to 8 inches thick.

Topography: Hill tops and single side slopes dominantly between 2 and 5 percent; it also occurs in minor areas on slopes up to 10 percent in association with Hector soils.

Drainage and permeability: Well-drained, runoff medium; permeability moderately rapid.

Vegetation: Postoak, Blackjack oak, Hickory (and minor amounts of Shortleaf Pine in the southeast part of Oklahoma east of the 44 inch rainfall line).

Use: Abandoned cropland, cropland, and brushy pasture. The cropland is used for growing small grains, bermuda grass, sorghums and peanuts.

Distribution: (In Oklahoma) Generally east of the 38 inch rainfall line and north of the Cretaceous geologic materials.

2. Miles: The Miles series comprises sandy reddish normal reddish chestnut soils developed on sandy calcareous earths in the Rolling Plains of western Texas and Oklahoma. The parent material is mostly plains outwash or old alluvium of the Quaternary and Pliocene but some areas are developed on petrographically similar earths of other formations or mode of accumulation. The principal associated series are Abilene, Sentinel, Mansker, Potter, Tivoli, probably Brownfield and various series developed on red beds.

1. Soil profile (Miles fine sandy loam)

A₁ 0-10" Brown (7.5 YR 4/3; 3/4, moist) fine sandy loam; neutral; weak medium granular; grades to horizon 2 through a transition 1 to 4 inches thick.

Range in
Thickness
6-15"

Topography: Nearly level to undulating upland with gradients up to about 5 percent, dominantly 1 to 3 percent; the surfaces are convex to plane.

Drainage: Moderate to rapid from the surface; moderate internally; very favorable for crop production.

Vegetation: Mainly Andropogons and other coarse bunch grasses plus a few shrubs of mesquite, lote, catclaw, Yucca, and others; some areas of loamy fine sand are covered with shin oak.

Use: Very largely in cultivation; with cotton and sorghums as strongly dominant crops; very productive.

Distribution: Rolling plains of Western Texas and Oklahoma; very extensive.

Type location: Dickens County, Texas.

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