THE DISTRIBUTION OF SOIL PHOSPHORUS COMPOUNDS, IN SOME REPRESENTATIVE SOILS OF OKLAHOMA

By

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1959

Submitted to the faculty of the Graduate School of the Oklahoma State University in partial fulfillment of the requirements for the degree of MASTER OF SCIENCE August, 1963

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Thesis Approved: Thesis Adviser

Dean of the Graduate School

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ACKNOWLEDGEMENTS

I wish to express my sincere gratitude to all who contributed to the realization of this report in any way whatsoever.

Mention must be made of Dr. H. F. Murphy, my first Principal Adviser for his encouragement and guidance in my early studies at Oklahoma State University; Messrs. C. C. Schaller and G. Laase for their invaluable technical assistance and help in various ways; Dr. B. Tucker, my adviser, and the other members of my committee Drs. D. Weibel and J. Gingrich for their suggestions and corrections of the manuscript.

I am very much indebted to my Principal Adviser, Dr. Lester Reed, for his advice, attention and guidance. My appreciation also goes to the Governments of Eastern Nigeria and the United States of America (through the Agency of International Development) who jointly sponsored my academic career at Oklahoma State University.

Godson Ebonine Chukuemeka Ohiaeri

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INTRODUCTION

Phosphorus is one of the key plant nutrients in the soil. Its relatively low availability to plants even in situations of high reserve in the soil, will pose a problem to man as long as man tills the soil for food.

For a long time scientists have realized that a knowledge of the forms and the distribution of phosphate compounds in the soil can be of significant value in understanding the chemistry of soil phosphorus and its availability to plants.

In fertilizer practice, various chemical extractants are used to measure the "available" phosphorus in the soil as a basis for fertilizer recommendations. Reports from various sources, however, have indicated that when crop yields or crop responses to phosphate fertilizers are correlated with phosphorus determined by the various chemical extractants, results have not always been satisfactory. Also the determination of "available" phosphorus by different chemical methods differs in respect to the phosphorus status of the soil concerned. The available phosphorus removed from the soil by the chemical extractants comes from the discrete chemical forms of phosphorus in the soil. The total and the relative amount of "available" phosphorus extracted is greatly influenced by the chemical forms, their relative amount, distribution, the specific surface area of the phosphorus forms in the extractant.

Therefore it becomes necessary to determine the amount and distribution of the various forms of phosphate in the soil in order to assess its phosphate potential (supplying power of "available" phosphate) and the suitability or adaptability of certain chemical extractants to determine the "available" phosphorus of a particular soil. The "Chang and Jackson" (13)¹ phosphorus fractionation procedure is so far the best chemical method in use to fractionate soil phosphorus. It is the aim of this investigation to employ these techniques to determine among other things, the amount and distribution of various forms of phosphate in five representative Oklahoma soil profiles, and fate of applied phosphate in short term "availability" studies.

¹Numbers in paranthesis refer to literature cited.

LITERATURE REVIEW

Soil Phosphorus Fractionation - Method

Phosphorus has long been recognized to occur in the soil in a large number of inorganic and organic compounds possessing various degrees of solubility and "availability." Many attempts have been made by several investigators to devise analytical methods that would estimate and differentiate between these various phosphorus forms.

The earliest attempt at separation of soil phosphorus fractions by selective extractants was by Fisher and Thomas (24). By the use of acetic acid-sodium acetate buffer at pH 5.0 and dilute H_2SO_4 at pH 2.0 for soil extraction, they attempted to fractionate soil phosphate¹ into three groups:

- a. Calcium, magnesium, and manganese phosphate
- b. Iron and aluminum phosphate
- c. Adsorbed phosphate and apatite

In 1937, Williams (73), used NaOH as an extractant and divided the soil phosphorus into (a) alkali soluble organic phosphate, exchangeable phosphate, and soluble inorganic phosphates such as those of sesquioxide, di-calcium phosphate and water soluble phosphate and (b) alkali insoluble

 $^{^{1}\}mathrm{Fe-PO}_{4}$ = all iron phosphates, Al-PO₄ = all aluminum phosphates, Ca-PO₄ = all calcium phosphates.

fractions such as apatites, titanium phosphate and crystal lattice phosphate.

Dean (20) made the first attempt at a complete systematic fractionation of soil phosphorus. From his analysis, he divided the phosphorus compounds of the soil into three fractions, Viz;

1. Organic phosphorus compounds soluble in 0.25N NaOH.

2. Inorganic compounds dissolved by extraction with sodium hydroxide followed by $0.5N H_2SO_4$.

3. Insoluble compounds

Ghani (26) modified Dean's procedure to obviate the interference effect of exchangeable calcium and magnesium in the alkali extraction. He first extracted with acetic acid and then by successive extractions with NaOH and finally with H₂SO₄. He obtained five phosphorus fractions which he identified as follows:

Acetic acid soluble phosphorus compounds consisting of mono-,
 di-, and tri-calcium phosphates.

2. Alkali soluble inorganic phosphorus compounds consisting of iron and aluminum phosphates.

3. Alkali soluble organic phosphorus compounds.

4. Sulfuric acid soluble phosphorus compounds.

5. Insoluble phosphorus compounds.

In a later study Ghani (28) suggested the use of 8 - hydroxy-quinoline to block the re-sorption or reprecipitation of phosphate by active iron and aluminum. This was necessary because some of the phosphate brought into solution by acetic acid was reabsorbed by iron and aluminum and then extracted in the NaOH extraction. Bray and Dickman (9) fractionated soil phosphorus into four fractions:

1. Fraction soluble in 0.1 N neutral NH₄F which contained all of the easily replaceable phosphates and some of the more strongly adsorbed forms.

2. Fraction soluble in 0.1N NH₄F and 0.01N HC1.

3. Fraction soluble in 1.0N neutral NH_4F . Fractions 2 and 3 are a measure of the strongly adsorbed phosphate.

4. Acid soluble (.002N H₂SO₄) fraction consisting of calcium and magnesium phosphates, iron, aluminum and manganese phosphates and other forms as fluor apatite, and rock phosphate (hydroxy apatite). Bray and Kurtz (10) fractionated soil phosphorus into acid soluble, adsorbed, and organic forms. Chirikov and Volkova (17) fractionated soil phosphorus into five fractions:

 Fraction soluble in CO₂ colution (alkali phosphates, acid phosphates, and di-phosphates of calcium, magnesium, and some phosphorites).

2. Fraction soluble in 0.5N acetic acid (some apatites, phosphorites and salts of alcohols, phosphoric acids and sugar phosphoric acids).

3. Fraction soluble in 0.5 N HCl (phosphorites, apatites, aluminum phosphates, Fe-phosphates, some of the more basic phosphates of iron and phytin).

4. Fraction soluble in 0.2N NaOH (organic phosphates - nucleins, nucleoprotein and similar compounds of humic acid).

5. Fraction insoluble in any of these solvents (titanium phosphate and phosphorus compounds of unweathered minerals of the parent material).

The fractionation method developed by Williams (70) was a further modification of Ghani's procedure. He used 8-hydroxy-quinoline as introduced by Ghani and extracted successively with 2.5% acetic acid - 1% 8-hydroxy-quinoline and 0.1N NaOH. His fractions were identified as:

1. Phosphorus extracted by 2.5% acetic acid containing 1% 8-hydroxyquinoline consisting primarily of calcium, magnesium, and manganese phosphates.

2. Phosphorus extracted by 0.1N NaOH following the #1 extraction, consisting of inorganic phosphates (adsorbed phosphates, basic iron and aluminum phosphates and titanium phosphates), and organic phosphorus.

3. Phosphorus insoluble in either of the above extractants consisting primarily of chloro and fluoro-apatites, crystal lattice phosphorus compounds and resistant phosphate minerals.

Bhango and Smith (6) fractionated the phosphorus in various Kansas soils into four fractions:

1. Phosphorus soluble in 0.1N HCl (calcium phosphate).

2. Cold alkali soluble phosphorus after the #1 extraction, was identified as adsorbed phosphrous.

Hot alkali soluble phosphorus after the #1 and #2 extraction
 was identified as aluminum phosphate.

4. Organic phosphorus compounds.

Mattson et al, (48) while investigating the forms of phosphorus in some profiles in Sweden determined seven forms of phosphorus as follows:

1. Acid oxalate soluble phosphorus (sesquioxide bound phosphorus which included some inorganic and organic phosphorus compounds).

2. Phosphorus soluble in 0.2N H₂SO₄ (mainly calcium bound and sesquioxide bound).

3. Organic phosphorus compounds.

4. Phosphorus soluble in 2.5% acetic acid (mainly calcium bound and aluminum bound phosphorus).

5. Neutral 0.5N NH₄F - soluble phosphorus which was identified as more active forms of sesquioxide bound phosphorus.

6. Lactate soluble phosphorus.

7. Water soluble phosphorus in 1:10 extracts.

Vahtras (62) another Swedish soil scientist modified Mattson's fractionation into five fractions:

1. 0.2N H₂SO₄ soluble phosphorus.

2. Organic phosphorus compounds.

- 3. 2.5% acetic acid soluble phosphorus.
- Lactate soluble phosphorus.
- 5. 0.02N CaCl₂ soluble phosphorus.

These methods are a few of the various attempts to fractionate the soil phosphorus into discrete chemical forms. All of these investigations had limited success, however, in 1956, Chang and Jackson (13) introduced a new phosphorus fractionation procedure based on the solubilities of the discrete phosphorus compounds in various solutions. Since then the "Chang and Jackson" phosphorus fractionation procedure has found extensive application and has remained the most widely adopted method of soil phosphorus fractionation.

The discrete chemical forms of phosphate according to Chang and Jackson are:

1. Aluminum phosphate extracted by neutral (pH 7.0) 0.5N $\rm NH_4~F.$

Iron phosphate extracted by 0.1N NaOH after the extraction with #1.

3. Calcium phosphate extracted with 0.5N H₂SO₄ after the extraction with #1 and #2.

 Reductant soluble iron phosphate extracted with 0.3M citrate and sodium dithionite, Na₂S₂O₄.

5. Occluded aluminum phosphate extracted with neutral NH₄F or Al=Fe=phosphate extracted with 0.1N NaOH, after extraction with #1 through #4.

6. Organic phosphate is separately determined.

Several criticisms and suggestions for modifications have been made in their fractionation. In the extraction of aluminum phosphate, use of alkaline NH_4F in the pH range of 8 to 8.5, as an extractant has been very strongly suggested by Glenn et al. (29), Fife (22, 23), and Khin and Leeper (43). Glenn et al. suggested 9 to 17 hours extraction of iron phosphate rather than the 17 hours originally proposed, and the extraction of all occluded phosphate before removal of calcium phosphate as the 0.5N H_2SO_4 used to extract calcium phosphate tends to remove some of the occluded phosphate. Jackson (39) further modified the dithionitecitrate extraction for the removal of iron oxide from soils and clays (1), in the determination of reductant soluble iron phosphate, to include a sodium-bicarbonate buffer at pH 8.2 according to Mehra and Jackson (50).

Chu and Chang (18) while fractionating some soils of Taiwan (Formosa) modified the "Chang and Jackson" procedure to exclude separate fractionation of reductant soluble iron phosphate and occluded aluminum phosphate. After the extraction of aluminum, iron, and calcium phosphates, they analyzed their samples for total occluded phosphate by digesting the residual sample with 6N HCl and after precipitation of the soluble iron

with 2N NaOH, determined the phosphorus in the extract. The phosphorus determined represented the occluded phosphate (reductant soluble iron phosphate and occluded aluminum phosphate). Chang (11) after reviewing all the criticisms and suggestions so far made, described a systematized extraction sequence and proposed a modification of the original "Chang and Jackson" procedure as follows:

Removal of exchangeable calcium and the more soluble phosphates
 largely mono- or di-calcium phosphates, with N NH₄Cl after shaking for
 hour (in place of 30 minutes as originally proposed).

2. Extraction of aluminum phosphate with 0.5N NH₄F of pH 7.0 for paddy soils and pH 8.2 for upland soils for one hour.

3. Extraction of Fe-PO4 with 0.1N NaOH for 9 to 17 hours.

4. Extraction of reductant soluble Fe-PO₄ with dithionite-citrate with a bicarbonate buffer at pH 8.0. The extract is treated with activated charcoal if colored by organic matter.

5. Extraction of occluded iron-aluminum-phosphate complex with 0.1N NaOH for 9 to 17 hours.

6. Extraction of calcium phosphate with 0.5N H_2SO_4 for one hour. Chang and Liaw (16) remodified the "Chang and Jackson" procedure to accept the original proposal of extracting Al-PO₄ with neutral 0.5N NH₄F. According to them, their own experiments indicated that within limits of experimental error, the pH of NH₄F in the range of 7 to 8.5 does not affect the amount of phosphate extracted. In neutral NH₄F they found that reprecipitation of phosphate occurs when released from Al-PO₄ by the ferric ion as shown by Fife (23), and at the same time the dissolution of FePO₄ as found by Chang and Jackson (13). The phosphate form extracted by neutral NH₄F rather than the alkaline NH₄F, may represent the total amount of aluminum phosphate with no more need for correction for dissolved iron phosphate assuming that the two amounts are approximately counter balanced.

Sen Gupta and Cornfield (31) analyzing for the different forms of phosphorus in calcareous soils adopted the "Chang and Jackson" procedure but differentiated between apatitic calcium phosphate and non-apatitic.

Saunders (57), Yuan and Fiskell (76) maintained that the use of neutral citrate-dithionite or alkaline buffered citrate-dithionite removed considerable aluminum from the soil and that the procedure should not be used uncritically for the study of soil phosphate. This probably indicates that what was determined to be reductant soluble iron phosphate actually contained some occluded A1-PO₄.

Concerning all the criticisms and the attendant problems in soil phosphorus fractionation, Chang (11) wrote: "Fractionation of soil phosphorus into the total amount of each discrete form by use of the selectivity of different extraction solutions has unsurmounted difficulties. The exact discreteness is subject to doubt. Nevertheless by use of the proper extractant, solid-solvent ratio, extraction time and extraction sequence, the result obtained would be very close to the truth".

Distribution of Forms of Phosphorus in the Soil

Several investigations have been made on the distribution of forms of phosphorus in studies mainly related to chemistry of soil phosphorus and soil fertility.

Dean (21) fractionated 36 soils from locations in Africa, Britain,

Hawaii, Soviet Union and the United States, and found that the amount of phosphorus in the insoluble form constituted a large part of the phosphorus in the soil. Ghani and Aleem (27) fractionated some Indian soils using Ghani's procedure and found that the acetic acid soluble fraction (calcium phosphate) was extremely small in acid soils over the pH range of 4.2 to 5.8, but was highest at the neutral point and then decreased again as the pH rose towards the alkaline side of the pH scale. Iron and aluminum phosphate were more abundant in acid soils and decreased with pH increase. The same was true of organic phosphate, but after attaining a minimum at neutrality it increased again as the pH increased toward the alkaline side. These authors attributed organic phosphate accumulation to microbial activities. Godfrey and Reicken (30) from their studies on the vertical distribution of phosphates on some genetically related Iowa soils, observed that total phosphate decreased vertically in all the profiles.

Bauwin and Tyner (4) investigated the chemical nature of the insoluble phosphorus fraction, and fractionated the native phosphates of some Illinois soil profiles into inorganic (acid soluble) adsorbed or replaceable; organic; and insoluble phosphates. They observed that the insoluble fraction was about 50% of the B horizon phosphates of the soils investigated.

In Sweden, Matson et al. (49) investigated the forms of phosphorus in the soil series of the Dala brown earth and Unden Podsol and also (48) the Brannalt limed and unlimed podsol series. Wiklander et al. (69) investigated the different forms of phosphorus in the "gytta" soils of Northern Sweden. Wiklander and Hallgren (68) also determined the phosphorus forms on a "gytta" soil from Kungsangen and found organic phosphate

fairly constant throughout the profile; acetic acid soluble phosphate (Ca and Al-PO₄) was higher in the surface soil and decreased with depth and rose again with increasing depth while the 0.2N H₂SO₄ soluble fraction (mainly calcium phosphate and sesquioxide bound phosphates) did not show great variations with depth. Vahtras (62) fractionated Swedish soils into 5 fractions and correlated these with several soil properties.

IL'IN, (38) fractionated the chestnut brown soils of Central Kulunda (USSR) and found total phosphate highest in the topsoil and decreased with depth. Organic phosphate continued to decrease with depth and virtually disappeared at a depth of about 190 to 210 cm. depth. In the inorganic fractions, calcium phosphate was about 50 to 80% of the total and the rest was Al-PO4 and Fe-PO4. Chang and Jackson (13, 14) introduced the "Chang and Jackson" procedure, now most widely accepted, and used it to fractionate some 10 representative soils and found that the phosphorus fractions in latosols were dominantly iron phosphates a majority of which were "occluded". This was the same fraction as Bauwin and Tyner's "insoluble" (4) or Dean's "inert" (20) phosphate. The quantities of calcium and aluminum phosphate were small in the latosols. Phosphate in the chernozems was dominantly Ca-PO4, with no occluded phosphate and little Al-PO4, while the rest of the soil that showed intermediate weathering had Al, Fe, and Ca-PO4 evenly distributed. Chu and Chang (18) fractionated some representative soils of Taiwan (Formosa) according to the "Chang and Jackson" procedure. Results showed that organic phosphate ranged from 10 to 25% in the surface and less than 10% in the subsoil. Occluded phosphate constituted about 33% of the total phosphate in the

surface and about 50% in the subsoil. Hamilton and Lassard (33) found that the total phosphate in some soils of Quebec increased with depth; while calcium phosphate was about 41% of the total phosphate in the surface and about 88% in the 18 to 24" depth. Aluminum phosphate was highest in the top 6" and dropped to 5% in the lower horizons. Iron phosphate was negligible throughout, organic phosphate decreased with depth while the quantity of occluded phosphate was a substantial portion of the whole in surface soil. MacKenzie (46) investigated the water soluble and inorganic phosphate associated with aluminum, iron and calcium in some Ontario soils. His findings indicated that aluminum phosphate supplied most of the phosphate found in the soil solution. Red'kin and Kubansk (56) showed in their work that organic phosphate constituted about 43 to 46% of the total phosphate in the tilled surface horizon of the Krasnoder Region (USSR), while calcium phosphate exceeded 20% of the total phosphate in the upper part of the soil and increased with depth; reaching 40-50% at the 200 cm. depth. The easily mobile phosphate did not exceed 10% throughout. Voikin (63) investigated 45 soils and found organic phosphate to comprise 40-50% of the total phosphate. The phosphorus in the "Forest" and "Podsol" soils was largely present as insoluble phosphorus compounds and the chernozem contained the least insoluble phosphorus compounds. Scheffer et al. (58) working on 9 German soils found that calcareous soils with high pH values were 46 to 64% calcium phosphate, 24 to 29% iron phosphate and a small quantity of aluminum phosphate. Bates and Baker (3) studied the forms of phosphorus in two tropical soil series of Western Nigeria and found high levels of phosphorus compounds throughout the profiles but the

concentration was higher in the topsoil. Organic phosphate decreased with depth and rose again at greater depth. Considerable amounts of iron phosphate, and small quantities of calcium phosphate were found throughout the profile. Nye and Bertheux (53) determined the phosphorus fractions in the soils of the forest and savannah lands of the Gold Coast (Ghana). They found the total phosphate was highest in the surface of the forest soils but no consistent change with depth was observed in Savannah soils. Ca-PO₄ decreased sharply with depth and alkali soluble inorganic phosphate (mostly Fe-PO₄) decreased more slowly. Hesse (36) analyzed the mangrove swamp soil of Sierra Leone and found that the distribution of phosphate in the mud to be as follows: Organic phosphate 87% of the total phosphate and the remainder was entirely Fe-PO₄ and Ca-PO₄. There was no occluded-PO₄ and practically no Al-PO₄.

Benavides (5) carried out soil phosphorus fractionation on some representative soils of Colombia, S. A. and found total phosphate was highest in the topsoil and lowest in the top layer of the parent material. Organic phosphate constituted the largest fraction (57 to 77%) of total phosphate, while the reductant soluble iron phosphate dominated the inorganic phosphorus fraction.

The above results despite some local variations are consistent with the generalization of Chang and Jackson (14) that the least weathered, or calcareous soils have Ca-PO₄ as the principal form of phosphate and the proportion of Al and Fe-PO₄ increases as weathering proceeds. In cases of extreme weathering occluded phosphate is the predominant fraction.

Forms of Phosphorus in the Soil and Soil Genesis

Soil phosphorus fractionation is now a new tool in the furthering of man's knowledge of soil genesis. Little research work has been done on soil phosphorus and soil genesis.

Chang and Jackson (14) fractionated 10 different soil profiles from different soil types and showed that the latosol samples (most weathered) had most of their phosphorus compounds as iron phosphate and most of it was occluded. The chernozem samples (the least weathered) had calcium phosphate dominant over iron and aluminum phosphate, while the soils of intermediate weathering had all the three types evenly distributed. This led them to postulate that the degree of or the stage of weathering of soils can be determined by the relative percentage of the discrete phosphorus forms in the soil and that the sequence of chemical weathering is in the order: Ca-PO₄----Al-PO₄----Fe-PO₄----occluded phosphate.

Chu and Chang (18) after fractionating some soils of Taiwan also 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. Hawkins and Kunze (35) fractionated the phosphorus compounds of Texas Grumusols and related the inorganic forms to soil weathering. Mattson (47) suggested that calcium phosphate was transformed into sesquioxide bound phosphate as a consequence of the increase in soil acidity during

soil genesis. Hsu and Jackson (37) investigating the inorganic phosphorus compounds in some major soil groups indicated that the distribution of the inorganic phosphate in the major soil groups is related to the degree of chemical weathering during soil development and confirmed the finding of Chang and Jackson (14). Significant also is the work of Hesse (36) who showed that the mangrove swamp of Sierra Leone contained practically no Al-PO4 and the comparatively unweathered situation was demonstrated by the complete absence of occluded phosphate.

In the process of weathering the relatively more stable aluminum phosphate, variscite, $\begin{bmatrix} A1 & (OH)_2 & H_2PO_4 \end{bmatrix}$ and iron phosphate, strengite, $\begin{bmatrix} Fe & (OH)_2 & H_2PO_4 \end{bmatrix}$ are formed, or are present as a mixed system of A1-Fe phosphate such as Barrandite $\begin{bmatrix} (A1, Fe) & (OH)_2 & H_2PO_4 \end{bmatrix}$. By processes of hydrolysis of iron phosphate, followed by dehydration of the resulting ferric hydroxide, a shell or coat of iron oxide is produced.

> $FePO_4 \neq 3 H_2O \longrightarrow H_3PO_4 \neq Fe (OH)_3$ 2 Fe(OH)_3 \longrightarrow Fe_2O_3 \neq 3 H_2O

This shell protects the inner phosphate nucleus from solvent action and in the course of soil chemical weathering iron phosphate accumulates in the "occluded form." Aluminum phosphate may precipitate, or coprecipitate with iron in barrandite-like form, having a solubility product close to the solubility product of iron phosphate. This can also be occluded by an iron oxide coating. Thus the occluded phosphate which marks the highest stage of weathering is of secondary origin, highly resistant to further weathering and is a product of accumulation during the centuries of soil development. This fraction is not influenced by fertilizer practice and can be said to be constant. "Available Phosphorus" in Relation to Forms of Phosphorus in the Soil

The forms and the amount of phosphorus in the soil whether native or applied as fertilizer have considerable effect on the amount that may be available to plants. The source of phosphate available to plants is probably that of the inorganic phosphate fractions although possibly the organic fraction by mineralization may contribute substantially particularly in areas of high weathering activity.

Fractionation of soil phosphorus has lately been employed to aid in the studies and evaluation of available phosphorus in the soil. The "Chang and Jackson" method is most widely used.

Chang and Jackson (14), Chang and Chu (12) have by soil phosphorus fractionation demonstrated that under flooded conditions, the phosphorus previously considered to be difficultly available is fairly available. Basak and Battacharya (2) adopted the soil phosphorus fractionation method of Bhango and Smith (6) and studied phosphorus transformation in rice soil under flooded condition. They concluded that in such a situation, there was an increase in the quantity of "available phosphorus" by a process of mineralization of organic phosphate and the reductive transformation of iron and aluminum phosphate. Another investigator Sperker (59) had shown that H₂S generated in the soil under anaerobic conditions could solubilize phosphate from soil minerals. This could partly account for the observation of Basak and Battacharya.

Chang and Juo (15) fractionated the phosphates of some soils of Taiwan and significantly correlated the different fractions with available phosphorus determined by the seven most commonly used methods. It illustrated that in a particular situation, the extractant which can dissolve selectively the forms of phosphorus which are the main supply of available phosphorus, would extract phosphorus which best represented the status of "available phosphorus" in the soil.

Williams (71) showed through his own fractionation procedure that in the acid redbrown earth (pH 5.6 to 6.1) he investigated, calcium phosphate was most utilized by wheat despite the predominant amount of A1-PO₄ and Fe-PO₄. MacKenzie (46) on the other hand showed that A1-PO₄ supplied most of the water soluble phosphate in the soils he investigated.

Laverty and McLean (45) correlated the soil phosphorus fractions with the uptake of phosphate by oat seedlings and to the available phosphorus as determined by the Bray #2 procedure (10). Westerman (67) carried out field and greenhouse tests with different levels of phosphate fertilizers in order to evaluate techniques for the determination of available phosphorus including "Chang and Jackson" phosphorus fractionation method. He found that short term nutrient absorption techniques and leaf analysis were not adequate for the determination of available soil phosphorus, and the phosphate needed for maximum yield.

Suzuki et al. (61) by chemical fractionation procedure, greenhouse experiments and chemical extraction measurements for "available" phosphorus correlated significantly the short term uptake of phosphorus and seasonal availability to the forms of phosphorus in the soil. Calcium and alumimum phosphate correlated significantly with short term uptake, and Al-PO₄ alone correlated significantly with the seasonal availability. Fe-PO₄ and organic phosphate did not contribute to any of the phosphorus removed

by the extractants of available phosphorus.

These examples serve to illustrate the importance of soil phosphorus fractionation in the studies of phosphate availability. It can, along with chemical determination of available phosphorus, greenhouse and field experiments, give a picture of the forms of phosphorus available to plants in a given situation. It can also show that where an extractant for the determination of available phosphorus has been shown to be significantly correlated with growth response them that same extractant or another with the same or similar selectivity for the forms of soil phosphorus, can be used in another situation with the same or similar phosphorus fraction distribution, regardless of pH, to determine the available phosphorus of the soil. This in turn will affect fertilizer recommendations.

Fate of water soluble phosphate applied to the soil

The study of the fate of applied phosphate in the soil is mainly one of phosphorus "fixation" and transformation. This is important in understanding more of the soil phosphorus chemistry (behavior) which is also relevant in soil phosphorus availability studies. Soil phosphorus fractionation is a useful tool, since phosphorus retention and "fixation" in the soil is mainly a chemical process as shown by Kittrick and Jackson (44).

Wright and Peech (74), employing a modified procedure of Chang and Jackson on some acid soils, showed that in some soils with predominantly native Fe-PO₄, the phosphate applied was converted principally to iron phosphate, while in others the fertilizer was usually converted into Al-PO₄. Ca-PO₄ in general was increased less by fertilization, and lime application had little influence on the course of chemistry of applied phosphorus. This illustrates clearly what Jackson (41) described as competition between Al and Fe for phosphate retention in the soil system.

Chang and Chu (12) fractionated native and applied phosphate forms in some soils of Taiwan and found that added phosphate in six soils with pH range of 5.3 to 7.5 at field capacity retained $A1-PO_4$ followed by iron phosphate and Ca-PO₄ in the short run but in the long run $A1-PO_4$ and Ca-PO₄ decreased while Fe-PO₄ increased. Under flooded or paddy conditions Fe-PO₄ was the dominant form fixed. They also reported Fe-PO₄ predominant over $A1-PO_4$ in two latosols, a deviation from the general trend. These results led them to conclude that the first stage of phosphate fixation was governed more by surface energy than ionic activity, but as time proceeded and in higher moisture condition the ionic activity became more appreciable and the principle of the "solubility product" takes over.

Chang and Jackson (14) had also determined the fate of applied phosphate by their fractionation method on a podzolic soil at a pH of 7.5. They found that the application of soluble phosphate fertilizer greatly increased the A1-PO4 and Fe-PO4 at all lime levels applied but increased the Ca-PO4 content only slightly at the highest lime level. Occluded-PO4 was not affected. In the long run, Ca-PO4 and A1-PO4 changed gradually into Fe-PO4 (the least soluble).

Laverty and McLean (45) by fractionation procedures, studied the fate of applied soluble phosphate. They reported "abnormal recovery" 20

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of applied phosphate for an average of 108% of the applied PO₄. They could not ascertain whether the abnormal recovery was due to random variation or to the solubilization of occluded phosphate.

Onken and Reed (54) also used Chang and Jackson's procedure. They studied the fate of applied rock phosphate and superphosphate fertilizer and found the major portion of phosphorus from superphosphate and lesser quantities from rock phosphate was converted to iron and aluminum phosphate regardless of lime level applied.

Volk and MacLean (64) studied the fate of applied phosphorus in four Ohio soils by "tracer techniques" and Chang and Jackson's procedure. They found that in acid soils about 90% of the applied phosphate was recovered as Al-PO₄ and Fe-PO₄. They showed that soils with higher "fixation capacity" converted applied phosphate to Fe-PO₄ while that with lower "fixation capacity" precipitated more phosphorus as Al-PO₄. This was also reported by Laverty and McLean (45) and has not been accounted for. They reported abnormal recovery of the applied phosphate and also justified the use of phosphorus fractionation procedures to study the fate of applied phosphorus.

The works of these people among others justify and recommend the use of phosphorus fractionation procedures in studying the fate of applied phosphate. The knowledge gained is of immense value in the study of the chemistry of soil phosphorus and availability to plants and the processes of soil genesis.

MATERIALS AND METHODS

The soil materials are soil profile samples from different locations in Oklahoma. They belong to the soil series - Carey, Hollister, Altus, Grant, Okemah and Norge. Their descriptions are contained in the appendix on pages 88-93.

Laboratory Method

Phosphate determinations:

1. <u>Total elemental phosphorus</u> was determined according to Harper's method (35) of digesting a soil sample with 72% perchloric acid. Color was developed by reducing the molybdenum which combined with the phosphate ion with hydrazine sulphate. 5 gm. of soil was used.

2. <u>Organic phosphate</u>: Phosphate was determined colorimetrically according to the procedure of Mehta et al. (51) by an alkaline extraction in NaOH following acid pretreatment. Two gm. of soil was used for Norge and 1 gm. for the remainder of the soils. The organic phosphate was determined by difference between the total phosphate (determined from the combined acid and alkali extractions along with flocculated organic materials) and inorganic phosphate (determined from the acid and alkali extraction excluding the flocculated material).

Total - inorganic phosphate : organic phosphate.

3. <u>Inorganic phosphorus fractions</u>: Were determined according to the procedure developed by Chang and Jackson (13) with some modifications.

a. <u>Aluminum phosphate</u>: 1 gm of soil (2 gms. for Norge) was extracted with 50 ml. 1N NH₄Cl for 1 hour on a reciprocating shaking machine to remove water soluble and loosely bound phosphorus. The quantity determined was considered to be very small and negligible. The ammmonium soil was extracted with 50 ml. neutral (pH 7.0) 0.5N NH₄F; the soil suspension centrifuged and the phosphorus determined on the supernatant by chloromolybdic acid and stannous chloride. Boric acid was added to eliminate flouride interference in the molybdenum blue.

b. <u>Iron phosphate</u>: The soil sample saved after aluminum phosphate extraction was washed twice with 25 ml. portions of saturated NaCl solution. The soil was extracted with 50 ml. 0.1N NaOH for 17 hours on a reciprocating shaking machine. The soil suspension was centrifuged and phosphate determined on the supernatant using sulfomolybdic acid and stannous chloride.

c. <u>Calcium phosphate</u>: The soil saved after iron phosphate extraction was washed twice with 25 ml. portions of saturated NaCl and the phosphate extracted with 50 ml. of 0.5N H₂SO₄ for one hour on a shaking machine. The suspension was centrifuged again and the phosphate determined colorimetrically on the supernatant using sulfomolybdic acid and stannous chloride.

d. <u>Total occluded phosphate</u>: Was determined according to the method used by Chu and Chang (18). The soil saved after calcium phosphate extraction was washed twice with 25 ml. portions of saturated NaCl. The sample was digested with 6N HCl and the iron precipitated with 2N NaOH. After removing the precipitate by filtration the phosphate was determined by Jackson's No. 2 (39) method using chloromolybdic acid and stannous chloride.

e. <u>Occluded aluminum phosphate</u>: In order to determine the portion of occluded phosphate attributed to occluded aluminum phosphate, a separate

sample was run. After the removal of Al-, Fe-, Ca-PO₄ and reductant soluble iron phosphate according to Chang and Jackson, the occluded aluminum phosphate was determined by washing the residual soil with two 25 ml. portions of saturated NaCl and the phosphate extracted and determined as Al-PO₄. Where further extraction with 0.1N NaOH indicated more phosphorus, the occluded Al-PO₄ extracted was present as a complex of occluded AlFe-PO₄.

f. <u>Reductant soluble iron phosphate</u> was obtained by difference between total occluded phosphate and occluded Al-PO4.

Soil Properties

Physical properties:

 Mechanical Analysis: Determined by method of Day et al. (19) using the hydrometer with Bouyoucos scale and 2% Na₂CO₃ was used as a dispersion agent. Carbonate and bivalent cations were removed by use of 1N Na-acetate buffered at pH 5.0.

Chemical properties:

1. <u>Soil pH</u>: Determined by the paste method and 1:1 soil:1N KCl method using the Beckman Zeromatic pH meter.

2. <u>Cation Exchange Capacity</u>: Was determined by Bower's method (8) using 1N Na-acetate at pH 8.2. Na^{\neq} was the displacing cation and determined by flame method using Beckman quartz-spectrophotometer model DU with photomultiplier. 4 gm. sample for the soil samples and 6 gm. for Norge was used.

3. <u>Exchangeable Cations</u>: $Ca^{\neq \neq}$, $Mg^{\neq \neq}$, K^{\neq} , Na^{\neq} determined by flame photometry on the 1.0N NH₄ acetate extract.

4. Exchangeable Acidity, H⁺ and Al⁺⁺⁺: By the method of Yuan (75).

5. <u>Free Iron Oxide</u>: The soil saved from the calcium phosphate extraction in phosphorus fractionation procedure was washed twice with saturated NaCl. Iron oxide (in form of hematite Fe_2O_3 and geothite FeO_2H) was extracted by dithionite - citrate - bicarbonate method, sodium dithionite ($Na_2S_2O_4$) being employed for reduction, sodium bicarbonate as a buffer and sodium citrate as a chelating or complexing agent for ferrous and ferric iron. Iron was determined by the Tiron method (40).

6. Total Nitrogen: Was determined by Kjeldhal's method (34).

7. <u>Organic Matter</u>: Was determined by Schollenberger - Allison Volumetric method as modified by Harper (34). Organic carbon was derived by the factor -

Carbon x 1.724 = 0.M

Fate of Applied Water Soluble Phosphate

Fate of applied phosphate in the short run was determined as follows:

1. 50 gm. of soil was treated with KH₂PO₄ (potassium dihydrogen phosphate) at 500 ppm in order to give concentrations of 200 ppm in the soil (20 mls. KH₂PO₄ to 50 gm. soil). The moisture was kept at approximately field capacity for 3 days at room temperature. After 3 days the soil was air dried, ground and mixed and 1 gram taken for phosphorus fractionation.

Another 50 gm. of soil was similarly treated but kept for 30 days.
 The soil phosphorus was also fractionated by Chang and Jackson's method.
 There was no fractionation for occluded phosphate.

Available Phosphorus

Available phosphorus was determined on the original and treated soil

samples according to Brays #1 method. (10) Statistical analyses were carried out according to the method of Steel and Torrie (60).

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RESULTS AND DISCUSSION

Physical Properties of the Soils

With regard to particle size distribution (Table Ia-e), all the soils are loams. The individual horizon analysis ranged from sandy loam in Norge to clay in Okemah. The clay fraction increased from the surface soil to the deeper layers. The higher level of clay in the subsurface horizons was perhaps due to clay formed in place, and clay elluviated from the surface soil and deposited in the deeper horizons. The plow layer in all the soils contained the least amount of clay.

Chemical Properties of the Soils

The pH increased with depth except in Norge and Okemah soils as shown in Tables IIa-e. The high pH in the plow depth of the Norge soil was due to increase in base saturation due to liming. The pH of Okemah decreased with depth unlike the rest. The soil reaction of the horizons analyzed ranged from an extremely acid condition with a pH of 4.60 (paste) in B_{21} horizon of Okemah to a highly alkaline condition, pH 8.30 (paste) in C_{ca} horizon of Carey.

Cation exchange capacity ranged from 6.04 m.e./100 gm. (oven dry) in A_{12} horizon of Norge to 34.10 in Okemah B_{21} horizon. The high level of the cation exchange capacity in this horizon was due mainly to a high level of exchangeable magnesium and sodium. Cation exchange capacity

Lab. no. Depth inches Horizon	61 -S- 79 0 - 12 ^A 1	61-S-80 12-22 B ₂₁	61 - S-81 22-28 B ₂₂	61 - S-82 28-34 C ₁	61 -S-83 34 - 54 C _{ca}
Particle size distribution %					
Clay < 2 🎮	14	18	20	26	19
Silt 2-50 H	41	51	49	49	50
Sand >50 M	45	31	31	25	31
Textural class	Loam	Silt Loam	Loam	Loam	Silt Loan
% moisture	1.56	1.81	1.61	1.00	1.28

PHYSICAL PROPERTIES: CAREY SILT LOAM

TABLE Ia

Lab. r Depth Horizo	inches	61 -S-73 0-5 ^A p	61-S-74 5-11 ^A 1	61-S-75 11-23 ^B 2	61-S-76 23-31 B ₃	61-S-77 31-44 C _{ca}	61 - S-78 44-50 C
Particle distribut							
Clay	<2 M	23	24	39	41	45	5 3
Silt	2-50M	38	46	25	28	29	3 0
Sand	>50M	39	3 0	3 6	31	26	17
Textural	class	Loam	Loam	Clay Loam	Clay	Clay	Clay
% moistur	ce	2.42	2.46	4.07	4.04	3.48	7.15

TABLE Ib

PHYSICAL PROPERTIES: HOLLISTER CLAY LOAM

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TABL.	R	Ic
TUDT	-	τ¢

Lab. no. Depth incl Horizon	ies	3219 0-5 ^A p	3220 5-12 ^A 12	3221 12-20 ^A 3	3222 20-36 B ₂	3223 36-48 C
article size istribution						
Clay <	2 M	10	14	18	25	23
Silt 2-	50 M	3 6	37	39	32	29
Sand >	50 M	54	49	43	43	48
extural clas	s	Sandy Loam	Loam	Loam	Loam	Loam
moisture		1.03	1,49	2,07	2.89	2.35

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PHYSICAL PROPERTIES: GRANT SILT LOAM

Lab. no. Depth inches Horizon		0-6 ^A p	6-14 ^A 12	14-24 ^B 2t	24-50 C
Particle					
distribut	ion %				
Clay	<2M	9	18	19	14
Silt	2-50 H	12	14	13	7
Sand	>50M	79	68	68	79
Textural	class	Sandy Loam	Sandy Loam	Sandy Loam	Sandy Loam
% moistur	e	0.95	1.61	2.18	1.92

PHYSICAL PROPERTIES: NORGE SANDY LOAM

TABLE Id

	PHYSICAL PRO	OPERTIES: OK	EMAH SILT LO	AM
Lab. no. Depth inche Horizon	2532 es 0-11 ^A 1	25 33 11-14 ^B 1	2534 14-20 ^B 21	2545 42 - 54 C
Particle size distribution %				
Clay <2/	Y 20	28	3 6	54
Silt 2-50,	H 64	58	42	34
Sand >50	H 16	14	22	12
Textural class	Silt Loam	Silt Clay Loam	Clay Loam	Clay
% moisture	2.26	2.81	5.01	5 .31

TABLE IE PHYSICAL PROPERTIES: OKEMAH SILT LOAM

TABLE IIa

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CHEMICAL PROPERTIES: CAREY SILT LOAM

Lab. no. Depth inches	61 -S-79 0 - 12	61 -S- 80 12 - 22	61-S-81 22-28	61-S-82 28-34	61-S-83 34-54
Horizon	A1	^B 21	B ₂₂	C1	C _{ca}
pH paste	7.00	7.80	8.05	8,15	8.30
pH 1:1 KC1	6.00	6,95	7.30	7.45	7.50
C.E.C.* m.e./100 gm.	9.61	9.85	9.39	8.57	8.92
Extractable cations					
m.e./100 gm.	16.13	20.44	28,47	32.75	32.02
Calcium	6.90	9.25	17.55	21.00	18.75
Magnesium	8.41	10.58	10,41	11.25	12.75
Potassium	0.64	0.38	0.28	0.28	0.30
Sodium	0.08	0.13	0.13	0.17	0.17
Hydrogen	0.10	0,10	0.10	0.05	0.05
Aluminum	0.00	0.00	0.00	0.00	0.00
% Base saturation	166.81	206.50	302.13	381.56	358.40
Exch. acidity					
m.e./100 gm.	0.10	0.10	0.10	0.05	0.05
% Organic matter	1.51	1.01	0.74	0.61	0.79
% Carbon *	0,87	0.59	0.43	0.35	0.46
% Nitrogen	0.08	0.06	0.05	0.04	0.05
C/N	10.88	9.83	8.60	8.75	9.20
% Free Fe ₂ 03	0,78	1.14	1.07	1.05	1.03
Bray's #1 phosphorus					
ppm	9.00	3.00	3.00	0.00	2.00

* Cation Exchange Capacity

TABLE IIb

CHEMICAL PROPERTIES: HOLLISTER CLAY LOAM

Lab. no. Depth inches Horizon	61 -S-73 0 - 5 ^A p	61-S-74 5-11 ^A 1	61-S-75 11-23 ^B 2	61-S-76 23-31 ^B 3	61 -S-77 31 - 44 ^C ca	61 - S-78 44-50 C
pH paste	6.50	6.40	6.95	7.50	7.75	7.90
pH 1:1 KC1	6.00	5.90	6.30	6.85	7.00	7.20
C.E.C.* m.e./100 gm.		10.70	17.45	17.22	17.57	18.73
Extractable cations	10.92	10.70	17,45	17.22	17.57	10.75
m.e./100 gm.	21.56	22.65	33.83	52.26	38.97	44.78
Calcium	10.00	10.20		15.90	17.25	21.00
Magnesium	9.00	10.00	16.08	16.60	18.75	19.50
Potassium	1.38	1.33	1.05	0.84	0.84	0.71
Sodium	1.08	1.04	1.65	1.60	2.00	3.47
Hydrogen	0.10	0.08	0.05	0.10	0.13	0.10
Aluminum	0.00	0.00	0.00	0.00	0.00	0.00
% Base saturation	196,52	210.93	193.58	202.32	221.06	238.55
Exch. acidity						
m.e./100 gm.	0.10	0.08	0.05	0.10	0.13	0.10
% Organic matter	1.76	1.74	1.31	0.88	0.56	0.45
% Carbon	1.02	1.01	0.76	0.51	0.33	0.26
% Nitrogen	0.09	0.09	0.07	0.04	0.03	0.04
C/N	11.33	11.22	10.86	12.75	11.00	6.50
% Free Fe203	0.61	0.70	0.94	0.84	0.79	0.89
Bray's #1 phosphorus				an an an the second second second		
ppm	13.00	14.00	3.00	2.50	2.50	2.00

* Cation Exchange Capacity

TABLE IIC

CHEMICAL PROPERTIES: GRANT SILT LOAM

Lab. no. Depth inches	3219 0-5	3220 5-12	3221 12-20	3222 20-36	3223 36-48
Horizon	Ap	A12	A3	B2	04-40 C
an a	P				ويتحكيهم ومعطيتها ومعرفه المراجعية المتكافية
pH paste	6.15	6.00	6.60	7.40	7.50
pH 1:1 KC1	5.50	4.95	5.80	6.60	6.60
C.E.C.* m.e./100 gm.	8.24	8.57	10.76	11.42	10.24
Extractable cations					
m.e./100 gm.	10.43	12.64	17.11	22.34	21.10
Calcium	5.00	6.20	8.65	11.10	9,85
Magnesium	4.25	5.50	7.66	10.41	10.41
Potassium	1.00	0.76	0.61	0.56	0.53
Sodium	0.08	Q.08	0.13	0.17	0.21
Hydrogen	0.10	0.10	0.06	0.10	0.10
Aluminum	0.00	0.00	0.00	0,00	0.00
% Base, saturation	125.36	146.32	158.46	194.75	205.09
Exch. acidity					
m.e./100 gm.	0.10	0.10	0.06	0.10	0.10
% Organic matter	1.46	1.33	1.24	1.01	0.63
% Carbon	0.85	0.77	0.72	0.59	0.37
% Nitrogen	0.07	0.07	0.07	0.06	0.06
C/N	12.14	11.00	10.29	9.83	6.17
% Free Fe2O3	0.43	0.45	0.53	0.66	0.60
Bray's #1 phosphorus					
ppm	14.00	13.00	5.00	2.50	5.00

*Cation Exchange Capacity

TÆ	B	LE	II	d

CHEMICAL	PROPERTIES:	NORGE	SANDY	LOAM

Lab. no.		<i>c</i> . <i>i</i>			
Depth inches	0-6	6-14	14-24	24-50	
Horizon	A _p	A12	B _{2t}	C	
pH paste	7.15	5.70	5.80	5.70	
pH 1:1 KC1	6.30	5.10	5.00	4.90	
C.E.C.* m.e./100 gm.	5.85	6.04	6.22	7.09	
Extractable cations					
m.e./100 gm.	9.57	12.56	14.82	11.36	
Calcium	6.00	6.55	6.90	4.90	
Magnesium	3.08	5.33	7,25	5.91	
Potassium	0.28	0.30	0.30	0.23	
Sodium	0.13	0.13	0.17	0.17	
Hydrogen	0.03	0,25	0.20	0.10	
Aluminum	0.05	0.00	0.00	0.05	
% Base saturation	162.22	203,81	235.05	158.11	
Exch. acidity					
m.e./100 gm.	0.08	0.35	0.20	0.15	
% Organic matter	0.79	1.25	0.88	0.43	
% Carbon	0.25	0.51	0.73	0.46	
% Nitrogen	0.05	0.06	0.05	0.03	
C/N	5.00	8.50	14.60	14.33	
% Free Fe ₂ 03	0.24	0.35	0.39	0.28	
Bray's #1 phosphorus					
ppm	5.00	2.50	1.00	2.50	

* Cation Exchange Capacity

TABLE IIe

Lab. no.	2532	25 33	2534	2545
Depth inches	0-11	11-14	14-20	42-54
Horizon	A1	^B 1	^B 21	С
oH paste	5.10	4.70	4.60	5.00
pH 1:1 KC1	4.90	4.35	4.10	4.50
C.E.C.* m.e./100 gm.	14.46	14.99	34.10	19.05
Extractable cations				
m.e./100 gm.	17.55	22.50	47.65	44,92
Calcium	6.35	6.90	14.40	25.50
Magnesium	9.00	10,58	21.25	15,00
Potassium	0.21	0,21	0.46	0.38
Sodium	1.86	4.26	9.78	3.69
Hydrogen	0.10	0.25	0.33	0.05
Aluminum	0.03	0.30	1.43	0.30
% Base saturation	120.47	146.43	232.60	129.31
Exch. acidity				
m.e./100 gm.	0.13	0.55	1.76	0.35
% Organic matter	2.68	1.60	2.05	0.50
% Carbon	. 1.55	0.93	1,19	0.29
% Nitrogen	0.13	0.09	0.10	0,05
C/N	11.92	10.33	11.90	5.80
% Free Fe ₂ O ₃ Bray's #1 phosphorus	1.00	1.80	3.00	5.20
ppm	5.00	2.50	1.00	2,50

CHEMICAL PROPERTIES: OKEMAH SILT LOAM

* Cation Exchange Capacity

increased with depth, and there was a highly significant correlation between cation exchange capacity and clay content for all the samples, of r (correlation coefficient) = $\neq 0.72^1$.

Base saturation was generally more than 100%, and it increased with depth. This super saturation was because the extractable cations included soluble and exchangeable cations. Exchange acidity was low throughout except in Norge and Okemah soils where exchangeable aluminum was an important contributing factor.

Organic matter accumulated at the surface and decreased with depth. It varied from 0.43% in C horizon of Norge to 2.68% in A₁ horizon of Okemah. The percentage of carbon and nitrogen followed the same trend. "Available phosphorus" by Bray's #1 method (10) was generally low but was highest in the surface soil and decreased with depth. Bray's #1 method is the standard technique used in this study for available phosphorus.

Phosphorus Forms and Distribution

The results of the amount and the distribution of the various forms of phosphorus compounds are shown on Table IIIa-e. The percentages of each form contributed to total phosphorus are shown in Table IVa-e.

Phosphates in the soil are divided into two main portions - the organic phosphates and the inorganic phosphates. The inorganic are further divided into active and inactive fractions. The active fraction represents that which can be readily extracted by ordinary laboratory "soil test" techniques, and which supplies most of the phosphorus required by plants. The inactive

¹Significant at 1% level of confidence.

TABLE IIIa

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DISTRIBUTION OF FORMS OF PHOSPHORUS

Carey Silt Loam									
Lab. no. Depth inches Horizon	61 -s- 79 0 - 12 ^A 1	61-S-80 12-22 B ₂₁	61 -S- 81 22-28 ^B 22	61-S-82 28-34 C ₁	61-S-83 34-54 ^C ca				
Total phosphorus ppm	37 0.00	530.00	586.00	59 6.00	5 30. 00				
Organic phosphorus ppm	130.00	190.00	186.00	186.00	150.00				
Inorganic phosphorus fractions	3								
A1-PO4 ppm	13.44	4.06	4.06	4.06	4.06				
Fe-PO4 ppm	11.25	6.25	0.00	0.00	0.00				
Ca-PO4 ppm	150.00	256.25	337.50	362.50	318.75				
Occluded phosphates									
R. Sol. Fe-PO4 ppm	58.12	57.50	66.87	29.37	31.87				
Oc A1-PO4 ppm	0.00	0.00	8.13	8.13	5.63				
Oc Al-Fe-PO ₄ ppm	4.38	5.00	0.00	0,00	0.00				
Total additive ppm	367.19	519.06	602.56	5 9 0.06	510.31				

TABLE IIIb

DISTRIBUTION OF FORMS OF PHOSPHORUS

	Holli	ster Clay	Loam			
Lab. no. Depth inches Horizon	61-S-73 0-5 ^A p	61-S-74 5-11 ^A 1	61 -S- 75 11-23 ^B 2	61-S-76 23-31 ^B 3	61 - S-77 31-44 C _{ca}	61-S-78 44-50 C
Total phosphorus ppm	300.00	310.00	270.00	240.00	230.00	225.00
Organic phosphorus ppm	120.00	150.00	85.00	110.00	95.00	85.00
Inorganic phosphorus fractions	14 60	12 50	2 91	2.20		1 / 1
A1-PO ₄ ppm	14.69	12.50	2.81	2.20	Trace	1.41
Fe-PO4 ppm Ca-PO4 ppm	16.25 63.75	15.6 3 65.00	5.63 56.25	3,44 67,50	1.25 7 0.00	0.00 85.00
Occluded phosphates						
R. Sol. Fe-PO4 ppm	81.25	62.50	99.38	56.87	45.63	56.87
Oc A1-PO4 ppm	0.00	0.00	0.00	0.00	0.00	5.63
Oc Al-Fe-PO4 ppm	6.25	6.25	6.88	5.63	4.38	0.00
Total additive ppm	295.94	311.88	255.95	245.64	216.26	233.91

Grant Silt Loam								
Lab. no. Depth inches Horizon	3219 0-5 ^A p	3220 5-12 ^A 12	3221 12-20 ^A 3	3222 20-36 ^B 2	3223 36-48 C			
Total phosphorus ppm	300.00	295.00	3 00.00	220.00	156.00			
Organic phosphorus ppm	115.00	115.00	125.00	80.00	36.00			
Inorganic phosphorus fractio	ns							
A1-PO4 ppm	18.75	7.47	2.81	2.20	4.06			
Fe-PO4 ppm	13.75	9.38	6.88	5.00	7.81			
Ca-PO4 ppm	107.50	97,50	87.50	44.50	22.50			
Occluded phosphates								
R. Sol. Fe-PO4 ppm	46.25	60.26	81.25	85.94	78.75			
Oc Al-PO4 ppm	0.00	0.00	0.00	0.00	0.00			
Oc Al-Fe-PO4 ppm	3.75	5.00	6.25	7.81	8.75			
Total additive ppm	3 05.00	294.61	309.69	225.45	157.87			

TABLE IIIC

DISTRIBUTION OF FORMS OF PHOSPHORUS

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TABLE	IIId

DISTRIBUTION OF FORMS OF PHOSPHORUS

Norge Sandy Loam								
Lab. no. D ept h inches Horizon	0-6 ^A p	6 - 14 ^A 12	14-24 ^B 2t	24 - 50 C				
Total phosphorus ppm	140.00	168.00	144.00	132.00	grafi. 47162967444			
Organic phosphorus ppm	65.00	98.00	69.00	67.00				
Inorganic phosphorus fraction	ns							
A1-PO4 ppm	5.62	2.81	1.41	Trace				
Fe-PO4 ppm	11.25	4.38	5.63	5.63				
Ca-PO4 ppm	5.63	8.75	6.88	3.75				
Occluded phosphates								
R. Sol. Fe-PO4 ppm	39.38	56.88	43.13	45.63				
Oc A1-PO4 ppm	0.00	0.00	0.00	0.00				
Oc Al-Fe-PO4 ppm	4.38	5.63	6.88	4.38				
Total additive ppm	1 3 1,26	176.45	132.93	126.39				

TABLE IIIe

DISTRIBUTION OF FORMS OF PHOSPHORUS

Okemah Silt Loam									
Lab. no. Depth inches	2532 0 - 11	25 33 11 - 14	25 3 4 14 -2 0	2545 42 - 54					
Horizon	A1	^B 1	B ₂₁	C					
Total phosphorus ppm	430.00	370.00	3 40.00	670.00					
Organic phosphorus ppm	255.00	220.00	205.00	160.00					
Inorganic phosphorus fractic	ons								
A1-PO4 ppm	2.81	Trace	Trace	1.41					
Fe-PO4 ppm	51.25	25.63	22.50	165.00					
Ca-PO4 ppm	15.00	1 3. 75	15.00	45.00					
Occluded phosphates									
R. Sol. Fe-PO4 ppm	101.25	98.75	59.38	236.25					
Oc A1-PO4 ppm	0.00	0.00	0.00	0.00					
Oc Al-Fe-PO4 ppm	11.25	1 3.7 5	15.63	51.25					
Total additive	436.56	371.88	317.51	658.91					

TABLE IVa

FRACTIONS OF THE SOIL PHOSPHORUS AS PERCENTAGE OF THE TOTAL PHOSPHORUS

Carey Silt Loam									
Lab. no. Depth inches Horizon	61 - S-79 0-12 ^A 1	61-S-80 12-22 ^B 21	61-S-81 22-28 B ₂₂	61-S-82 28-34 C ₁	61-S-83 34-54 C _{ca}				
Inorganic phosphorus fractions	9	5 9 (- 1900) - 1900 (- 1900) 19	6	19 / 19 - 19 - 19 - 19 - 19 - 19 - 19 - 					
Active A1-PO4 %	3.66	0.78	0.67	0.68	0.79				
Active Fe-PO4 %	3.06	1.20	0.00	0.00	0.00				
Active Ca-PO ₄ %	40,85	49.37	56.01	61.43	62.46				
Inactive R. Sol. Fe-PO ₄ %	15.82	11.07	11.09	4.97	6.24				
Inactive OcAl-PO ₄ %	0.00	0.00	1 .3 5	1.37	1.10				
Inactive OcAl-Fe-PO4 %	1.19	0.96	0.00	0.00	0.00				
Fotal inorganic phosphorus %	64.58	63.38	69.12	68.45	70.59				
Organic phosphorus %	35.42	36.62	30.88	31.55	29.41				

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TABLE IVb

FRACTIONS OF THE SOIL PHOSPHORUS AS PERCENTAGE OF THE TOTAL PHOSPHORUS

	Ho	llister C	lay Loam			
Lab. no. Depth inches Horizon	61 -S-73 0-5 ^A p	61 -S-7 4 5 - 11 ^A 1	61 - S-75 11-23 ^B 2	61-S-76 23-31 B ₃	61-S-77 31-44 ^C ca	61 -S- 78 44-50 C
Inorganic phosphorus fractions						
Active Al-PO ₄ %	4.96	4.00	1.09	0.89	0.00	0.60
Active Fe-PO ₄ %	5.49	5.01	2.19	1.40	0.57	0.00
Active Ca-PO ₄ %	21.54	20.84	21.97	27.47	32.36	36.33
Inactive R. Sol. Fe-PO ₄ %	27,45	20.03	38.82	2 3. 15	21.09	24.31
Inactive OCA1-PO4 %	0.00	0.00	0,00	0.00	0.00	2.40
Inactive OcAl-Fe-PO4 %	2.11	2.00	2.68	2.29	2.02	0.00
Total inorganic phosphorus %	61.55	51.88	66.75	55.20	56.04	6 3. 64
Organic phosphorus %	38.45	48.12	33.25	44.80	43.96	36.36

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TABLE IVc

FRACTIONS OF THE SOIL PHOSPHORUS AS PERCENTAGE OF THE TOTAL PHOSPHORUS

	Gra	nt Silt I	Joam	ched. Million & Mildon against	
Lab. no. Depth inches	3219 0 - 5	3220 5 - 12	3221 12 - 20	3222 20 - 36	3223 36-48
Horizon	Ap	A ₁₂	^A 3	^B 2	C
Inorganic phosphorus fractions					
Active Al-PO4 %	6.14	2.54	0.91	0,97	2.57
Active Fe-PO4 %	4.50	3.18	2.22	2.21	4.94
Active Ca-PO ₄ %	35.24	33. 10	28.25	19.73	14,25
Inactive R. Sol. Fe-PO ₄ %	15,16	20.45	26.24	38.11	49.88
Inactive OcA1-PO ₄ %	0.00	0.00	0.00	0.00	0.00
Inactive OcAl Fe-PO4 %	1.22	1.70	2.02	3.46	5.54
Total inorganic phosphorus %	62.26	60.97	5 9. 64	64.48	77.18
Total organic phosphorus	37.74	39.03	40.36	35.52	22.82

TABLE IVd

FRACTIONS OF THE SOIL PHOSPHORUS AS PERCENTAGE OF THE TOTAL PHOSPHORUS

No	orge San	dy Loam			Strategy of the state
Lab. no. Depth inches Horizon	0 - 6 A	6 - 14 ^A 12	14-24 ^B 2t	24 - 52 C	
Inorganic phosphorus fractions					
Active Al-PO4 %	4.28	1.59	1.06	0.00	
Active Fe-PO ₄ %	8.57	2.48	4.23	4.45	
Active Ca-PO ₄ %	4,28	4.96	5.17	2.96	
Inactive R. Sol. Fe-PO ₄ %	30.00	32.24	32.44	36.10	
Inactive OcAl-PO4 %	0.00	0.00	0.00	0.00	
Inactive OcAl-Fe-PO ₄ %	3.33	3.19	5.17	3.46	
Total inorganic phosphorus %	50.46	44.46	48.05	46.97	
Organic phosphorus %	49.54	55.54	51.95	53.03	

TABLE IVe

FRACTIONS OF THE SOIL PHOSPHORUS AS PERCENTAGE OF THE TOTAL PHOSPHORUS

Ok	emah Si	lt Loam			
Lab. no. Depth inches Horizon	25 3 2 0-11 ^A 1	25 33 11-14 ^B 1	2534 14 - 20 ^B 21	2545 42 - 54 C	
Inorganic phosphorus fractions					
Active Al-PO4 %	0.64	0.00	0.00	0.21	
Active Fe-PO4 %	11.73	6.89	7.80	25.04	
Active Ca-PO ₄ %	3.43	3.69	4.72	6.82	
Inactive R. Sol. Fe-PO4 %	23.19	26.55	18.70	3 5.85	
Inactive OcAl-PO4 %	0.00	0.00	0.00	0.00	
Inactive OcAl-Fe-PO4 %	2.57	3.69	4.92	7.77	
Total inorganic phosphorus %	41.56	40.82	35.42	75.69	
Organic phosphorus %	58.44	59.18	64.58	24.31	

or inert portion cannot readily be extracted by ordinary laboratory methods; it is highly insoluble in the common solvents used in phosphorus extraction, and it is strongly resistant to further weathering. This phosphate does not under ordinary circumstances contribute to plant nutrition. The active phosphates include; aluminum phosphate (A1-PO₄), iron phosphate (Fe-PO₄), and calcium phosphate (Ca-PO₄). The inactive phosphate includes the occluded phosphates. Occluded phosphates occur as reductant soluble iron phosphate (Re Sol Fe-PO₄) and occluded aluminum phosphate (Oc A1-PO₄), or as the occluded aluminum-iron phosphate complex (Oc A1-Fe-PO₄).

Total Phosphorus

There was a difference in the distribution of total phosphorus within and among the soil profiles. In Carey Silt Loam, the total phosphorus in the A horizon was less than that in B and this in turn was less than that in C horizon. The relationship can be represented as follows: P-A < P-B < P-C (P represents total phosphorus; A, B and C, the genetic horizons). In Hollister, Grant and Norge the relationship was in the reverse order: P-C < P-B < P-A. Okemah had a totally different relationship: P-B < P-A < P-C. Considering the solum which is comprised essentially of the A and B horizons and which is important in plant nutrition, the results indicated that generally the surface soils were richer in total phosphorus reserve than the subsurface soils.

The average total phosphorus for each horizon of the profiles was as follows: Carey 522.4 ppm, Okemah, 452.5 ppm, Hollister 262.5 ppm, Grant 254.4 ppm and Norge 148.5 ppm. Carey and Okemah were the richest in total phosphorus, Norge the poorest; Hollister and Grant occupied intermediate positions. The average total phosphorus for all the horizons analyzed was 327.2 ppm.

Several factors such as physical and chemical properties, geologic origin and agricultural practice were largely responsible for the distribution of total phosphorus within and among the soil profiles.

Organic Phosphorus

Because of the low rate at which microbial organisms mineralize organic phosphates in the temperate regions, it has not been considered very important in phosphorus nutrition of the plant. However, in the tropical regions and in areas of high weathering activities, organic phosphates contribute very substantially to plant nutrition. In most soils organic phosphates constitute a relatively large proportion of the total phosphorus in the soil. Unfortunately the true nature of about half of the total organic phosphates in the soil remains obscure. The other fraction consists of 3 types of phosphates: inositol phosphate, ribonucleic acid and their derivatives, and phospholipids.

Distribution of organic phosphorus in Oklahoma soils. With the exception of Carey, the organic phosphates were accumulated in the surface soils. The level in the surface soil exceeded that in the subsurface soil and this in turn exceeded the level in the C-material. The amount of organic phosphate varied from 65 ppm in the A_p horizon of Norge to 255 ppm in the A_1 horizon of Okemah. The organic phosphate contribution to total phosphorus ranged from 35.42% in A1 horizom of Carey to 59.10% in the B_1 horizon of Okemah. The peculiar distribution pattern in Carey soil can be compared to that in Pima Clay Loam soil reported by Fuller and

McGeorge (25) in their work on Arizona calcareous soils. In the Pima soil the level of organic phosphate rose with increase in depth. In most of the soils Fuller and McGeorge analyzed, organic phosphate as percentage of total phosphorus also increased with depth. Wiklander and Hallgren (68) reported organic phosphate fairly constant throughout the profile while Gupta (32) found organic phosphate significantly correlated with percentage of CaCO₃ in the calcareous soils investigated.

The average total organic phosphate for all the soils analyzed was 129 ppm and its average percentage of the total phosphorus was 41.7%. Thus one can conclude that organic phosphate constituted a large part of the total phosphorus in the soils investigated.

<u>Carbon: Phosphorus ratio</u> (C:P). The results obtained by comparing carbon, nitrogen and phosphorus ratios are shown in Table V. Organic phosphorus is related to carbon and nitrogen in the soil organic matter. In the soils analyzed C:P varied markedly within the individual profiles, and also among the profiles. The extreme variation was from 18.1:1 in the C horizon of Okemah to 105.8:1 in the B_{2t} horizon of Norge. The soil variation was from 34.10:1 in Carey to 74.86:1 in Grant when averaged over the profile. However, the variation in C:P for the surface soils was not great. The range was from 45:1 to 76:1 (Hollister 76:1, Carey 67:1, Grant 66:1, Okemah 61:1, Norge 45:1). Several workers (42, 55, 66, 72) have also reported wide variation in C:P for soils.

<u>Nitrogen Phosphrous Ratios (N:P)</u>. This ratio has been reported to be less variable than C:P (42, 66, 72). Results showed that N:P variation was generally small in all the samples; and within individual profiles this variation was less marked than C:P. The N:P was fairly uniform

between the surface soils of the different profiles (Norge 6.9:1, Hollister 6.7:1, Carey 6.2:1, Okemah 5.1:1, and Grant 5.9:1). The range was between 5.1:1 and 6.9:1. This was comparable to the results of Walker and Adams (66) on some British soils where N:P ratio for the 0-7" layer for all soils analyzed varied from 10:3.2 to 10:1.2.

Carbon, Nitrogen, Phosphorus ratios (C:N:P). The results indicated that in all the surface soils analyzed, the C:N:P ratio was not very variable: Hollister 76:7:1, Carey 67:6:1, Grant 66:6:1, Okemah 61:5:1 and Norge 45:7:1. The average C:N:P for all the surface soils was approximately 63:6:1, subsurface or B horizon 59:6:1 and C-material 44:6:1. Average C:N:P for all the samples analyzed was 56:6:1. Williams et al. (72) reported C:N:P 147:10:2.5 for Scottish soils. Black and Goring (7) reported average C:N:P for organic matter in mineral soils as 100:9:1. Results from tropical soils reported by Nye and Bertheux (53) show ratios of 233:22:1 and 247:20:1 for the Forest and Savannah soils respectively, of Ghana. Benavides (5) showed 81:10:1 for tropical soils of Colombia, South America.

The significance of C:N:P ratio is that, it showed that organic phosphorus was an important factor in the build up of organic matter in the soil. Walker and Adams (66) emphasized that "the major factor governing the accumulation of organic matter in the soil was the phosphorus content of the parent material." The higher the C:P and N:P ratios of a soil, the more deficient the soil is likely to be in phosphorus. This deficiency will affect the build up of micro-organisms which require high phosphorus in the presence of carbon and nitrogen, to meet their narrow C:P and N:P ratios of 20:1 and 3:1 respectively. Walker (65)

Lab. No.	Depth Inches	Horizon	C:N	C:P	N:P	C:N:P
	(*)	Care	y Silt Loa	am		
61-S-79 61-S-80 61-S-81 61-S-82 61-S-83	0-12 12-22 22-38 28-34 34-54	A1 B21 B22 C1 Ca	11.20 10.37 9.20 8.21 8.67	66.9 31.1 23.1 18.8 30.7	6.2 3.2 2.7 2.2 3.3	67:6:1 31:3:1 23:3:1 19:2:1 31:3:1
		Hollis	ter Clay I	Loam		
61-S-73 61-S-74 61-S-75 61-S-76 61-S-77 61-S-78	0-5 5-11 11-23 23-31 31-44 44-50	Ap Al B2 B3 Cca C	11.33 11.22 11.08 11.86 10.46 7.44	85.0 67.3 89.4 46.4 34.7 34.7	7.5 6.0 8.2 3.6 3.2 5.3	85:8:1 67:6:1 89:8:1 46:4:1 35:3:1 35:5:1
		Gran	t Silt Lo	am		
3219 3220 3221 3222 3223	0-5 5-12 12-20 20-36 36-48	A A 12 A 3 B 2 C	12.78 10.95 10.51 10.02 5.90	73.9 67.0 57.6 73.0 102.8	6.1 6.1 5.6 7.5 16.7	74:6:1 67:6:1 58:6:1 73:8:1 103:17:1
		Norg	e Sandy L	Dam		
	0-6 6-14 14-24 24-50	$\begin{array}{c} {}^{A}\mathbf{p} \\ {}^{A}12 \\ {}^{B}\mathbf{2t} \\ {}^{C} \end{array}$	9.8 11.6 10.4 9.1	38.5 52.0 105.8 68.7	7.7 6.1 7.2 4.8	39:8:1 52:6:1 106:7:1 69:5:1
		Oken	ah Silt L	oam		
25 32 25 33 25 3 4 2545	0-11 11-14 14-20 42-54	$ \begin{array}{c} A_1 \\ B_1 \\ B_{21} \\ C \end{array} $	11.9 10.3 11.9 5.9	60.8 42.3 58.1 18.1	5.1 4.1 4.9 3.1	61:5:1 42:4:1 58:5:1 18:3:1

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CARBON, NITROGEN AND ORGANIC PHOSPHORUS RATIOS IN SOME OKLAHOMA SOIL PROFILES

TABLE V

noted that either a deficiency of sulfur or phosphorus will limit nitrogen fixation by micro-organisms.

Inorganic Phosphorus Fractions

Results indicated that all the forms of phosphorus analyzed were distributed in the 5 soil profiles regardless of soil reaction.

<u>Aluminum phosphate</u>. Aluminum phosphate was very low in all the soils, and within some profiles it was completely absent or present in trace quantities in some horizons. It was most highly accumulated within the surface soils, particularly in the plow depth and it decreased with increase in depth. Its contribution to the total phosphorus content was not appreciable: (Range: 0-6.2%).

<u>Iron phosphate</u>. Like aluminum phosphate, the level of iron phosphate was very low and its contribution to the total phosphorus was rather small except in the Okemah soil where it was substantial. It was totally absent in the calcareous horizons despite the high level of iron oxide. Range of iron phosphate level was from 0.0 ppm in calcareous horizons of the Carey and Hollister soils to 165 ppm in the C horizon of the Okemah soil, and its contribution to total phosphorus ranged from 0% in the calcareous horizons to 25% in the C horizon of Okemah. In the Okemah soil iron phosphate constituted the largest fraction of active inorganic phosphorus.

<u>Calcium phosphate</u>. This constituted a very large portion of total phosphate and the active inorganic fraction. In the calcareous soils it increased with depth. The total amount ranged from 3.75 ppm in C horizon of Norge to 362.50 ppm in C_1 horizon of Carey and its portion of the total phosphate varied from 2.96% in C horizon of Norge to 62.46%

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in C_{ca} horizon of Carey.

<u>Occluded phosphate</u>. This was well distributed in all the profiles but remarkably high in Okemah. It ranged from 37.50 ppm in C_{ca} horizon of Carey to 287.50 ppm in C horizon of Okemah, but as a percentage of total phosphorus, the range was from 6.34% in C_1 horizon of Carey to 55.42% in C horizon of Grant. It occurred mainly as reductant soluble iron phosphate and a complex of occluded aluminum and iron phosphate which Chang and Jackson (13) described as barrandite-like.

Reductant soluble iron phosphate. This constituted the larger fraction of the occluded phosphate. With the possible exception of Okemah where it was very high, it was well distributed in all the profiles. Its contribution to total phosphate was low in Carey, but fairly constant in the other soils. In the Reddish Chestnut soils it was concentrated more in the surface soils and decreased with increased depth, but in the Reddish Prairie and Prairie soils it tended to be higher in the lower horizons. It ranged from 39.38 ppm in the plow layer of Norge to 236.25 ppm in the C horizon of Okemah, and its percentage of total phosphorus varied from 4.97% in the C_1 horizon of Carey to 49.88% in the C horizon of the Grant soil.

<u>Occluded aluminum phosphate</u>. This was not important in any of the soils. It was mostly absent and where it occurred it tended to be concentrated in the C horizon.

Occluded aluminum-iron phosphate complex. Occluded aluminum phosphate occurred mainly as a complex. It was low for all soils, but was quite appreciable in Okemah profile. In the calcareous soils it was concentrated in the surface soils and decreased with increased depth, while in the rest of the profiles it tended to concentrate in the subsurface and deeper horizons.

From the results of the analyses, it was found that organic phosphorus contributed most to the total phosphorus reserve with an average value of 42%. Occluded phosphate and calcium phosphate contributed about evenly to the total phosphorus: occluded phosphate 28% and calcium phosphate 25%. Iron phosphate and aluminum phosphate contributed very little to total phosphorus, the average values being 4% and 2% respectively. In the surface soils organic phosphate contributed most to total phosphorus followed by occluded phosphate and calcium phosphate. The contribution of iron phosphate and aluminum phosphate was small: (Organic phosphate 46%, Oc-PO4 25%, Ca-PO4 20%, Fe-PO4 6%, Al-PO4 3%). In the subsurface soil layers the contribution of the various phosphorus forms showed again organic phosphate. Iron phosphate contributed little while the aluminum phosphate contributed little while the aluminum phosphate contribution was negligible: (O.P. 44%, Oc-PO4 28%, Ca-PO4 21%, Fe-PO4 5%, Al-PO4 <1%).

Among the individual profiles the relationships of the various forms of phosphorus were as follows:

Carey:Ca-PO4 > 0.P > 0c-PO4 > A1-PO4 > Fe-PO4.Hollister: $0.P. > 0c-PO_4 > Ca-PO_4 > Fe-PO_4 > A1-PO_4.$ Grant: $0.P. > 0c-PO_4 > Ca-PO_4 > Fe-PO_4 > A1-PO_4.$ Norge: $0.P. > 0c-PO_4 > Fe-PO_4 > Ca-PO_4 > A1-PO_4.$ Okemah: $0.P. > 0c-PO_4 > Fe-PO_4 > Ca-PO_4 > A1-PO_4.$

0.P. = organic phosphates, Oc-PO₄ = occluded phosphates, A1-PO₄ = aluminum phosphates, Fe-PO₄ = iron phosphates, Ca-PO₄ = calcium phosphates.

The dominance of occluded phosphate over each of the inorganic forms was not expected in the soils of Reddish Chestnut and Reddish Prairies. Possibly the cause was geological, occluded phosphate being inherited directly from the parent material. This will be discussed in full in the next chapter on soil weathering. The manner of distribution of active phosphate fractions which will influence the determination of available phosphorus is shown in Table VI.

Therefore any chemical extractant that would extract Ca-PO₄ selectively would best give indication of available phosphorus for Carey, Hollister and Grant. In Norge any chemical extractant that would dissolve the 3 phosphate fractions selectively would give the best indication of the available phosphorus of the soil. For Okemah the best test extractant should be one that will dissolve Ca-PO₄ and Fe-PO₄ selectively. The chemical extractant can be determined from experiments or from the findings of Chang and Juo (15).

TABLE VI

FORMS OF PHOSPHATES AS PERCENTAGE OF TOTAL ACTIVE PHOSPHATES

Soil Profile	A1-P04 %	Fe-PO ₄ %	Ca⇔PO ₄ %
Carey Silt Loam	7.60	6.36	85.86
Hollister Clay Loam	14.46	16.97	67.80
Grant Silt Loam	9.96	9.01	81.02
Norge Sandy Loam	21.29	38.73	39.39
Okemah Silt Loam	4.06	74.21	21.72

Soil Phosphorus Forms and Soil Genesis

Chang and Jackson (14) have postulated that the degree of, or the stage of weathering of a soil can be determined by the relative percentages of the discrete phosphorus forms, and that the sequence of chemical weathering is in the order: Ca-PO4--A1-PO4--Fe-PO4--Oc-PO4. The B horizons of the profiles were investigated because the B horizon best represents the stage of development or weathering of a mature soil. The results of the analysis of the distribution of inorganic soil phosphate are shown in Table VII. Applying the "Chang and Jackson" postulation, results indicated that the soils ranged from weakly weathered to highly weathered soils. Carey silt loam represented a soil not strongly weathered, Grant, Norge and Okemah represented soils more strongly weathered, while Hollister represented a moderately weathered soil. The relative percentages of the discrete phosphorus forms of the total inorganic phosphate are shown in Table VIII and the graphs of percentage of chemical forms of inorganic soil phosphorus plotted as a chemical weathering sequence shown in Figures I and II.

Two explanations are possible for the relatively high level of occluded phosphate in the profiles of the Reddish-Chestnut and Reddish Praiire soils. 1. It could be a result of weathering activities considering the climate of Oklahoma in which they are found. Results from other places might strengthen this point. Data from Chang and Jackson (14) for a Dewey A₂ horizon, a podzolic soil developed from calcareous material showed

TABLE VII

Lab. No.	Depth Inches	Horizon	A1-P04 %	Fe-P04 %	Ca - P0 ₄ %	0c-P04*	Added Total Inorganic P p.p.m.
			Care	y Silt Loa	am		
61-S-79 61-S-80 61-S-81 61-S-82 61-S-83	0-12 12-22 22-28 28-34 34-54	A ₁ B ₂₁ B ₂₂ C C _{ca}	5.66 1.23 0.97 1.00 1.12	4.74 1.89 0.00 0.00 0.00	63.24 77.87 81.02 89.71 88.46	26.35 18.99 18.00 9.28 10.40	237.19 329.06 416.56 404.06 360.31
			Hollist	er Silt]	Loam		
61-S-73 61-S-74 61-S-75 61-S-76 61-S-77 61-S-78	0-5 5-11 11-23 23-31 31-44 44-50	Ap Al B2 B3 Cca C	8.34 7.72 1.64 1.62 0.00 / 0.94	9.23 9.65 3.29 2.53 1.03 0.00	36.23 40.15 32.90 49.76 57.72 57.08	49.73 42.46 62.15 46.07 41.24 41.97	175.94 161.88 170.95 135.64 121.26 148.91
		- 1999-1999 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 -	Grant	Silt Loa	am		
3219 3220 3221 3222 3223	0-5 5-12 12-20 20-36 36-48	Ap A12 A3 B2 C	9.86 4.15 1.52 1.51 3.33	7.23 5.22 3.72 3.43 6.40	56.57 54.28 47.37 30.59 18.46	26.31 36.33 47.37 64.45 71.79	190.00 179.61 184.69 145.45 121.87
			Norge	Sandy Lo	oam		
	0-6 6-14 14-24 24-50	Ap A12 B2t C	8.48 3.58 2.20 0.00	16.97 5.58 8.80 9.47	8.49 11.15 10.76 6.31	66.04 79.68 78.22 84.20	66.26 78.45 63.93 59.39
			Ok ema	ah Silt Lo	oam		
25 3 2 25 33 2534 2545	0-11 11-14 14-20 42-54	A ₁ B ₁ B ₂₁ C	1.54 0.00 0.00 0.28	28.22 16.88 19.99 33.07	8.26 9.05 13.33 9.01	61.96 74.09 66.66 57.62	181.56 151.83 112.51 498.91

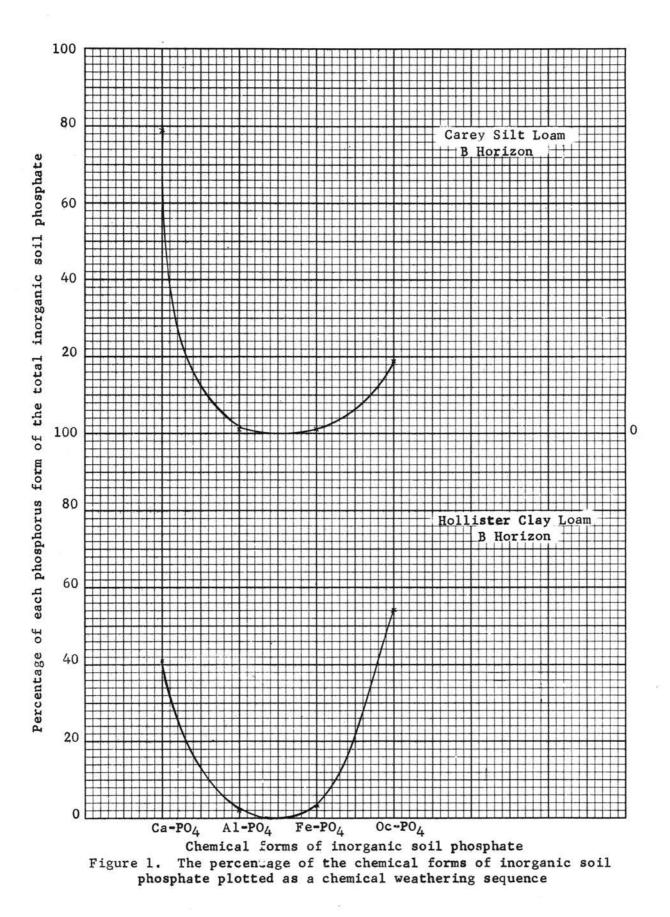
DISTRIBUTION OF INORGANIC SOIL PHOSPHORUS FORMS AS A PERCENTAGE OF THE TOTAL INORGANIC PHOSPHATE

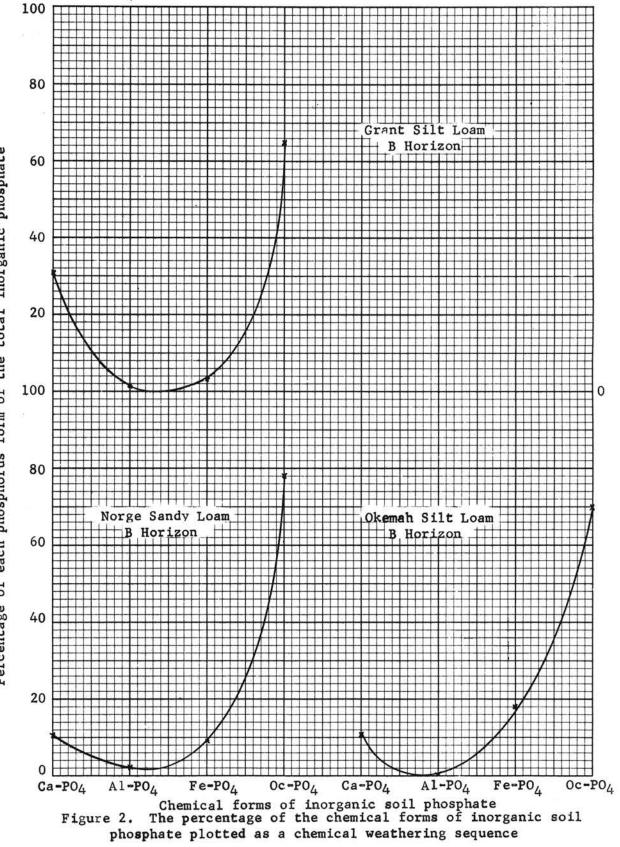
* Total occluded phosphate

TABLE VIII

				det en
Soil	A1-P04	Fe-PO ₄	Ca-PO ₄	0c-P04
Carey Silt Loam	1.0	0.9	79.0	19.0
Hollister Clay Loam	2.0	3.0	41.0	54.0
Grant Silt Loam	1.5	3.0	31.0	65.0
Norge Sandy Loam	2.0	9.0	11.0	78.0
Okemah Silt Loam	0.0	18.0	11.0	70.0

PHOSPHORUS FORMS OF THE SOILS AS PERCENTAGE OF TOTAL INORGANIC PHOSPHATE





Percentage of each phosphorus form of the total inorganic phosphate

occluded phosphate dominant over each of the other inorganic phosphorus forms. Miami silt loam (a grey brown podzol) and Scott (ground water podzol) were both derived from calcareous material and showed intermediate weathering. Therefore the results could be comparable although these soils are mostly podzolic. On the other hand the occluded phosphate might have been derived directly from the parent material. Weathering or soil development might not have been wholly responsible considering the fact that the quantities of iron or aluminum phosphates were very low or even absent in the B-horizon of some of the soils (unlike the Okemah where Fe-PO4 was substantial although for other reasons A1-PO4 was absent). The reports of Molthan and Gray (52) showed two soils usually considered similar, arising from the Permain redbed and belonging to Reddish Prairies had all of their clay unaltered with little evidence of weathering. They postulated that the clay minerals were possibly inherited directly from the clay minerals in the parent material. One of their profiles had a higher level of total phosphorus because the Permain redbed close to the gypsiferous deposits of the retreating Permian sea in Weatern Oklahoma is rich in phosphorus. 2 Permain redbeds contain much iron oxide, therefore a question might be raised; whether the occluded phosphate had not been formed long before soil development (possibly by a slow process) in the parent material and was inherited directly as a part of the clay. Some of the soils like Carey, Grant and Hollister were developed on Permian redbeds rich in phosphorus but the Norge soil was not. This might also account for the low phosphorus level of Norge. Therefore it is possible that the occluded phosphate of these soils excepting

2 Fenton Gray - private communication.

Norge and Okemah was not mainly a result of soil development or soil weathering but mostly inherited directly from the parent material.

The problem needs more investigation, first to determine the type of clay minerals in these soils, and to investigate whether other profiles derived from Permian redbeds rich in phosphorus contained high or reasonable levels of occluded phosphate even in soils known to be young. If the latter was applicable, then the "Chang and Jackson" postulation should be modified to accomodate a situation where clay materials rich in iron oxide and phosphorus, and shown to contain occluded phosphate, is derived directly from the parent material and not a product of weathering in the course of soil development.

Chemical Distribution of Water Soluble Phosphate Applied to the Soil

Results of the chemical distribution of water soluble phosphate applied to the soil, for 3 and 30 days are shown in Tables IXa-e and Xa-e respectively. Results showed that in 3 and 30 days the water soluble phosphate was retained as phosphate soluble in NH₄Cl or "saloid bound" phosphate, aluminum phosphate, iron phosphate and calcium phosphate. There was a great increase in the level of saloid bound phosphate and aluminum phosphate in the native soil phosphorus. A large portion of the applied phosphate was retained as aluminum phosphate. In the Carey soil, the applied phosphate was retained mostly as "saloid bound" phosphate with aluminum phosphate and calcium phosphate about equal in quantity. In the Hollister, Grant and Norge soils, the applied phosphate was retained mostly as aluminum phosphate while in Okemah it was retained mostly as iron phosphate. Results are shown in Table XI. The average total percentage

TABLE IXa

RETENTION OF 200 PPM OF PHOSPHORUS ADDED AS KH₂PO₄ FROM SOIL HELD AT FIELD CAPACITY FOR THREE DAYS

Depth inches 0-12 12-22 22-28 28-34 34	S=83 =54 C _{ca} 55
	55
pH paste 6.40 7.10 7.50 7.60 7.	
pH 1:1 KC1 5.80 6.60 6.95 7.20 7,	10
Net increase of P	
in each form in ppm "saloid bound"	
PO4 85.00 65.00 100.00 100.00 117.	50
A1-PO ₄ 89.06 93.44 52.19 39.69 49.	69
Fe-P04 17.50 33.75 0.00 0.00 0.	00
Ca-PO ₄ 6.25 43.75 100.00 87.50 93.	70
Total phosphorus	
recovered ppm 197.81 235.94 252.19 227.19 260.3 % phosphorus	39
recovery 98.90 117.97 126.09 113.59 130.	44
Bray #1 available	
bhosphorus ppm 194.00 167.00 0.00 0.00 0.	50
% rendered "fixed" 3.00 16,50 100.00 100.00 99.	75

TABLE IXb

RETENTION OF 200 PPM OF PHOSPHORUS ADDED AS KH₂PO₄ FROM SOIL HELD AT FIELD CAPACITY FOR THREE DAYS

Hollister Clay Loam								
Lab. no.	61-S-73	61-S-74	61-S-75	61-S-76	61-S-77	61-S-78		
Depth inches	0-5	5-11	11-23	23-31	31-44	44-50		
Horizon	Ap	A1	^B 2	^B 3	C _{ca}	C		
pH paste	6.40	6.10	6.60	7.10	7.20	7.40		
pH 1:1 KC1	5.50	5.45	5.90	6.40	6.90	6.90		
Net increase of P								
in each form in ppm								
"saloid bound"								
PO4	57.50	50.00	17.50	32.50	42.50	57.50		
A1-PO4	114.06	116.25	125.94	121.55	102.50	84.84		
Fe-PO4	23.75	26.87	39.37	41.56	38.75	21.25		
Ca-PO4	16.25	8.75	6.25	0.00	15.00	22.50		
Total phosphorus								
recovered ppm	211.56	201.87	189.06	195.61	198.75	186.09		
% phosphorus								
recovery	105.78	100.93	94.53	97.80	99.37	93.04		
Bray #1 available				9 (419 (40) E				
phosphorus ppm	190.00	165.00	158.50	159.50	145.50	143.00		
% rendered "fixed"	5.00	17.50	20.75	20.25	27.25	28.50		

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TABLE IXc

RETENTION OF 200 PPM OF PHOSPHORUS ADDED AS KH₂PO₄ FROM SOIL HELD AT FIELD CAPACITY FOR THREE DAYS

Grant Silt Loam					
Lab. no. Depth inches Horizon	3219 0-5 ^A p	3220 5-12 ^A 12	3221 12-20 ^A 3	3222 20 - 36 ^B 2	3223 36-48 C
pH paste	6.20	5.90	6.35	6.88	7.10
pH 1:1 KC1	5.40	5.20	5.60	6.00	6.20
Net increase of P	- •				
in each form in ppm					
"saloid bound"			42		
PO4	75.00	60.00	53.75	23.75	25.00
A1-P04	105.00	116.28	115.94	136.55	145.94
Fe-PO4	15.00	19.37	20.62	28.75	29.69
Ca-PO4	17.50	17.50	7.50	0.50	0.00
Total phosphorus					
recovered ppm % phosphorus	212.50	213.15	197.81	189.55	200.63
recovery	106.25	106.57	98.90	94.77	100.31
Bray #1 available	1999-1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1 1997 -	1999	1900000 0020000	5 (10155 (N.S.)	99999999999999999999999999999999999999
phosphorus ppm	189.00	166.00	156.00	158.50	163.00
% rendered "fixed"	5.50	17.00	22.00	20.75	18.50

TABLE IXd

RETENTION OF 200 PPM OF PHOSPHORUS ADDED AS KH₂PO₄ FROM SOIL HELD AT FIELD CAPACITY FOR THREE DAYS

Norge Sandy Loam					
Lab. no. Depth inches Horizon	0 -6 Ap	6-14 ^A 12	14-24 ^B 2t	24 - 52 C	
pH paste	6.60	5.50	5,60	5.60	
pH 1:1 KC1	6.15	4.90	4.90	5.00	
Net increase of P					
in each form in ppm "saloid bound"					
PO4	47.50	22.50	10.00	23.75	85.
A1-P04	118.13	158.44	148.59	133.75	
Fe-PO4	20.00	33.12	41.87	31.87	
Ca-PO4	8.12	6.25	6.87	13.75	
Total phosphorus			1000		
recovered ppm % phosphorus	193.75	220.31	207.33	203.12	
recovery	96.87	110.15	103.66	101.56	
Bray #1 available	250 A B A B				
phosphorus ppm	147.00	158.50	143.00	165.50	
% rendered "fixed"	26.50	20.75	28.50	17.25	

TABLE IXe

RETENTION OF 200 PPM OF PHOSPHORUS ADDED AS KH₂PO₄ FROM SOIL HELD AT FIELD CAPACITY FOR THREE DAYS

1	Oke	mah Silt Lo	oam		
Lab. no. Depth inches Horizon	2532 0-11 ^A 1	2533 11-14 ^B 1	25 3 4 14 - 20 ^B 21	2545 42 - 54 C	
pH paste	5.20	4.80	4.50	5.00	
pH 1:1 KC1	4.80	4.20	3.80	4.30	
Net increase of P					
in each form in ppm "saloid bound"					
PO4	10.00	0.00	0.00	0.00	
A1-PO4	88.44	70,00	48.75	31.09	
Fe-PO4	104.00	115.00	118.13	260.00	
Ca-PO4	5.00	0.00	0.00	0.00	
Total phosphorus					
recovered ppm % phosphorus	207.44	185.00	166.88	291.09	
recovery	103.72	92.50	83.44	145.54	
Bray #1 available					
phosphorus ppm	83.00	61.50	52.00	16.50	
% rendered "fixed"	58.50	69.25	74.00	91.75	

TABLE Xa

RETENTION OF 200 PPM OF PHOSPHORUS ADDED AS KH2PO4 FROM SOIL HELD AT FIELD CAPACITY FOL 3THIRTY DAYS

	Ca	rey Silt L	oam		
Lab. no. Depth inches Horizon	61 - 5-79 0-12 ^A 1	61-S-80 12-22 ^B 21	61-S-81 22-28 ^B 22	61 - S-82 28-34 C ₁	61 - S-83 34-54 C _{ca}
pH 1:1 KC1	5.80	6.70	7.10	7.20	7.20
Net increase of P in each form in ppm					
"saloid bound"					
PO4	72.50	61.30	92.50	92.50	100.00
A1-PO4	99.06	87.19	44.70	39.69	49.69
Fe-PO4	16.25	25.00	0.00	0.00	0.00
Ca-PO4	6.25	43.75	112.50	87.50	91.25
Total phosphorus					
recovered ppm	194.06	217.24	249.70	219.69	240,94
% phosphorus recovery	97.03	108.62	124.85	109.84	120.47

TABLE Xb

RETENTION OF 200 PPM OF PHOSPHORUS ADDED AS KH2PO4 FROM SOIL HELD AT FIELD CAPACITY FOR3 THIRTY DAYS

The manufacture of the Second system of the Second s	Hol1:	ister Cla	y Loam			
Lab. no. Depth inches Horizon	61 -S-73 0-5 ^A p	61 -S- 74 5-11 ^A 1	61-S-75 11-23 ^B 2	61 -S- 76 2 3-3 1 ^B 3	61-S-77 31-44 ^C ca	61-S-78 44-50 C
pH 1:1 KC1	5.40	5 .3 0	5.70	6.50	6.80	6 .9 0
Net increase of P in each form in ppm						
"saloid bound"						
PO4	40.00	35.00	11.30	22.50	32.50	50.00
A1-P04	119.06	116.25	125.94	121.55	102.50	84.84
Fe-PO4	26.25	29,40	39.37	36.56	32.50	20.00
Ca-PO4	16.25	8.75	6.25	7.50	32.50	50.00
Total phosphorus						
recovered ppm	201.56	189.40	182.86	188.11	200.00	204.84
% phosphorus recovery	100.78	94.70	91.43	94.06	100.00	102.42

TABLE Xc

RETENTION OF 200 PPM OF PHOSPHORUS ADDED AS KH2PO4 FROM SOIL HELD AT FIELD CAPACITY FOR THIRTY DAYS

		Grant Silt	Loam		
Lab. no. Depth inches Horizon	3219 0-5 A p	322 0 5-12 ^A 12	3221 12-20 ^A 3	3222 20-36 ^B 2	3223 36-48 C
pH 1:1 KC1	4.80	5,10	5.40	6.20	6.30
Net increase of P each form in ppm	in				
"saloid bound"					
POL	50.00	44.00	43.80	20.00	22.50
A1-PO4	105.00	116.00	116,00	121.50	134.69
Fe-PO4	15.00	20.00	20,62	32.50	37.19
Ca-PO4	17.50	27.50	12.50	10.50	5.50
Total phosphorus					
recovered ppm	187,50	207,50	192.92	184.50	199.88
% phosphorus recov	very 93.75	103.75	96.46	92.25	99.94

Norge Sandy Loam					
Lab. no. Depth inches Horizon	0 - 6 ^A p	6-14 ^A 12	14-24 ^B 2t	24 - 52 C	
pH 1:1 KC1	5.55	4.80	4.80	4.80	
Net increase of P in each form in ppm	đ		¥Ĵ.		
"saloid bound"					
PO4	40.00	15.00	7.50	22.50	
Al-PO4	118.13	153.20	144.60	133.75	
Fe-PO4	24.00	35.00	43.87	30.37	
Ca-PO4	8.00	6.25	6.50	13.50	
Total phosphorus					
recovered ppm	190.13	209.45	202.47	200.12	
% phosphorus recovery	95.06	104.73	101.24	100.06	

TABLE Xd

RETENTION OF 200 PPM OF PHOSPHORUS ADDED AS KH2PO, FROM SOIL HELD AT FIELD CAPACITY FOR THIRTY DAYS

TABLE Xe

RETENTION OF 200 PPM OF PHOSPHORUS ADDED AS KH2PO4 FROM SOIL HELD AT FIELD CAPACITY FOR THIRTY DAYS

	Ok	emah Silt Los	am		
Lab. no. D ept h inches Horizon	2532 0-11 ^A 1	2533 11-14 ^B 1	2534 14-20 ^B 21	2545 42 - 54 C	
pH 1:1 KC1	4.45	4.30	3.85	4.35	
Net increase of P in each form in ppm					
"saloid bound"					
PO4	6.30	Trace	0.00	0.00	
A1-P04	83.50	70.00	50.13	31.09	
Fe-PO4	96.50	120.62	122.00	255.00	
-Ga-BO4	5,00	0.00	0.00	0.00	
Total phosphorus					
recovered ppm	191.30	190.62	172.13	286.09	
% phosphorus recovery	95.65	95 .3 1	86,06	143.05	

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Soil	"Saloid bound" - PO ₄	A1-P04	Fe-PO ₄	Ca=PO4
Carey Silt Loam	39.82	27.60	4.36	28.21
Hollister Clay Loam	21.76	56,22	16.19	5.81
Grant Silt Loam	23,43	61.14	11.19	4.24
Norge Sandy Loam	12.58	67.78	15.38	4.24
Okemah Silt Loam	1,17	28.01	70,20	0.58

PERCENTAGE OF ADDED WATER SOLUBLE PHOSPHATE RETAINED BY EACH PHOSPHORUS FORM AFTER 3 DAYS

of the applied phosphate retained by each chemical form is: aluminum phosphate 48,15, iron phosphate 23,46, saloid bound phosphate 19.75, calcium phosphate 8,62.

There was no appreciable difference between the net increase in retained phosphate in 3 days and 30 days. This period was very short for the transformation of phosphate from one form to another.

pH: There was a general drop in pH level after application of the water soluble phosphate but the pH remained about the same after 3 and 30 days. The pH comparisons were made in N KCl.

Phosphate recovered: Results showed that after 3 and 30 days it was possible to recover all of the applied phosphate in the phosphorus forms discussed. In most samples, the percentages of the phosphate recovered exceeded that applied. This had also been observed by other workers (45, 64). There are four probable causes:

1. Some occluded phosphate might have been solubilized, but this is not very likely since reports of Chang and Jackson (14) showed that fertilizers have no effect on the amount of occluded phosphate.

2. Organic phosphorus might have been mineralized. However, no lime was applied to the acid soils and there was therefore no stimulation of microbial activilies, and the time was too short to produce any appreciable amount of phosphorus from the organic phosphorus.

3. Inherent errors associated with colorimetric techniques. Where "tracer techniques" were used for a similar investigation, the recovered phosphorus had remained lower than that by colorimetric technique (64).

4. The most likely reason is the difference in solubilities between freshly formed phosphate compounds and the more aged cyrstalline native

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phosphorus compounds in the soil.

There was little or no increase in the calcium phosphate when soils were treated with water soluble phosphate as had been reported be several workers (12, 13, 74). Chang and Chu (12) reported this even for calcareous soils. When water soluble phosphate is applied to the soil, the first stage of the phosphate fixation is governed more by surface energy of the solid phases associated with aluminum, iron and calcium rather than the ionic activities of aluminum, iron and calcium ions in the soil solution (12). Since clay is the main site of phosphate fixation and the content of aluminum in clay is much higher than either iron or calcium, water soluble phosphorus added to the soil is likely to be retained more as aluminum phosphate than iron phosphate or calcium phosphate at the initial stage.

Forms of Phosphorus Compounds and Available Phosphorus

The correlation analysis between available phosphorus determined by Bray's #1 method and the forms of phosphorus in the surface soils of the profiles is shown in Table XII.

Results showed that by Bray's #1 method, aluminum phosphate and calcium phosphate were associated with the available phosphorus but aluminum phosphate more significantly. Organic phosphate and iron phosphate did not contribute to available phosphorus.

After the water soluble phosphate was applied to the soil it was retained mostly as aluminum phosphate and saloid bound phosphate in the surface soils. If the relative amounts and the quantities of the active phosphorus forms indicate their relative availabilities to plants (though

TABLE XII

Forms of Phosphorus	Correlation Coefficient	Remarks
Aluminum phosphate	≁ 0 .83 47	Significant at 1% level
Iron phosphate	- 0.0946	No correlation
Calcium phosphate	≠ 0.2848	Not significant
Organic phosphate	- 0.0045	No correlation

CORRELATION BETWEEN FORMS OF PHOSPHORUS AND BRAY'S #1 AVAILABLE PHOSPHORUS

availability is largely governed by the specific surface area), then aluminum phosphate and saloid bound phosphate would form the main reserve of available phosphorus in the surface soils. However, reaction time studied should be followed by a very long reaction interval in an effort to check on further changes in quantities of phosphate compounds. The use of Bray's #1 as a selective extractant for available phosphorus in these soils needs more investigation since it is the distribution pattern of phosphorus forms that would indicate the suitable soil test extractant for available phosphorus. Chang and Juo (15) observed that in soils dominated by calcium phosphate, the available phosphorus determined by Bray's #1 was highly correlated with aluminum phosphate and considerably less with calcium phosphate and iron phosphate. In soils dominated by calcium phosphate and iron phosphate, Bray's #1 available phosphorus was more significantly correlated with aluminum phosphate and much less with iron phosphate and least with calcium phosphate. Only in soils dominated by iron phosphate was there a high correlation between Bray's #1 available phosphorus and calcium phosphate or iron phosphate.

SUMMARY AND CONCLUSION

The main objective of this research was to fractionate soil phosphorus of five soil profiles of Oklahoma into chemical compounds and determine the relative amounts and the distribution of these compounds in the soils. Other investigations included the stage of soil weathering according to the relative amounts and the distribution of the phosphorus compounds in the soil, chemical distribution of water soluble phosphate applied to the soil, and forms of phosphorus in relation to available phosphorus.

A modified Chang and Jackson method was employed and the soil phosphorus compounds fractionated into aluminum phosphate, iron phosphate, calcium phosphate, occluded phosphate, and organic phosphate. Total phosphorus was higher in the surface soils than in the subsurface soils. With the possible exception of Norge Sandy Loam, all soils investigated were high in total phosphorus. Organic phosphorus decreased with depth. About 42% of the total phosphorus was organic phosphorus. This was the largest individual phosphorus form contributing to total phosphorus. It was concentrated in the surface soils of all profiles. The average C:N:P ratio for all horizons of all soil profiles was 56:6:1.

Aluminum phosphate and iron phosphate were of little importance and contributed 2% and 4% respectively to the total phosphorus. Aluminum phosphate was accumulated most in the plow layer of all the soils. Calcium phosphate contributed about 25% of the total phosphorus and it was highest in the Carey, Hollister and Grant soil profiles. Occluded

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phosphate was present mainly as reductant soluble iron phosphate and a complex of occluded aluminum-iron phosphate. It was high in all profiles. It contributed about 28% of the total phosphate and was next in rank to organic phosphate and about equal to calcium phosphate. Calcium phosphate dominated the active phosphate fractions.

The soils ranged from weakly weathered to strongly weathered soils with Carey Silt Loam representing the weakly weathered profile. Hollister Clay Loam was moderately weathered, Grant Silt Loam more than moderately weathered but not as strongly weathered as Norge Sandy Loam and Okemah Silt Loam.

It was possible to recover in 3 and 30 days all of the applied water soluble phosphate as aluminum phosphate, iron phosphate, calcium phosphate and "saloid bound" phosphate. The application of water soluble phosphate greatly increased the level of aluminum phosphate and saloid bound phosphate in the soil. Aluminum phosphate and calcium phosphate contributed to the available phosphorus in the surface soils, as determined by Bray's #1 method. Iron phosphate and organic phosphates were not important. Aluminum phosphate and saloid bound phosphate constituted the main supply of available phosphorus in the surface soil after application of water soluble phosphate in 30 days.

While it was not possible to fractionate the soil phosphorus compounds into chemically discrete forms by the Chang and Jackson method, it was possible to fractionate them into general compounds of aluminum, iron and calcium and these were present in all the soils regardless of soil reaction. The relative amounts and the distribution pattern of phosphorus forms in the soil can be of great help in studies related to soil chemistry, soil genesis and soil fertility.

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APPENDIX

CAREY SERIES

Field Description¹

- 1. Plot near Custer, Oklahoma. Wheat.
- A₁ 0-12" Dark reddish brown (5 YR 3/3 moist) silt loam, moderate medium and fine granular structure; friable moist; pH 6.5 (Hellige); gradual boundary.
- B₂₋₁ 12-22" Dark reddish brown (2.5 YR 3/4 moist) heavy silt loam; moderate medium granular; friable moist; many worm casts and roots; pH 7.0, noncalcareous; gradual boundary.
- B₂₋₂ 22-28" Dark red (2.5 YR 3/6 moist) light silty clay loam; weak medium prisms separating easily to moderate medium granules; slightly firm moist; hard when dry; few faint films and organic stains on ped faces; many worm casts and roots; pH 7.0, noncalcareous; clear boundary.
- C1 28-34" Red (2.5 YR 4/6 moist) silt loam; weak medium granular; friable moist; calcareous, with few streaks and blotches of segregated lime; gradual boundary.
- C_{ca} 34-54" Similar to above; porous massive; strongly calcareous with 5-10% lime concretions. This horizon rests on a slightly heavier and darker (buried) layer, not sampled.

Remarks: This is modal Carey silt loam.

Great Soil Group: Reddish Chestnut.

Parent Material: Calcareous permeable sandy Permian redbeds.

Topography: Very gently sloping convex surfaces in erosion upland. Gradient 1-3%.

Drainage: Well drained on surface and internally.

- Vegetation: Coarse bunch grasses, mainly little bluestem; some gama grasses.
- Use: Very largely in cultivation to cotton, sorghums and small grains. Moderately to highly productive.
- Distribution: Western Oklahoma east of the High Plains.

1 Description by Roy M. Smith

HOLLISTER CLAY LOAM

0-1% slopes

Sample S63-OK-33-1-1

- A p 0-8" Very dark grayish brown (10 YR 3/2) clay loam, dark yellowish brown (10 YR 4/4) dry; weak medium granular; friable moist, slightly hard dry; pH 8.0; clear boundary.
- Sample S63-OK-33-1-2
- B₁ 8-13" Dark brown (7.5 YR 3/2) light clay, brown (7.5 YR 4/2) dry; moderate medium blocky; very firm moist, hard when dry; small lime concretions; weakly calcareous; pH 8.0; gradual boundary.

Sample S63-OK-33-1-3

B_{2t-1} 13-28" Dark brown (7.5 YR 3/2) clay, brown (7.5 YR 4/2) dry; weak medium and coarse blocky; very firm moist, hard when dry; calcareous; pH 8.0; gradual boundary.

Sample S63-OK-33-1-4

B_{2t-2} 28-34" Dark reddish brown (5 YR 3/3) clay, reddish brown (5 YR 4/3) dry; weak medium and coarse blocky, few pink granite pebbles and lime concretions present; calcareous in mass; pH 8.0; gradual boundary.

Sample S63-OK-33-1-5

B₃ 34-54" Dark reddish brown (5 YR 3/3) clay loam, reddish brown (5 YR 4/3) dry; massive; calcareous; pH 8.0.

Location: Altus Irrigation Station Oklahoma.

Great Soil Group: Reddish Chestnut.

Parent Material: Reddish calcareous clay mainly Permian

Topography: Nearly level to very gently sloping with gradients not exceeding 3%, dominantly less than 2%.

Drainage and Slow to very slow from surface and internally, but the soil is well drained.

Vegetation: Short grasses mainly buffalo and grama grasses with scattered mesquite trees.

Distribution: Rolling plains of Western Oklahoma.

PS: The profile described here is not exactly the profile used in this work, but they come from the same area and have many characteristics in common. Description by Roy Smith and Ben Cunningham.

GRANT SERIES

Field Description²

- 1. From Cherokee Station wheat fertility (long time) tests.
- Ap 0-5" Dark brown (7.5 YR 3/2) coarse silt loam, brown (7.5 YR 4/2) dry; very weakly granular; friable moist, tends to crust or "set up" when dry; pH 6.0 (Hellige); plowed boundary.
- A₁₂ 5-12" Dark brown (10 YR 3/3 moist) silt loam; weak medium granular; friable; pH 5.8; gradual boundary.
- A₃ 12-20" Dark brown (7.5 YR 3/3 moist) silt loam; moderate medium and fine granular; friable moist; pH 6.5; clear boundary.
- B₂ 20-36" Dark reddish brown (5 YR 3/4 moist) light clay loam; weak medium prisms separate to weak subangular blocks; friable to slightly firm moist; pH 7.0; gradual boundary.
- C 36-48" Reddish brown (5 YR 4/4 moist) loam, with few small gravels; porous massive; friable moist; pH 7.5; noncalcareous.

Remarks: This is Grant Silt Loam

Great Soil Group: Reddish Prairie.

- Parent Material: Late Pleistocene of loess that originated largely in silty Permian redbeds. Parent material may be calcareous.
- Topography: Very gently to moderately sloping erosional uplands; surfaces convex to plane gradients 1-4%.

Description by Roy Smith

Drainage: Free from the surface and internally.

Vegetation: Originally of tall prairie grasses.

Use: Practically all in cultivation, very largely to winter wheat; very fertile productive and highly valued.

Distribution: N.W. Central Oklahoma.

Remarks: Grant series are submature soils with weak textural profiles developed for the most part in deposits younger than middle Pleistocene. Generally classed as Reddish Prairie but are less acid than typical of that soil; and lack the distinct carbonate zone characteristic of Reddish Chestnut soils.

NORGE SERIES

Field Description

- Ap0-6"Dark brown (7.5 YR 3/2) light loam or fine sandy loam;
brown (7.5 YR 5/4) dry; weak fine granular structure;
very friable moist; pH 6.0 (Hellige); clear boundary.
- A₁₂ 6-14" Dark brown (7.5 YR 3/2) loam, brown (7.5 YR 4/2) dry; moderate medium granular structure; friable moist; pH 6.0; gradual boundary.
- B_{2t} 14-24" Dark reddish brown (5 YR 3/4) clay loam, reddish brown (5 YR 4/4) dry; weak medium subangular blocky; slightly firm moist; pH 5.5; clear boundary.
- C 24-50" Strong brown (7.5 YR 5/6) fine sandy loam, reddish yellow (7.5 YR 6/6) dry; weak granular, almost structureless; friable moist; pH 5.5; weakly stratified with browner and slightly heavier lenses.

Location: Perkins Experiment Station, Oklahoma.

Great Soil Group: Reddish Prairie.

Parent Material: Calcareous or alkaline old alluvium.

Topography: Nearly level to gently sloping erosional uplands. Convex with gradients 1-7%.

Drainage: Moderate to rapid from the surface, moderately internally.

Vegetation: Originally coarse grasses mainly little bluestem.

Use:	Less sloping lands largely farmed to cotton, corn, sorghum, oats, peanuts and sudan grass; some used for vegetable crops and fruits. Only moderate fertility but very responsive to management; very susceptible to erosion under usual cultural practices.
Distribution:	Reddish Prairie sections of Oklahoma.

PS: Description by Roy Smith. He considered B_{2t} quite light textured and thin for Norge, suggested Teller.

OKEMAH SILT LOAM

Soil Description

S63-OK-18-1(5 horizons)

- A 0-15" Very dark grayish brown (10 YR 3/3) silt loam, grayish brown (10 YR 5/2) dry; weak medium granular structure; friable moist; pH 5.5 (Hellige); gradual boundary.
- B₁ 15-24" Dark grayish brown (10 YR 4/2) clay loam, brown (10 YR 5/3) dry; common fine distinct strong brown (7.5 YR 5/6) and light brownish gray (10 YR 6/2) mottles; strong medium and coarse granular structure; friable moist, hard when dry; pH 5.0; few small black concretions; clear boundary.
- B_{2t} 24-35" Dark gray (10 YR 4/1) clay, gray (10 YR 5/1) dry; many (greater than 20 percent of the soil mass) medium (from 5 to 15 mm. in size) prominent (matrix and mottles vary several units in hue, value and chroma) red (2.5 YR 4/6) and strong brown (7.5 YR 5/6) mottles; moderate medium subangular blocky structure; firm moist, very hard dry; pH 5.0; clear boundary.
- B₃₁ 35-45" Finely mottled strong brown, grayish brown and gray clay loam; weak medium and coarse subangular blocky structure; friable moist, hard when dry; pH 4.8; many black nodules and concretions; gradual boundary.
- B₃₂ 45-54" Color and structure similar to the above horizon; clay; firm moist; pH 4.5; many black concretions.

Location: Vinita, Oklahoma out-state test plot.

Great Soil Group: Prairie

- Parent Material:Olive and gray mildly alkaline to slightly calcareous
weakly consolidated shales and clays generally of
Pennsylvanian origin.Topography:Nearly level to gently sloping erosional uplands.
Surface weakly convex to planes.Drainage:Slow to moderate from the surface.Vegetation:Thick cover of tall grass mainly bluestems.Use:Mainly cultivated. Principal crops are corn, cotton
and small grains. Moderately fertile and productive.PS:The profile described here is not exactly the profile
- PS: The profile described here is not exactly the profile used in the experiments but they come from the same area and have many characteristics in common. Description by Roy M. Smith and Ben Cunningham.

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