PHOSPHORUS FRACTIONATION AND METABOLISM STUDIES IN A LATERITIC SOIL OF EAST PAKISTAN

by

SYED FAZLE ELAHI, B.Sc., M.Sc. (Dacca).

THESIS

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A B S T R A C T

Several aspects of phosphorus were studied in a lateritic silty clay loam (pH 5.3) from the Dacca district of East Pakistan.

A comparison was made of two published methods and a modified method of fractionating inorganic phosphorus (Al-, Fe- and Ca-bound phosphate) after addition of water-soluble phosphate in the original Dacca soil and after adjustment to higher pH.

Changes in inorganic P forms of soils of original and higher pH were determined during incubation after addition of water-soluble phosphate. The effects of addition of organic materials (straw, compost, sewage sludge and cellulose) immediately and sometime before incubation was started were also determined. Several chemical extractants for determining "available" P were compared on these soils and correlation coefficients between available P as determined by each extractant and the three forms of inorganic P were calculated.

The effects of varying static and changing moisture contents on available P were determined during incubation of original and treated soils.

The effects of temperature of incubation and of alternate wetting and drying on availability of native and added P were studied in Dacca soil alone and after pretreatment with straw, compost and water-soluble phosphate.

D E D I C A T E D

T O

M Y G R A N D M O T H E R

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INTRODUCTION

REVIEW OF LITERATURE

A. Source and nature of soil P.

B. Factors affecting transformation of phosphorus in soils.

CHAPTER I

INTRODUCTION

The soil used in this study is from the Dacca district of East Pakistan. The area involved is about 600 square miles and is sparsely populated and only small portions are cultivated. With increasing population and availability of irrigation water, it is likely that the area will soon come into intensive cultivation.

Very little work has been done on this acid lateritic soil. This thesis reports on studies made on (i) the mode of fixation of added inorganic phosphate during incubation of soil as affected by pH and organic materials, (ii) comparison of a number of chemical reagents for determining "available" phosphorus and (iii) effects of soil pH, moisture content and temperature on "available" phosphorus.

REVIEW OF LITERATURE

A. SOURCE AND NATURE OF SOIL P

The total amount of phosphorus in the earth is of the order of 10^{19} tons, of which 10^{15} tons are present in the crust which on average contains 0.12 percent phosphorus (Van Wazer, 1958). There are localized concentrated deposits of phosphorus compounds which amount to 10^{9} tons of phosphorus.

Phosphorus in the lithosphere always occurs in the quinque-

valent oxidation state, that is, corresponding to the anhydrite P_2O_5 (Landergren, 1962). Condensed phosphates occur in nature by thermal dehydration of acid phosphates, by polymerisation on the surface of phosphate minerals at low temperature (Miller & Parris, 1964), and by excretion and release during the decay of dead cells. However, in soils and natural water, condensed phosphate will be hydrolysed comparatively quickly to orthophosphate by microbial action (Sutton & Larsen, 1964; Clesceri & Lee, 1965) and natural minerals containing phosphates other than orthophosphate are virtually nonexistent.

Although the total phosphorus content of soil can be determined with reasonable precision, the determination of the nature of phosphorus compounds in soil is beset with many difficulties. It is, however, possible to divide the total phosphorus into two broad fractions, inorganically and organically bound phosphorus.

(a) INORGANICALLY BOUND PHOSPHORUS :- The nature of the inorganically bound phosphorus is a subject of great interest to students of soils. Determination of its nature cannot be done by direct methods, such as X-ray diffraction analysis and optical methods, without prior concentration; this generally brings about changes in phosphorus forms. The fractionation methods of inorganic phosphorus based on such methods are therefore arbitrary.

Inorganic phosphorus in soil is considered to be present in two forms : (i) soil solution and (ii) phosphorus minerals.

i) Phosphorus in soil solution :- The inorganic phosphorus in soil solution takes part in many equilibria; some of these are

within the liquid phase only (homogeneous equilibria) and others occur between the solid and the liquid phases (heterogeneous equilibria) (Larsen, 1967). The overall equilibrium,

$$P_{solid} \rightleftharpoons P_{liquid}$$

is heavily biased in favour of P_{solid}, and soil phosphorus can therefore be classified as "sparingly soluble".

The concentration of phosphorus in the soil solution is of the order of 0.1 to 1.0 ppm. It varies with the properties of both the solid and the liquid phases and also with the ratio between solid and solution. The forms in which phosphorus exists in solution are governed by the reactions of protonation and complex formation. These forms are phosphoric acid, H_3PO_4, the corresponding ions $H_2PO_4^-$, HPO_4^{2-}, PO_4^{3-}, and the soluble complexes of these ions.

The distribution of phosphorus between phosphoric acid and the phosphorus ion is determined primarily by pH. Phosphoric acid being a tribasic acid has three dissociation constants from which the proportion of the free acid and the phosphorus ion which exists at various pH levels can be calculated. Thus, Larsen (1967) showed that the ionic species $H_2PO_4^-$ and HPO_4^{2-} are the most abundant in the pH ranges encountered in soil and that the ionic strength encountered in nonsaline soil does not alter this distribution significantly.

Phosphorus forms soluble complexes with many metallic ions, and part at least of phosphorus in the soil solution may be complexed. No information concerning soluble phosphorus complexes in the true

soil solution is available, but based on the meagre experimental evidence (Taylor & Gruney, 1962; Larsen, 1965, 1966) and known solubility constants of phosphorus complexes (Sillen & Martell, 1964) it seems likely that a significant proportion of phosphorus in the soil solution may sometimes be present in this form. Further, it would be expected that this proportion would be high both in acid soils (due to the high stability of Fe-P and Al-P complexes) and in calcareous soils (due to the high proportion of HPO_4^{2-} ions). Complex formation will be lowest in slightly acid soils where $H_2PO_4^-$ ions predominate and where the concentration of iron and aluminium are low.

ii) Phosphorus minerals :- Nearly 200 phosphorus minerals have been found in nature. Of these only one group is of significance, namely the apatites. The apatite unit cell has the chemical composition $M_{10}(PO_4)_6X_2$ and most frequently the metal ion M is calcium and X is fluorine. Thus calcium fluorapatite $Ca_{10}(PO_4)_6F_2$ is the commonest phosphorus mineral (Larsen, 1967).

Fluorapatite is classified among the easily weathered minerals (Mitchel, 1964); therefore it very rarely occurs as a primary mineral in sediments. The secondary phosphorus minerals present also belong to the apatite group, but they generally exist in poorly crystalline forms with many substitutions in the lattice (Degens, 1964).

Chang and Jackson (1957b) classified inorganic soil phosphorus into different categories according to their solubility in different reagents. But as the reorientation of phosphorus during extraction is inevitable, the classification is thought to be arbitrary.

Of the available evidence concerning the nature of phosphorus in intact soil, the most relevent is that obtained from the application of solubility product principle. On this basis, the occurrence of phosphorus compounds of Ca, Al and Fe has been suggested (Larsen, 1967).

The preponderance of various phosphates in soil depends largely on the degree of weathering. Again, the degree of weathering is related to such soil factors as pH, activity of various cations (particularly of calcium, aluminium and iron), the solubility products of the various phosphates, and fertilizer and liming practices, pH especially being a controlling factor (Hsu & Jackson, 1960). As weathering proceeds and acidity develops in soil the phosphate becomes increasingly bound to aluminium and iron ions released from the silicate minerals (Ensminger, 1949; Haseman et al., 1950; Kittrick & Jackson, 1954, 1955; and Low & Black, 1947). Reactions of this type are complex ion exchange reactions in which PO_4^{3-} replaces $(OH)^-$ from hydroxy minerals or oxygen from oxide minerals from which trivalent ions are derived. The chemical properties of phosphate in this form resemble those of minerals, e.g., variscite $Al(OH)_2H_2PO_4$ or $AlPO_4.2H_2O$ (Cole & Jackson, 1951; and Lindsay et al., 1959), strengite $Fe(OH)_2H_2PO_4$ or $FePO_4.2H_2O$ (Chang & Jackson, 1957a) and isomorphous intermediate, barrandite $(Al,Fe)(OH)_2H_2PO_4$ or $(Al,Fe)PO_4.2H_2O$ (Cole & Jackson, 1957; and Wright & Peech, 1960). When K or NH_4 is high, as in fertilizer bands, these ions are incorporated as taranakite, $K_3Al_5H_6(PO_4)_8.18H_2O$, or its ammonium analogues (Wada, 1959) or other (K,NH_4) salts such as $(K,NH_4)(Al,Fe)_3H_8(PO_4)_6.6H_2O$ (Haseman et al., 1950; Lindsay & Stephanson, 1959). Wavellite,

$Al_6(F,OH)_6(PO_4)_4 \cdot 9H_2O$, has also been identified in soils (Dyal, 1953).

Under reducing conditions, vivianite, $Fe_3(PO_4)_2 \cdot 8H_2O$, forms in soil and, being fairly soluble, may be deposited in the lower levels of the soil profile. Reduction of ferric iron renders the oxides soluble and the phosphate becomes more available to plants, as to rice in paddy culture. The phosphate which had been associated with iron may leach out of highly reduced soils while the relative amount of aluminium phosphate form increases in acid gley soils (Chang & Jackson, 1958).

The solubility of phosphate from calcium, aluminium and iron compounds are close to each other in soil of pH 6–7. Below this pH range, the aluminium and iron phosphates are more stable than calcium phosphate; above this range, the various calcium phosphates are formed. The calcium phosphates formed are hydroxyapatite, $Ca_{10}(PO_4)_6(OH)_2$, dicalcium phosphate, $CaHPO_4$, and complex phosphates intermediate between these two, one of which is known as octocalcium phosphate (Lindsay & Moreno, 1960).

Lindsay and Moreno (1960) developed a solubility diagram for variscite, strengite, fluorapatite, hydroxyapatite, octocalcium phosphate and dicalcium phosphate dihydrite. The resulting solubility diagram indicates the important effect of pH on all the systems. Although the solubility diagram is supported in general by phosphorus solubility data in acid and alkaline soils, they suggested that kinetic considerations during equilibration in soils could more often than not preclude the obtaining of solubility data which would correspond to any known solubility product.

iii) Fractionation of inorganic soil phosphorus :- The earliest work on the fractionation of inorganic phosphate in soil appears to be that reported by Fisher and Thomas (1935). They claimed that extraction of soil with acetic acid-sodium acetate at pH 5.0 removed calcium, magnesium and manganese phosphates. Extraction of a separate soil sample with ~~dilute~~ sulphuric acid at pH 3.0 removed iron and aluminium phosphate in addition to the forms already mentioned.

R. Williams (1937) used NaOH solution as the extracting reagent and divided the soil phosphorus into alkali-soluble and alkali-insoluble fractions. Dean (1937, 1938) suggested that the alkali-soluble fraction contained mainly iron and aluminium phosphates and mono- and di-calcium phosphates as well organic forms of phosphorus. He extended the method by using dilute sulphuric acid extraction of the residue following alkali extraction and claimed that H_2SO_4 removed tri-calcium phosphate and apatite.

Ghani (1943a) modified Dean's method by extracting the soil with acetic acid prior to the NaOH and H_2SO_4 extractions. Ghani (1943b) modified the acetic acid extraction by addition of 8-hydroxy-quinoline to the reagent in order to block readsorption or precipitation of phosphate during the extraction. Ghani's modified method was examined by C.H. Williams (1950) who confirmed that 8-hydroxyquinoline effectively blocked readsorption of phosphate during acetic acid extraction. He also found that a single extraction with NaOH was usually as effective as multiple extractions used by Ghani.

C.H. Williams (1950) also studied the solubility of phosphates

of various rocks and minerals and synthetic phosphate compounds in acetic acid-8-hydroxyquinoline and sodium hydroxide and concluded that these two reagents extracted the following forms of phosphates :

(a) 2.5% v/v acetic acid + 1% w/v 8-hydroxyquinoline. Water-soluble phosphate; mono-, di- and tri-calcium phosphates; magnesium and manganese phosphates; hydroxy- and carbonate-apatite; and to some extent chloro- and fluoro-apatite.

(b) 0.1N NaOH. Adsorbed phosphate; basic iron and aluminium phosphates; titanium phosphate and organically bound phosphorus.

(c) The forms insoluble in either extract include chloro- and fluoro-apatite, crystal lattice phosphorus and resistant phosphate minerals such as turquois, monazite and amblygonite.

Rennie (1956) modified C.H. Williams' (1950) procedure to simplify the determination of phosphorus in the extracts .

Fractionation methods up to this time made no effort to separate aluminium-bound and iron-bound phosphorus. Turner and Rice (1952) found that neutral 0.5N NH_4F reacted with $Al(OH)_3$ gels to form $(NH_4)_3AlF_6$, and phosphate adsorbed by the gels were more or less completely released and brought into solution. $Fe(OH)_3$ gels, on the other hand, were apparently not attacked by the fluoride reagent and there was little release of adsorbed phosphate.

Chang and Jackson (1957b) used a different order of extraction of the inorganic phosphate forms after first removing water-soluble phosphate by N NH_4Cl. They first extracted aluminium phosphate with neutral 0.5N NH_4F, and next iron phosphate with 0.1N NaOH. They based their separation of aluminium and iron phosphates on the works of Turner and Rice (1952) mentioned above. Their next

extracting reagent was 0.5N H_2SO_4 which removed the various forms of calcium phosphate. They considered that these extraction procedures did not remove iron and aluminium phosphates occluded in iron oxide. They therefore treated the residue of the soil from the 0.5N H_2SO_4 extraction with sodium dithionite-citrate reagent, which reduces and dissolves the protective iron oxide coating and also reduces the ferric phosphate to ferrous phosphate, thus bringing the phosphate into solution. This treatment extracts negligible amount of original occluded aluminium phosphate which is then extracted with neutral 0.5N NH_4F.

Various modifications of Chang and Jackson's original procedure have been put forward (Peterson & Corey, 1966; Frink & Peech, 1962; Smith, 1965; J.D.H. Williams et al., 1967), but these involve minor changes, or the application of correction factors for obtaining more correct estimates of particular form of phosphate, or modified methods of analysis of the extracts for phosphate.

(b) ORGANICALLY BOUND PHOSPHORUS :- Plants, animals, microorganisms and their metabolic products are the sources of soil organic phosphorus. The organic phosphorus compounds present in the soil may be classified as phospholipids, nucleic acids, inositol phosphates,"metabolic" phosphates and phosphoproteins.

In contrast to nitrogen and sulphur the assimilated ions, nitrate and sulphate, of which are reduced within the cell, the plant does not reduce phosphate and this ion enters into organic combination largely unaltered (Alexander, 1961).

In studies of organic phosphorus compounds present in soil, most importance has been given to the phospholipids, nucleic acids

and inositol phosphates.

It has not been possible to isolate any of the organic phosphorus compounds present in soil as a whole; but indirect evidence for the presence of these compounds in soil has been put forward by various investigators.

Two types of evidence exist for the presence of phospholipids in soil. Firstly, cholin, a product of hydrolysis of the phospholipid, lecithin, has been isolated from soil by Aso (1905), Shorey (1913) and Hance and Anderson (1963). Secondly, organic phosphorus has been found in ether extracts of soil by a number of investigators. Solubility in ether and alcohol has been used as qualitative and quantitative test for phospholipids. Results obtained by various investigators including Drachev (1933), Vincent (1937) and Sokolov (1944, 1948) indicate that the amount of phospholipid-phosphorus in soil is small, rarely exceeding 3 ppm, although Stoklasa (1911) found levels of up to 34 ppm phospholipid-phosphorus.

Evidence for the presence of nucleic acid in soil has been shown by Auten (1923), Wrenshall and Dyer (1941) and Anderson (1958). Their evidence is based on the identification of the constituent parts of nucleic acids in the hydrolysis of soil extracts.

Quantitative data on the amount of nucleic acid phosphorus in soils are few because of the uncertainity connected with the nature of soil organic phosphorus. However, Sokolov (1948) estimated that 38 to 58% of the organic phosphorus was present as nucleic acid phosphorus.

The presence of inositol phosphate in soils is evident in several ways. A number of workers, including Smith and Clark (1951)

and Caldwell (1956), have obtained chemical and microbiological evidence for the presence of inositol in the hydrolysate of soils. Inositol is the completely dephosphorylated nucleus of inositol hexaphosphate. The calcium hydroxide precipitation test of Bower (1949) verified the presence of inositol hexaphosphate in soils.

Attempts to determine quantitatively the amount of inositol phosphates in soil were made by Vincent (1937), Bower (1945) and Jackman (1949). However, Smith and Clark (1951, 1952) showed that chemical fractionation used by the workers to separate soil inositol phosphates was inadequate for obtaining inositol phosphate uncontaminated by soil inorganic phosphorus. Caldwell (1956) found that an average of 16% of organic phosphorus was inositol phosphate. Anderson (1956), using chromatographic analysis, found that inositol phosphate accounted for 33% of the organic phosphates in the soils he studied.

Determination of total organic P in soil :- The total organic P in soil has been determined by two types of methods. The direct method involves extraction of organic phosphorus and its determination. The indirect method involves extraction of inorganic phosphate before and after oxidation of organic P into inorganic phosphate.

In the direct method Mehta et al. (1954) extracted the soil sample successively with conc. HCl and then 0.5N NaOH and combined the extracts. The combined extract was then diluted to a known volume and after vigorous shaking a suitable aliquot was taken, the organic P oxidized to phosphate with perchloric acid and the total phosphorus determined. The remainder of the combined extract was filtered to remove organic matter (including organic P) and

phosphate determined in an aliquot of the filtrate. The difference between the phosphate in the original extract and that in the oxidized aliquot is considered to be the organic P. The method was modified by Hance and Anderson (1962) who eliminated the HCl extraction and extracted the soil only with 0.3N NaOH, and continued the method as described by Mehta et al. (1954).

In the indirect method described by Saunders and Williams (1955) a sample of soil is ignited at 550°C to convert organic P to phosphate. This sample and a comparable unignited sample are shaken with 0.2N H_2SO_4 for 16½ hours to extract phosphate. The difference between the inorganic P in the ignited and the unignited samples is taken as organic P.

B. FACTORS AFFECTING TRANSFORMATION OF PHOSPHORUS IN SOILS

Phosphorus found in the soil, as discussed earlier, is always present in either the inorganic or the organic form. The immediate source of phosphorus utilized by crops growing in a soil is that of the inorganic phosphate ions in the soil solution. Plants cannot take up phosphorus from the soil organic matter. It is necessary for phosphorus to go into inorganic combination for uptake by plants.

Alexander (1961) produced a phosphate cycle where he depicted the various stages that phosphorus goes through in soil (Fig. 1, overleaf).

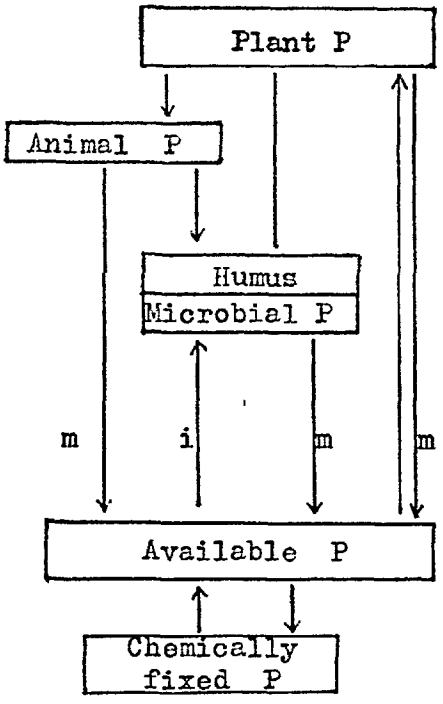


FIGURE 1

Mineralization (m) and immobilization (i) of phosphorus.

Transformation of soil phosphorus from organic to inorganic form and vice versa takes place through the biological activities in the soil. By their actions, the bacteria, fungi and actinomycetes make the phosphorus bound in crop residues and soil organic matter available to succeeding generation of plants.

More emphasis has been given to the mineralization of organic phosphorus than to its build-up by microorganisms. This tendency is probably because the assumption that there is a fairly definite pool of available phosphate in the soil fails for soils in which most of the potentially available phosphate is in the soil organic matter (Russel, 1961). But, it is evident that environmental and other factors affecting the multiplication of these organisms will have a definite effect on the interconversion of organic and inorganic phosphorus in soil.

MINERALIZATION OF ORGANIC PHOSPHORUS :- Many soils contain relatively large anount of phosphorus in the organic fraction. Phosphorus from these organic forms cannot be utilized unless it has been mineralized.

Many investigators believe that increased phosphorus availability to plants effected by addition of organic materials can be explained by the mineralization of organic phosphorus through bacterial decomposition. Schollenberger (1920), Garman (1948), Thompson and Black (1950), Thompson, Black and Zoellner (1954) and Caldwell (1956) have found that in comparable cultivated and virgin soils, the cultivated soil generally had lower organic phosphorus content.

However, the decomposition of the soil organic matter is accomplished by microorganisms which themselves use large amounts of phosphorus and compete directly with the plant roots for it (Drake, 1964). Mineralization of organic phosphorus by the decomposition of organic matter in itself does not appear to be a sizable source of phosphorus to plants. A more fundamental explanation of the role of soil organic matter in the uptake of phosphorus is that the organic anions produced by microorganisms complex the aluminium, calcium and iron and thereby solublize the relatively insoluble soil inorganic phosphorus (Drake, 1964)

As mineralization of organic phosphorus is biological, the factors that affect the biological population of the soil will also affect the mineralization of organic phosphorus. The major influencing factors are soil pH, moisture, temperature and the addition of organic materials.

Temperature :- There ~~are~~ is evidence that mineralization of soil organic phosphorus is favoured by increasing temperature. Thompson and Black (1947) showed that the release of mineral phosphate is markedly increased by raising temperature above 30°C. McCall et al. (1956) also obtained similar results. Acquaye (1963) found that during the laboratory incubation of some cocoa soils from Ghana, more organic phosphorus was mineralized at 50°C than at 27°C or 40°C.

Heating, drying or freezing the soil, known to increase the solubility of soil organic matter, may affect the mineralization of soil organic phosphorus. De Long et al. (1940) found that previous heating of the soil increased the amount of both organic and inorganic phosphorus extracted by Truog's dilute sulphuric acid-ammonium sulphate extractant. The finding of Yuen and Pollard (1951b) that the content of organic phosphorus in soil solution was highest in the spring and lowest in the autumn suggests an effect of winter freezing on the susceptibility of a part of the organic phosphorus to mineralization. Investigations by Birch (1958, 1959 & 1960) on the effect of drying or heating the soil on humus decomposition suggest the susceptibility of soil organic phosphorus to mineralization on drying. He found that the more intensely the soil was dried, the higher the temperature it was heated to and longer the soil was kept dry, the larger was the magnitude of the flush of decomposition when the soil was remoistened.

Moisture :- Nearly all studies done on native and added phosphorus in relation to soil moisture indicate that phosphorus transformation under various soil moisture regimes is mainly by

chemical and physico-chemical processes, soil microbial activity being of little importance in the short-term but probably of importance in the long-term.

Dunnewald (1935) and Trumble (1947) reported the fixation of phosphorus to increase with drying of the soils. Rydkii (1938), using red-earths and podzols, suggested that the degradation of soil colloidal surfaces during drying enabled the phosphate ions to penetrate the soil particles.

Contrary to these observations, Grava et al. (1961), Aderichin (1960) and Themlitz (1953) found increases in native available phosphorus or decrease in the fixation of added phosphorus on drying the soil or the hydrated iron oxides. Yuan et al. (1960) reported increase in the aluminium-fixed and decrease in the iron-fixed phosphorus with increase in soil drying temperature.

Reitemier (1946) observed increases in the solubility of several ions including phosphate with increase in soil moisture content.

Under water-logged conditions, phosphate has been reported to be greatly mobilized by Aoki (1941), Kereszteny (1953), Shapiro and Armiger (1958), Davide (1960) and Ekpete and Cornfield (1966).

Gasser and Bloomfield (1955) noticed no release of aluminium or phosphorus from aluminium phosphate, but reported release of iron and phosphorus from iron phosphate under anaerobic conditions. Egawa et al. (1951) and Popovic (1958) found that under anaerobic conditions, produced either by water-logging or by reducing the oxygen pressure, added phosphates were fixed and lactate soluble phosphate reduced, especially in soils originally high in phosphates.

Kawaguchi (1944) showed that water-logging increased the availability of phosphate to a greater extent than air-drying the soil. He showed a predominence of iron phosphate when the solubility of phosphate was high, under water-logged, than under dry field conditions.

Several workers have reported increases in available phosphate when soilswere subjected to a number of cycles of alternate wetting and drying (Tendille & Eynard, 1959; Eynard & Tendille, 1960; and Khanna, 1960). Tendille (1959), in another experiment, showed that the transformation of phosphate from exchangable to non-exchangable form was accelerated by alternate wetting and drying.

Yuan et al. (1960) reported that increasing the number of cycles of wetting and drying reduced the percentage of aluminium-fixed phosphate in two soils and increased that of iron-fixed phosphate in two others.

Soil pH :- Soil reaction controls the mineralization of soil organic phosphorus in two ways. Firstly, it controls the type and number of organisms in the soil and secondly, it exerts an influence on the stability of certain organic phosphorus compounds in the soil. The result of interaction between these two effects shows up in the generally observed fact that organic phosphorus mineralization increases with increasing pH up to neutrality (Ghani & Aleem, 1943; Kaila, 1948; and Thompson et al., 1954).

Highly acid and alkaline conditions tend to inhibit many common bacteria as the optimum for most species is near neutrality (Alexander, 1961). However, it is thought (Russel, 1961; Kotelev et al., 1960; and Jackman & Black, 1952) that acid soils carry a

larger fungal but a smaller bacterial flora than neutral soils. Since bacteria and fungi have different requirements for phosphorus (Kaila, 1948), it is reasonable to assume that they will vary in their ability to dephosphorylate organic phosphorus.

A number of investigators (Jackman & Black, 1952; Casida, 1959; and Halstead, 1964) observed that phosphatase and phytase activities are greater in acid soils than in neutral soils. Janossy (1963) found that enzymatic activity of fungi and actinomycetes were nearly five times greater than that of bacteria. But Kotelev et al. (1960) found that in soils and rhizospheres the phosphatase activity of bacteria and actinomycetes was greater than that of fungi.

The solubility of organic phosphorus has been attributed mainly to the formation of insoluble compounds with polyvalent ions (Neuberg & Roberts, 1949; Jackman & Black, 1951a & b; and Wittcoff, 1951) and the reaction of organic constituents with clay (Swenson et al., 1949; Scarseth, 1935; and Sieling, 1947). Metzger (1940) believed that active iron would be reduced in the presence of organic matter, thus making the phosphate more available. Swenson et al. (1949) observed that the relative effectiveness of the various organic anions changed with the variation in the pH values of the solutions. An increase of pH value from 3.6 to 6.3 increased the effectiveness of citrate and also decreased that of tartrate. Bower (1949) theorized that the relationship between the availability of the added inositol phosphate and the soil pH can be explained by the formation of insoluble iron and aluminium salts under strongly acid conditions and of rather more soluble

calcium and, possibly, magnesium salts under slightly acid or alkaline conditions, the influence being that such changes in solubility with pH should affect the rate of both direct absorption and microbial mineralization of the added inositol phosphate.

Added organic matter :- The addition of organic matter to soil helps in the release of phosphorus to plants in two ways : (a) by the release of native and added organic matter and (b) by forming complexes with phosphorus-fixing elements.

It is believed by Enwezor (1965) that the net result of an addition of organic materials to the soil depends to a certain extent on the phosphorus content of the added materials. Microorganisms require phosphorus for building up their bodies and during the breakdown of organic materials they make demands both on the native soil organic phosphorus and on the phosphorus contained in the added organic materials. A net increase in soil inorganic phosphorus (mineralization) will occur if the microbial demand is less than the organic phosphorus mineralized but a net decrease (immobilization) will occur in those circumstances where microbial demand exceeds the organic phosphorus mineralized. Thus mineralization will occur with such substances as nucleic acids and simple carbohydrate phosphates (which contain high percentages of organic phosphorus) as has been shown by the investigations of Dyer and Wrenshall (1941), Pearson et al. (1941), Pinck et al. (1941) and Saxena and Kasinathan (1956a & b). On the other extreme, immobilization will take place when high carbon/low organic phosphorus substances such as blood and carbohydrates are added (Taylor, 1946; Kaila, 1948; and Fuller & McGeorge, 1950)

The results of several investigators (Kurtz et al., 1946; Swenson et al., 1949; and Struther & Sieling, 1950) indicate that certain organic substances, principally the hydroxyorganic acids and other substances particularly effective in forming stable complex molecules with iron and aluminium, would effect the liberation of fixed phosphate. These organic substances are the very substances that are formed as a result of microorganic oxidation of carbohydrate materials in soils - tartaric acid, oxalic acid, citric acid, malic acid, malonic acid, galacturonic acid and many others (Waksman & Starkey, 1931; Waksman, 1938; and Shorey, 1939).

Organic matter plays another important role in the release of phosphorus. It was suggested by Harter (1969) that phosphates added to soil react immediately with soil organic matter. The most likely exchange involved a substitution of phosphate ions for hydroxyl ions in the organic matter. It was also assumed that, with time, the phosphorus is transformed into soluble iron and aluminium phosphate, as well being incorporated into the organic matter.

C H A P T E R II

METHODS AND MATERIALS

CHAPTER II

METHODS AND MATERIALS

METHODS

Analytical methods used in this investigation were as follows :

1. Mechanical and mineralogical analysis :- The mechanical and mineralogical analysis of the soil was done using the method of Andrew et al. (1960).

In the procedure, the organic matter was destroyed by treating the soil with sodium hypochlorite solution (pH 9.5). Sodium hydroxide was used as a dispersing agent prior to the mechanical analysis.

2. Determination of pH :- The pH value of the soil was determined after shaking (2 minutes) 10 g of soil with 20 ml of boiled distilled water.

3. Maximum water-holding capacity (mwhc) :- 10 g of soil was placed in a crucible with a porous bottom, which was then weighed. The crucible was placed in a dish containing sufficient water to bring the level up to the porous bottom. After the soil had been saturated by capillary action the crucible was removed, the outside was dried and the crucible weighed again. Thus the amount of water in the soil was determined and was expressed as percentage of the air-dry soil.

4. Determination of organic carbon :- Organic carbon content of the soil was determined by Walkley and Black's rapid

titration method (1947).

5. Determination of total nitrogen :- The total nitrogen content of the soil was determined by micro-Kjeldahl digestion employing concentrated sulphuric acid and anhydrous potassium sulphate with selenium oxychloride as catalyst. Ammonia from the digest was distilled into 2% boric acid, after addition of alkali, and determined by titration with standard sulphuric acid.

6. Determination of total phosphorus :- Two methods, the dry oxidation method of Saunders and Williams (1955) and the wet oxidation method of Volk and Jones (1938) were examined. The descriptions and the results of these methods are given in Chapter III.

7. Fractionation of phosphorus :- Methods for fractionation of phosphorus in soil were compared. The descriptions and the results are given in Chapter III.

8. Extractable ("available") phosphorus :- The following extraction reagents were used for determining "available" P.

(a) Truog's reagent (Truog, 1930) :- One gram of the soil was shaken with 200 ml of Truog's reagent (0.002N H_2SO_4 buffered by addition of 3 g of $(NH_4)_2SO_4$ per litre to produce a pH of 3) for 30 minutes and filtered through a dry filter paper.

(b) Morgan's reagent (Morgan, 1937):- 5 g soil was shaken with 10 ml of Morgan's reagent (0.5N acetic acid-0.75N sodium acetate) for two minutes and filtered immediately through a dry filter paper.

(c) 0.5M Sodium bicarbonate (pH 8.5) (Olsen et al., 1954) :- One gram of the soil was shaken with 20 ml of the reagent and 0.5 g of activated carbon for 30 minutes and then filtered through

a dry filter paper.

(d) 0.2N Sulphuric acid (Saunders and Williams, 1955) :- One gram of soil was shaken with 20 ml of 0.2N H_2SO_4 solution for two hours. After shaking, the suspension was filtered through a dry filter paper.

9. Determination of phosphorus in soil extracts :- Phosphorus in the extracts were determined by Fiske-Subbarow's method (1925) as modified by Yuen and Pollard (1951a).

When the ferric iron concentration of the aliquot taken for analysis was greater than 0.05 mg, a preliminary reduction of ferric to ferrous iron with sodium metabisulphite and dilute H_2SO_4 was made (Yuen & Pollard, 1951a).

In those extracts whose pH values were appreciably different from 3, pH was adjusted to 3 by adding 2N H_2SO_4 or 2N NaOH as necessary, using 2,4-dinitrophenol as an internal indicator.

10. Method used for incubation of soils :- In incubation experiments, 10 g of air-dry soil (alone or mixed in bulk with finely ground organic materials where indicated) was placed in 4"x1" inch diameter flat bottom tube and water added to give the desired moisture content, i.e. a particular %mwhc. The BaO_2 method (Cornfield, 1961) was used for aeration and absorption of CO_2 during incubation of the stoppered tube.

Sufficient tubes of each treatment were prepared to allow for analysis in duplicate initially and after each incubation period.

In some experiments 1 or 5 g portions of soil were used for incubation.

11. Method used for increasing soil pH :- In order to give a rough indication of the "lime requirement" of the Dacca soil (to be used in the experiments where soils of different pH were to be studied), 10 g portions of soil were shaken for 48 hours with 20 ml of water and graded levels of $CaCO_3$ (0.1 to 1.0 g) and the pH then determined. Based on these results, 500 g portions of 2 mm sieved soil were mixed with 0.2% and 0.5% finely ground $CaCO_3$. The two treated soils and a control soil were placed in amber glass pots and water added to bring the moisture content to 50% mwhc. The pots were held at room temperature (18-22°C) for 8 months with water being added when necessary to maintain soil moisture content between 40-50% mwhc. The soils were then air-dried and were found to have pH values of 5.3, 6.5 and 7.7 for the control, 0.2% $CaCO_3$-treated and 0.5% $CaCO_3$-treated soils respectively.

MATERIALS

The soil used was obtained from the Dacca district of East Pakistan. The soil has not been classified but is a red laterite. The land is sparsely forested with a thin grass cover which dries in the summer. The soil was sampled to 6 inches over an area of about an acre. The samples were mixed air-dried and ground to pass a 2 mm sieve before dispatch (in a polythene bag) to the United Kingdom.

Mechanical and mineralogical analysis of the soil :- Mechanical analysis of the soil showed that it contained 0.5% coarse sand (>200 μ), 6.8% fine sand (50-200 μ), 57.0% silt (2-50 μ) and

31.2% clay (<2 μ).

The main components of the clay fraction are mica, kaolinite and expanding lattice silicate minerals (mainly vermicullite). The clay also contains a little quartz, goethite and a trace of chlorite. It is very probable that the soil contains appreciable amount of allophanic materials.

Chemical analysis of the soil and organic materials :-
The soil contained 1.00% total organic carbon, 0.140% total nitrogen and 0.0175% total phosphorus.

The "total" content of mineral elements was determined by boiling (1 hour) the soil with 6N HCl and analysing the extract by atomic absorption spectroscopy. The results obtained on the air-dry soil basis were 133 ppm potassium, 250 ppm calcium, 120 ppm magnesium, 172 ppm manganese, 11 ppm copper, 30 ppm zinc and 2.05% iron.

The organic materials used during incubation studies contained the following levels of total phosphorus on dry basis :- oat straw 1,000 ppm, green grass 1,560 ppm, compost 2,180 ppm and sewage sludge 8,100 ppm.

C H A P T E R III

ANALYTICAL METHODS STUDIED

CHAPTER III

ANALYTICAL METHODS STUDIED

Three methods for determination of total phosphorus and three methods for fractionation of inorganic phosphorus in soils were studied and their results compared.

1. Determination of total phosphorus in soil :- Three methods were compared on soil alone and soils treated with 2% w/w of finely ground compost and straw. All analyses were in duplicate.

(a) Dry oxidation method of Saunders and Williams (1955) :- One gram sample of soil was weighed into a porcelain crucible and ignited in a furnace at 550°C for 1 hour. After cooling, the residue was transformed to a 100-ml graduated flask with the aid of 50 ml of 0.2N H_2SO_4. The flask was shaken for 16½ hours. The contents were diluted to 100 ml and filtered through a dry filter paper and a small aliquot analysed for phosphorus.

(b) H_2SO_4-HNO_3 digestion method of McClean (1936) as adapted by Rennie (1956) :- The H_2SO_4-HNO_3 digestion method of McClean was modified by Rennie (1956) for use in micro-Kjeldahl digestion flasks.

One gram of soil was treated in a micro-Kjeldahl digestion flask with 4 ml of conc. H_2SO_4, followed by 3 ml of conc. HNO_3 with gentle heating at first, and then more strongly for 5 minutes after the appearance of white fumes. After cooling, a further 3 ml of conc. HNO_3 was added and heating continued to the fuming stage as before. This was repeated once more and heating with

fuming continued for 15 minutes, when the digest was faintly greenish-yellow. After cooling, about 20 ml of water was added and the whole gently warmed for 5 minutes (to convert any pyrophosphate to orthophosphate). The contents of the flask were then quantitatively transferred to a 100-ml graduated flask, diluted to the mark and a suitable aliquot used for analysis of phosphorus.

(c) HNO_3-$HClO_4$ digestion method of Volk and Jones (1938) :- The nitric-perchloric acid digestion method of Volk and Jones (1938) was adapted for micro-Kjeldahl digestion.

One gram sample of air-dried soil was weighed into a micro-Kjeldahl digestion flask and digested with 5 ml of conc. HNO_3 for 10 minutes. After cooling, 10 ml of 60% perchloric acid was added and the digestion continued until the solution was colourless and white fumes of perchloric acid filled the flask. After cooling, the digest was quantitatively transferred with the aid of water to a 100-ml graduated flask, diluted to the mark and a suitable aliquot used for analysis of phosphorus.

The results (in duplicate) are shown in Table 1 for each method.

TABLE 1

Sample	Dry oxidation method.	H_2SO_4-HNO_3 digestion.	HNO_3-$HClO_4$ digestion.
Dacca soil alone	153 151	157 170	175 175
Dacca soil + 2% compost	167 163	205 222	220 225
Dacca soil + 2% straw	159 158	204 180	195 198

It is seen that the dry oxidation method gave consistently lower results for total P than did the two wet oxidation methods. The H_2SO_4-HNO_3 method gave poor reproducibility and the average results were lower than those obtained by the HNO_3-$HClO_4$ method.

It was, therefore, decided to use the HNO_3-$HClO_4$ method in this study for the determination of total P in the soil alone or in soils treated with organic materials.

2. Fractionation of inorganic phosphorus in soil :- Three methods were compared. All analyses were in duplicate.

(a) Fractionation method of Chang and Jackson (1957b) :-

Separation of inorganic phosphate forms :- One gram of soil was treated with 50 ml of N NH_4Cl in centrifuge tube and was shaken for 30 minutes in a shaker to extract the water-soluble phosphorus. Then it was centrifuged and the supernatant liquid was discarded. Then 50 ml of 0.5N NH_4F (pH 7) was added to the soil and shaken for 1 hour. The suspension was centrifuged and the supernatant liquid was kept for determination of aluminium-bound phosphate (Al-P). The soil sample was washed twice, with centrifuging, with 25 ml portions of saturated NaCl solution. It was then shaken with 50 ml of 0.1N NaOH for 17 hours. After centrifuging until clear, the supernatant liquid was decanted into a tube for determination of iron-bound phosphate (Fe-P). The soil was then washed twice, with centrifuging, with 25 ml portions of saturated NaCl solution. It was then shaken with 50 ml of 0.5N H_2SO_4 for 1 hour. The suspension was centrifuged and the supernatant liquid was used for the determination of calcium-bound phosphate (Ca-P).

Determination of phosphorus in the fractions :- A suitable aliquot of the extract containing Al-P was placed in a 50-ml graduated flask and 15 ml of 0.8M boric acid was added before the determination of phosphorus.

For the determination of Fe-P in the NaOH extract, the solution was treated dropwise with conc. H_2SO_4 until the organic colloids flocculated. After dilution to a known volume, the suspension was centrifuged and the supernatant liquid used for the determination of phosphorus.

For the determination of Ca-P in the H_2SO_4 extract, a suitable aliquot was placed in a 50-ml graduated flask before determining phosphorus.

(b) Partial fractionation method of Williams (1950) as modified by Rennie (1956) (Rennie's method) :-

Separation of inorganic fractions :- One gram of soil in a centrifuge tube was shaken with 50 ml of 8-hydroxyquinoline-acetic acid reagent (1 g of A.R. grade 8-hydroxyquinoline dissolved in 100 ml of aqueous 2.5% v/v A.R. grade acetic acid) for 16 hours. The suspension was centrifuged and the clear supernatant liquid was used for determination of Ca-P. The soil was drained of liquid and 50 ml of 0.1N NaOH reagent was added. After shaking for 16 hours and centrifuging, the clear liquid was used for determination of Al- plus Fe-P.

Determination of phosphorus in the fractions :- For the determination of Ca-P in the 8-hydroxyquinoline-acetic acid extract an aliquot was evaporated to 1-2 ml in a 50-ml beaker. After cooling, the organic matter was destroyed by heating with 1 ml

of conc. H_2SO_4 and 1 ml of conc. HNO_3. The solution was transferred to a 50-ml graduated flask for determination of phosphorus.

For determination of Al- plus Fe-P in the NaOH extract, the solution was neutralised with conc. HCl till organic matter flocculated. After dilution to a known volume, the suspension was centrifuged and a suitable aliquot of the supernatant liquid was used for the determination of phosphorus.

(c) Modification of Rennie's method (1956) for complete fractionation (Modified method) :- Since Williams' method (1950) and Rennie's (1956) modification of it do not distinguish between Al-P and Fe-P, a modification of these methods is described below which distingishes between Al-P and Fe-P. In addition, since neither of the original methods allows for removal or determination of water-soluble phosphorus, the removal of this with NH_4Cl treatment as described by Chang and Jackson (1957b) was included.

Separation of the inorganic fractions :- One gram of soil sample was shaken with 50 ml of N NH_4Cl in a centrifuge tube for 30 minutes to extract the water-soluble P. After centrifuging, the liquid was discarded and the residue was shaken with 50 ml of 8-hydroxyquinoline-acetic acid reagent (1 g of A.R. grade 8-hydrxyquinoline dissolved in 100 ml of aqueous 2.5% v/v A.R. grade acetic acid) for 16 hours. The suspension was centrifuged and the supernatant liquid was kept for determination of Ca-P. The residue was shaken with one portion of 25 ml of saturated NaCl solution followed by centrifuging and the liquid rejected. 50 ml of 0.5N NH_4F (pH 7) was then added and the tube shaken for 1 hour. After centrifuging, the supernatant liquid was kept for analysis of Al-P.

The residue was again washed, with centrifuging, with one 25 ml portion of saturated NaCl solution. Then 50 ml of 0.5N H_2SO_4 was added to the soil and the tube shaken for 1 hour. The suspension was centrifuged and the clear liquid was used for analysis of Fe-P.

Determination of phosphorus in the fractions :- For the determination of Ca-P in the 8-hydroxyquinoline-acetic acid extract, a suitable aliquot was evaporated to 1-2 ml in a 50-ml beaker. The organic matter present was destroyed by heating it with 1 ml of conc. H_2SO_4 and 1 ml of conc. HNO_3. After cooling, the liquid was transferred to a 50-ml graduated flask for the determination of phosphorus.

For the determination of Al-P in the NH_4F extract, an aliquot was placed in a 50-ml graduated flask and 15 ml of 0.8M boric acid was added before the determination of phosphorus.

For the determination of Fe-P in the H_2SO_4 extract, a suitable aliquot was placed in a 50-ml graduated flask and was adjusted to pH 3 with 2N NaOH before the determination of phosphorus.

The three fractionation methods used are summarised in Fig. 2.

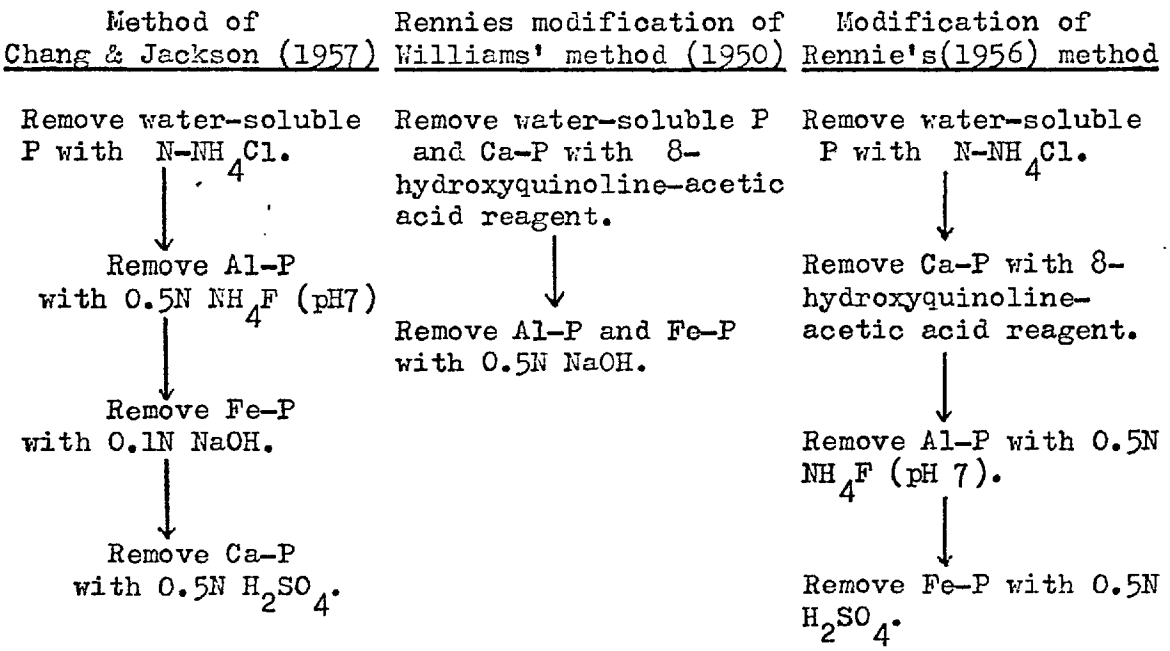
Comparison of the three fractionation methods using Dacca soil (pH 5.3 and 6.5) after treatment with inorganic phosphate.

The three fractionation methods were tested using the original soil (pH 5.3) and the original soil which had been treated with 0.2% $CaCO_3$, as described in Chapter II, to raise the pH to 6.5.

Ten gram portions of soil of each pH were shaken in centrifuge tubes for 48 hours with 20 ml of water containing sufficient phosphate to supply 1,000 ppm P on the soil basis. The phosphate was supplied as a mixture of KH_2PO_4 and K_2HPO_4 so that the pH

Figure 2

Summary of fractionation methods studied.



of the phosphate solution was same as the pH of the soils (5.3 and 6.5 for the untreated and $CaCO_3$-treated soils respectively). The tubes were centrifuged and the liquid poured off. The soils were then washed thrice with 25 ml portions of water with shaking followed by centrifuging. The residues were then allowed to air-dry and ground to pass a 1 mm sieve. One gram samples in duplicate were then subjected to phosphorus fractionation by the three methods previously described.

Results :- Results for soils of pH 5.3 and 6.5 are shown in Table 2. Total inorganic P values for each method were obtained by summing the Al-, Fe- and Ca-P values.

In the soil of pH 5.3, total inorganic P by Rennie's method was somewhat higher than those by other two methods; Chang-Jackson method gave slightly, though significantly, higher value than did the modified method for total inorganic P. Although the actual amounts of Ca-P and (Al+Fe)-P were somewhat lower by the modified method than by Rennie's method, the proportion of these two fractions was virtually the same for both methods. 49 to 50% of the total inorganic P was present as Ca-P. However, the Chang-Jackson method gave a very much lower proportion of Ca-P and a correspondingly higher proportion of (Al+Fe)-P than did the other two methods. Only 3% of the total inorganic P was present as Ca-P.

In the soil of pH 6.5, the total inorganic P was somewhat higher than in the soil of pH 5.3 with Chang-Jackson and Rennie's methods. The proportion of Ca-P and (Al+Fe)-P among the three methods in the soil of pH 6.5 were similar to those obtained with the soil of pH 5.3; the main difference was that Rennie's method

TABLE 2

Fractionation of phosphorus by three methods in original soil (pH 5.3) and soil treated with 0.2% $CaCO_3$ (pH 6.5), after treatment with 1,000 ppm P as potassium dihydrogen phosphate.

(All results are in ppm P on soil basis)

A. Chang and Jackson's method (1957) (Chang-Jackson method) :-

pH -	5.3				6.5			
	Al-P	Fe-P	Ca-P	Total inorganic P	Al-P	Fe-P	Ca-P	Total inorganic P
ppm P	441	275	20	736	450	319	30	779
% of total inorganic P	60	37	3		56	40	4	

B. Williams' method as modified by Rennie (1956) (Rennie's method):-

ppm P	440*	432	872	560*	375	935
% of total inorganic P	51	49		60	40	

* (Al+Fe)-P

C. Modification of Williams-Rennie method (Modified method) :-

ppm P	216	135	345	696	210	140	347	697
% of total inorganic P	31	19	50		30	20	50	

L.S.D. at Prob. < 0.05 for Al-, Fe- and Ca-P = 14 ppm.

L.S.D. at Prob. < 0.05 for total P = 35 ppm.

showed a somewhat lower proportion of Ca-P (40%) in the soil of pH 6.5 than in the soil of pH 5.3 (49% of the total inorganic P).

The ratio of Al-P to Fe-P can be seen only in Chang-Jackson and modified methods. Although the actual amounts of Al-P and Fe-P were considerably higher in the Chang-Jackson method than in the modified method, the Al-P/Fe-P ratio for both methods in both soils were of the same order, ranging from 1.41 to 1.60, with the pH 6.5 soil having a lower ratio than the pH 5.3 soil.

Only the Chang-Jackson method was used for further fractionation to determine the reductant soluble Fe-P and occluded Al-P and Fe-P. Negligible amounts (less than 1 ppm P) of these forms were found.

Discussion :- The chief point of difference obtained in this study was the very low proportion of Ca-P (and a correspondingly higher proportion of (Al+Fe)-P) as determined by the Chang-Jackson method when compared with Rennie's method and the modified method. It appears that in the Chang-Jackson method most of the Ca-P has been removed by 0.5N NH_4F and 0.1N NaOH extractants used to remove Al-P and Fe-P respectively. A comparison of the Chang-Jackson method (where Al-P and Fe-P were removed before the extraction of Ca-P) with the modified method (where Al-P and Fe-P were removed after the extraction of Ca-P) indicates that in the Chang-Jackson method Ca-P was removed during both 0.5N NH_4F and 0.1N NaOH extractions (to the extent of 26-29% and 18-20% respectively of the total inorganic P).

Williams (1950) found that Ca-P accounted for 47% of the total inorganic P in a soil of pH 4.5 which had been allowed to

react with 160 ppm phosphate-P before fractionation by his method. This proportion of Ca-P is of the same order as found with the original acid soil in this experiment. Appelt and Schalscha (1970), using the Chang-Jackson fractionation method, found that Ca-P accounted for 3% of the total inorganic P in a soil of pH 5.2 which had been allowed to react with 270 ppm phosphate-P. Thus, a comparison of the results in the original acid Dacca soil with other acid soils indicates that there was a fair agreement in the proportion of Ca-P present provided the same method of fractionation was used. It appears that no other worker has compared the Chang-Jackson method with Williams' method (1950) or Rennie's (1956) modification of Williams' method.

In the Dacca soil of pH 5.3, it was found that the amount of "Ca-P" found by Rennie's method and the modified method could not be fully accounted for by the calcium content of the soil, i.e., there was not sufficient Ca in the soil to precipitate the amount of Ca-P found (assuming that the phosphate was precipitated as $CaHPO_4$). However, if phosphate was precipitated as magnesium- and manganese-phosphate in addition to $CaHPO_4$, then the amounts of calcium, magnesium and manganese in the soil would be sufficient to account for the amount of "Ca-P" found. Williams (1950) states that magnesium and manganese phosphates, in addition to the calcium phosphate, are extracted from the soil by the 8-hydroxy-quinoline-acetic acid reagent.

It was necessary to choose a method for fractionation of phosphorus in Dacca soil to be used further in the present study. Since Ca-P (including Mg-P and Mn-P) is considered to be

the available form of phosphorus to plants, it seemed logical that the fractionation method (Rennie's (1956) modification of Williams' method) which removed Ca-P before removing Al- and Fe-P would be better than the Chang-Jackson method. In addition, Rennie's method was modified only to the extent of extracting and determining Al-P and Fe-P separately (Modified method).

CHAPTER IV

FRACTIONATION OF SOIL PHOSPHORUS DURING INCUBATION OF SOILS WITH ADDED ORGANIC MATERIALS.

Experiment 1 :

Changes in Al-, Fe-, Ca- and organic-P during incubation of Dacca soil of different pH levels treated initially with monocalcium phosphate (200 ppm P) and the effects of addition of 1% straw, sewage sludge and cellulose.

Experiment 2 :

Changes in Al-, Fe-, Ca- and organic-P during incubation, after addition of 400 ppm P as monocalcium phosphate, of Dacca soil previously held moist for 8 months after treatment with 2% straw and compost (plus 100 ppm urea-N).

CHAPTER IV

EXPERIMENT 1

CHANGES IN Al-, Fe-, Ca- AND ORGANIC-P DURING INCUBATION OF DACCA SOIL OF DIFFERENT pH LEVELS TREATED INITIALLY WITH MONOCALCIUM PHOSPHATE (200 ppm P) AND THE EFFECTS OF ADDITION OF 1% STRAW, SEWAGE SLUDGE AND CELLULOSE.

The purpose of this experiment was to determine the changes occurring in levels of Al-, Fe-, Ca- and organic-P during 20 weeks of aerobic incubation of Dacca soil (at its original pH of 5.3 as well as after adjustment to pH values of 6.5 and 7.7) treated with monocalcium phosphate, $Ca(H_2PO_4)_2.H_2O$, at 200 ppm P just before incubation. In addition, the effects of adding 1% levels of straw, sewage sludge and cellulose were determined.

METHODS

The original Dacca soil (pH 5.3) and soils which had been previously treated with $CaCO_3$ to increase pH to 6.5 and 7.7 (as described in Chapter II) were used. Bulk samples of the air-dry 2 mm sieved soils of each pH were mixed with finely ground $Ca(H_2PO_4)_2.H_2O$ to supply 200 ppm P and NH_4NO_3 to supply 100 ppm N on the dry soil basis. Each soil was divided into 4 portions. One portion (control soil) recieved no further treatment. Each of the other three portions were mixed with 1% w/w finely ground straw, sewage sludge and cellulose. Sufficient 10 g replicates of each treatment, including the control, were set up to allow for analysis

in duplicate initially (zero incubation) and after 6, 12 and 20 weeks of incubation at 30°C and 50% mwhc. The "zero incubation" samples were actually analysed 24 hours after addition of water to bring the soil to 50% mwhc. This was to allow time for the added water-soluble phosphate to react chemically with the soils. For analysis the soils were allowed to airdry for three days at room temperature, each 10 g sample was then finely ground and 1 g portion of each of these was used for fractionation.

RESULTS

CHANGES IN Al-, Fe- AND Ca-P DURING INCUBATION

Results are shown in Table 3 and Figure 3 for Al-, Fe- and Ca-P levels (in ppm P on dry soil basis) initially and after each incubation period. L.S.D. values are shown at probability (Prob.) <0.05.

A stated change in any form of P implies that the change is significant (at Prob. <0.05).

Soils without added organic materials (control soil).

At pH 5.3 Al-P increased with incubation time up to 20 weeks. Fe-P increased to 6 weeks, decreased to 12 weeks and increased again to 20 weeks, but the extent of change was small. Ca-P decreased considerably from 0 to 6 weeks of incubation and then increased up to 20 weeks, but the level after 20 weeks was considerably lower than the initial level.

At pH 6.5 Al-P showed only slight changes due to incubation. Fe-P increased to 6 weeks, but showed no further change to 20 weeks. Ca-P decreased to 6 weeks, but showed little further change

TABLE 3

Effect of addition of 1% straw, sewage sludge and cellulose on levels of Al-, Fe- and Ca-P during incubation of soils of pH 5.3, 6.5 and 7.7 treated with 200 ppm P as $Ca(H_2PO_4)_2.H_2O$. (All soils, including control, recieved 100 ppm N as NH_4NO_3)

(Results in ppm P on dry soil basis)

pH 5.3

Weeks of incubation – Soil Treatment	Al-P				Fe-P				Ca-P			
	0	6	12	20	0	6	12	20	0	6	12	20
Nil	55	63	70	81	54	71	59	76	124	28	48	64
Straw	54	58	77	81	51	72	62	83	112	24	58	63
Sewage sludge	67	102	113	119	57	94	77	97	181	84	126	123
Cellulose	53	61	68	78	52	75	58	71	98	32	56	52

pH 6.5

Weeks of incubation – Soil Treatment	Al-P				Fe-P				Ca-P			
	0	6	12	20	0	6	12	20	0	6	12	20
Nil	65	75	76	73	51	78	68	70	100	48	61	58
Straw	55	80	67	65	47	87	62	67	77	47	54	46
Sewage sludge	71	90	95	100	56	94	77	87	126	98	110	121
Cellulose	65	62	59	65	51	74	67	74	95	16	44	42

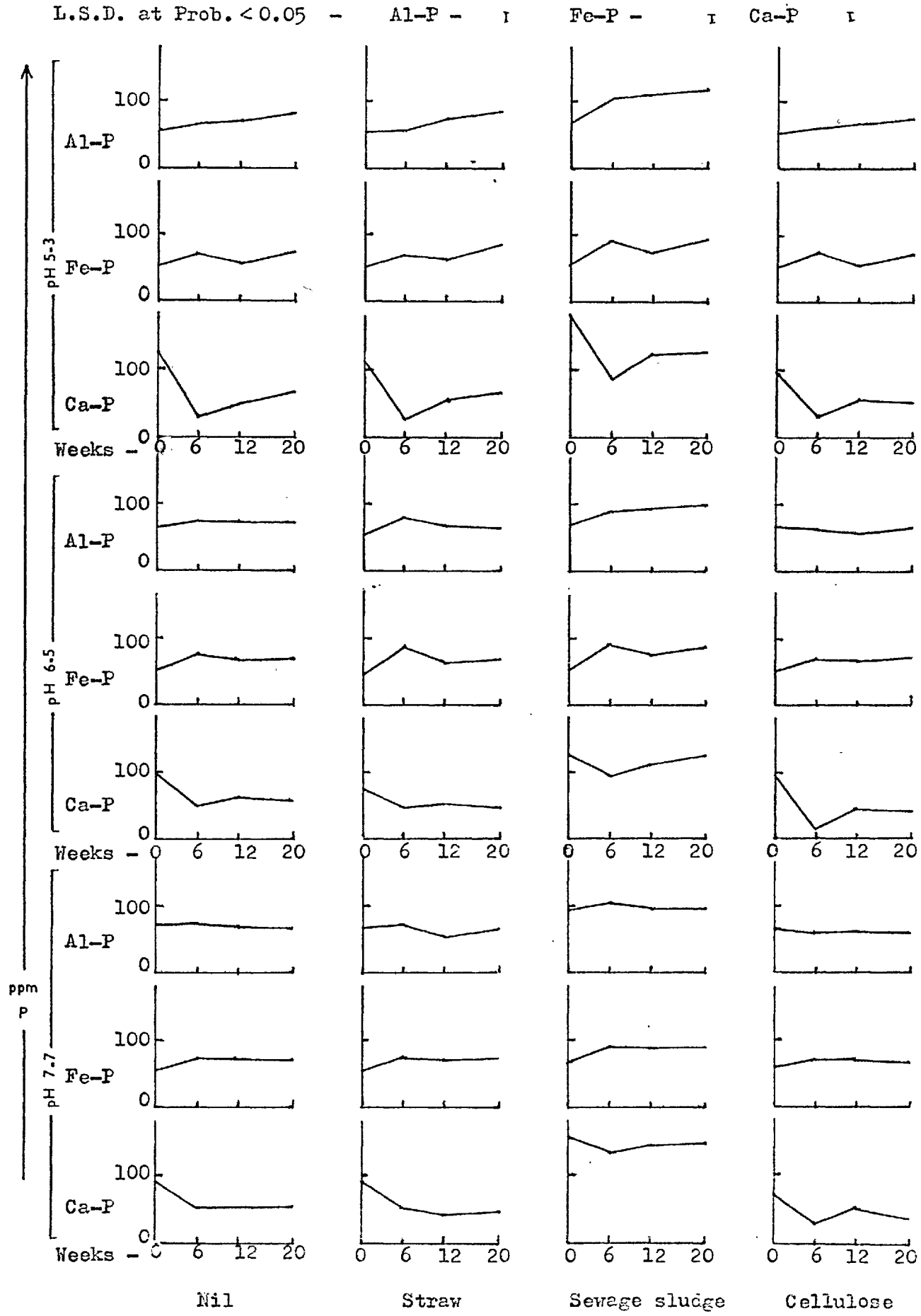
pH 7.7

Weeks of incubation – Soil Treatment	Al-P				Fe-P				Ca-P			
	0	6	12	20	0	6	12	20	0	6	12	20
Nil	71	74	72	68	56	75	73	70	91	54	57	57
Straw	68	72	55	63	57	78	72	74	93	53	43	49
Sewage sludge	93	103	98	98	67	90	88	88	155	132	141	145
Cellulose	66	60	63	60	58	70	72	68	74	37	57	40

L.S.D. at Prob. <0.05 Al-P = 8.8, Fe-P = 7.7 and Ca-P = 10.9

FIGURE 3

Effects of addition of 1% straw, sewage sludge and cellulose on levels of Al-, Fe- and Ca-P during incubation of Dacca soil of pH 5.3, 6.5 and 7.7 treated with 200 ppm P as $Ca(H_2PO_4)_2.H_2O$. (Results in ppm P on soil basis)



to 20 weeks.

At pH 7.7 Al-P showed no change with incubation. Fe-P increased whilst Ca-P decreased to 6 weeks, but there was little further change in either form to 20 weeks.

Soils treated with straw.

At pH 5.3 Al-P increased up to 20 weeks, but the main increase occurred during the 6-12 week period. Fe-P increased to a fair extent by 20 weeks, even though there was a decrease during the 6-12 week period. Ca-P decreased considerably to 6 weeks and increased to a moderate extent to 12 weeks, but showed no further change to 20 weeks.

At pH 6.5 Al-P and Fe-P increased to 6 weeks, but decreased somewhat to 12-20 weeks. Ca-P decreased to 6 weeks, but showed no further change to 20 weeks.

At pH 7.7 Al-P showed no change to 6 weeks but decreased slightly to 12-20 weeks. Fe-P increased whilst Ca-P decreased to 6 weeks, but neither form showed any further change to 12-20 weeks.

Soils treated with sewage sludge

At pH 5.3 Al-P increased considerably to 6 weeks and increased further to a small extent to 20 weeks. Fe-P increased to 6 weeks, decreased to 12 weeks and increased again to 20 weeks. Ca-P decreased considerably to 6 weeks, increased to a moderate extent to 12 weeks and did not change to 20 weeks.

At pH 6.5 Al-P increased with incubation time up to 20 weeks. Fe-P increased to 6 weeks, decreased to 12 weeks and increased to 20 weeks. Ca-P decreased to 6 weeks but increased to its initial level by 20 weeks.

At pH 7.7 Al-P and Fe-P increased slightly to 6 weeks, but showed no further change to 20 weeks. Ca-P decreased to 6 weeks, but increased slightly by 20 weeks.

Soils treated with cellulose.

At pH 5.3 Al-P increased slightly over 20 weeks. Fe-P increased to 6 weeks, decreased to 12 weeks and increased again to 20 weeks. Ca-P decreased to 6 weeks, increased somewhat to 12 weeks, but did not change to 20 weeks.

At pH 6.5 Al-P showed no change with incubation. Fe-P increased to 6 weeks, but showed no further change to 20 weeks. Ca-P decreased considerably to 6 weeks and increased again somewhat to 12-20 weeks.

At pH 7.7 Al-P showed no change with incubation. Fe-P increased to 6 weeks, but showed no further change to 20 weeks. Ca-P decreased to 6 weeks, increased to 12 weeks and decreased again to 20 weeks.

CHANGES IN Al-, Fe- AND Ca-P DURING INCUBATION EXPRESSED AS PERCENTAGE OF TOTAL INORGANIC PHOSPHORUS ((Al+Fe+Ca)-P).

Results are shown in Table 4.

The three forms of P expressed as percentage of total inorganic P will be referred to as Al-P%, Fe-P% and Ca-P%.

Soils of pH 5.3.

It is seen that Al-P% increased to 6 weeks to about the same extent in the control and the treated soils and there was little further change in any of the soils up to 20 weeks.

Initially Fe-P% was decreased slightly by sewage sludge but

TABLE 4

Results in Table 3 expressed as percentage of total inorganic phosphorus ((Al + Fe + Ca)-P).

pH 5.3												
Weeks of incubation - Soil Treatment	Al-P				Fe-P				Ca-P			
	0	6	12	20	0	6	12	20	0	6	12	20
Nil	24	39	39	37	23	44	34	34	53	17	27	29
Straw	25	38	39	36	23	46	32	36	52	16	29	28
Sewage sludge	22	36	36	35	19	34	24	28	59	30	40	37
Cellulose	26	36	37	39	26	45	32	35	48	19	31	26
pH 6.5												
Weeks of incubation - Soil Treatment	Al-P				Fe-P				Ca-P			
	0	6	12	20	0	6	12	20	0	6	12	20
Nil	30	37	37	36	24	39	33	35	46	24	30	29
Straw	31	37	37	36	26	41	34	38	43	22	29	26
Sewage sludge	28	32	34	32	22	33	27	29	50	35	39	39
Cellulose	31	41	35	36	24	48	39	41	45	11	26	23
pH 7.7												
Weeks of incubation - Soil Treatment	Al-P				Fe-P				Ca-P			
	0	6	12	20	0	6	12	20	0	6	12	20
Nil	33	36	36	35	25	37	36	36	42	27	28	29
Straw	31	35	29	34	26	39	48	40	43	26	23	26
Sewage sludge	29	32	30	30	22	27	26	26	49	41	44	44
Cellulose	34	36	33	36	29	42	37	40	37	22	30	24

was little affected by straw and cellulose. Fe-P% increased in all soils including the control up to 6 weeks, decreased somewhat to 12 weeks but showed only small changes to 20 weeks.

Ca-P% initially was decreased by cellulose, increased by sewage sludge and unaffected by straw. There were considerable decreases in Ca-P% in all soils up to 6 weeks followed by moderate increases up to 12 weeks and with little further change up to 20 weeks.

Soils of pH 6.5.

Initially all soils were similar in Al-P% followed by small increases up to 6 weeks and with little further changes up to 20 weeks.

Initially Fe-P% values were similar for all soils. With up to 6 weeks incubation the control, straw and cellulose treatments increased Fe-P% to a fair extent compared with the sewage sludge treatment. There were moderate decreases up to 12 weeks in all soils with little further changes up to 20 weeks.

Initially Ca-P% values were of the same order for all soils. There were fair decreases in Ca-P% in all soils up to 6 weeks with sewage sludge showing the least and cellulose greatest decrease. There were general small increases, particularly in cellulose treatment, up to 12 weeks with little further change to 20 weeks

Soils of pH 7.7

Al-P% in all soils were of the same order initially, increased slightly up to 6 weeks and showed little further change to 12 or 20 weeks.

Initially Fe-P% was decreased slightly by sewage sludge.

Up to 6 weeks Fe-P% increased to a moderate extent in the control, straw and cellulose treatments and to a slight extent in the sewage sludge treatment. There were little further changes in Fe-P% up to 12 or 20 weeks in the control, sewage sludge and cellulose treatments, whilst Fe-P% increased to a maximum after 12 weeks in the straw treatment.

Initially Ca-P% was highest in the sewage sludge treatment. Ca-P% decreased up to 6 weeks to a lesser extent in the sewage sludge treatment than in other treatments. There were only small further changes in Ca-P% up to 12 or 20 weeks.

CHANGES IN INORGANIC P((Al+Fe+Ca)-P) AND ORGANIC P DURING INCUBATION (COMPARED AS LEVELS AND AS PERCENTAGES OF TOTAL P).

Results are shown in Table 5. Total P values were obtained by summing up the total soil P, added water-soluble phosphate and total P in organic materials where they were applied. Inorganic P values were obtained by summing Al-P, Fe-P and Ca-P values. Organic P values were obtained by subtracting inorganic P from total P.

It must be borne in mind that any change during incubation in inorganic P is reverse of that which occurs in organic P. Since the main purpose of this section is concerned with organic P, the results will be described in relation to changes in organic P.

Soils of pH 5.3

In all soils including the control, organic P increased to a maximum by 6 weeks then decreased to 20 weeks. Organic P after 20 weeks was considerably lower than the initial value with the sewage sludge treatment, but with other treatments and the control

TABLE 5

Levels of inorganic P ((Al + Fe + Ca)-P) and organic P during 20 weeks of incubation (see Table 3).(Results on dry soil basis)

pH	Treatment	Weeks	Total P (ppm)	Inorg.P (ppm)	Inorg.P as % of total P	Org. P (ppm)	Org. P as % of total P
	Nil	0	375	233	62	142	38
		6		162	43	213	57
		12		177	47	198	53
		20		221	59	154	41
	Straw	0	385	217	56	168	44
		6		154	40	231	60
		12		197	51	188	49
		20		227	59	158	41
5.3	Sewage sludge	0	456	305	67	151	33
		6		280	61	176	39
		12		316	69	140	31
		20		339	74	117	26
	Cellulose	0	375	203	54	172	46
		6		168	45	207	55
		12		182	49	193	51
		20		201	54	174	46
	Nil	0	375	216	58	159	42
		6		201	54	174	46
		12		205	55	170	45
		20		201	54	174	46
	Straw	0	385	179	46	206	54
		6		214	56	171	44
		12		183	48	202	52
		20		178	46	207	54
6.5	Sewage sludge	0	456	253	55	203	45
		6		282	62	174	38
		12		282	62	174	38
		20		308	67	148	33
	Cellulose	0	375	211	56	164	44
		6		152	41	223	59
		12		170	45	205	55
		20		181	48	194	52
	Nil	0	375	218	58	157	42
		6		203	54	172	46
		12		202	54	173	46
		20		195	52	180	48
	Straw	0	385	218	57	167	43
		6		203	53	182	47
		12		170	44	215	56
		20		186	48	199	52
7.7	Sewage sludge	0	456	315	69	141	31
		6		325	71	131	29
		12		327	72	129	28
		20		331	73	125	27
	Cellulose	0	375	198	53	177	47
		6		167	45	208	55
		12		192	51	183	49
		20		168	45	207	55

the values were of the same order.

Soils of pH 6.5

In the control soil organic P increased slightly to 6 weeks, but changed little up to 20 weeks. With straw treatment organic P decreased to 6 weeks and increased again to its original level by 12-20 weeks. In the sewage sludge treatment organic P was at the maximum initially and decreased to 20 weeks. In the cellulose treatment organic P increased considerably to 6 weeks and then decreased to a moderate extent to 20 weeks.

Soils of pH 7.7

In the control and straw-treated soils organic P was at maximum initially and increased to 12-20 weeks. With sewage sludge there was only slight decrease in organic P from 0 to 20 weeks. With the cellulose treatment organic P increased to 6 weeks, decreased to 12 weeks and then increased again to 20 weeks.

DISCUSSION

When water-soluble phosphate is added to soil, it is presumed to react fairly rapidly and is precipitated from solution. The literature indicates that at low pH water-soluble phosphate would tend to precipitate in Al- and Fe-bound forms (Al- and Fe-P), whilst at higher pH levels it would tend to precipitate as Ca-bound form (Ca-P). At "zero" incubation the lateritic soil used in this study did not, however, show this effect in relation to increasing pH. In general the Ca-P level and its proportion of the total inorganic P was highest at the lowest pH (5.3) and tended to decrease with increasing pH. It must be borne in mind

that the "zero" incubation in this study represents 24 hours moist contact between the soil and the added water-soluble phosphate. It was assumed that this period would be long enough to allow complete conversion of water-soluble phosphate to water-insoluble forms, but not sufficiently long enough to allow any significant conversion of phosphate by microbial activity. The fact that no water-soluble phosphate was found in any of the soils after this initial 24 hour period confirms the former point. In addition, the relatively small changes in organic P in the control soils after the 24 hour period confirms the latter point.

With incubation, particularly the first 6 weeks, there were considerable changes in the proportions of Ca-P and Fe-P. At all pH levels Ca-P decreased to 6 weeks and there were general concomittant increases in Fe- and Al-P. The changes were generally greater at pH 5.3 than at pH 6.5 or 7.7. This indicates that in time one form of inorganic phosphate may be converted to another form. It is also seen that at pH 5.3 the decreases in Ca-P were not, except for the sewage sludge treatment, accompanied by comparable increases in Al-P and Fe-P. This is presumably due to immobilization of inorganic phosphate by microbial activity. At pH levels of 6.5 and 7.7, on the other hand, with the exception of cellulose treatment, decreases in Ca-P in the first 6 weeks were generally balanced by increases in Al- and Fe-P. This indicates that microbial activity involving immobilization of inorganic phosphate was generally greater in the soil at its original pH of 5.3 than at the higher pH levels. This is confirmed by the fact that the highest level of organic P after 6 weeks of incubation

in all, except the cellulose-treated soil, occurred in soils of pH 5.3.

In soils of pH 5.3 increases in organic P during the first 6 weeks of incubation were accounted for entirely by decreases in Ca-P with all including the control treatment. This indicates that P-immobilizing organisms were only utilizing Ca-P and not Al- or Fe-P forms. The lesser increases in organic P where organic materials were added than in the control soil were probably due to adsorption of Ca-P forms by the organic materials resulting in decreased availability of the phosphate to microorganisms. Sewage sludge had the greatest effect in this respect and ~~the~~ straw the least effect. The 0-6 week period can be considered as the immobilization phase in all soils of pH 5.3. With further incubation up to 20 weeks organic P declined in all soils of pH 5.3 indicating a mineralization phase.

In soils of pH 6.5 changes in organic P during the first 6 weeks differed depending on treatments. Organic P increased in the control and, in particular, with the cellulose treatment, but decreased with straw and sewage sludge treatments. This indicates that considerable decomposition of cellulose was occurring resulting in immobilization of phosphate. On the other hand, apparently, no decomposition of straw and sewage sludge was occurring and it appeared that these materials were stimulating mineralization of organic P. With incubation beyond 6 weeks organic P decreased with the cellulose treatment indicating a mobilization phase. On the other hand with the straw treatment organic P increased somewhat beyond 6 weeks indicating that straw was decomposing

during this later period of incubation. With all treatments there was still preference by the immobilizing organisms for Ca-P over Fe- or Al-P.

At pH 7.7 there was a trend for all soils to show increased levels of organic P with time of incubation up to 20 weeks (except with sewage sludge where only slight changes in organic P occurred). When compared with soils of pH 5.3 where the immobilization process was complete by 6 weeks, in the soils of pH 7.7 immobilization process appeared to be taking place over the whole 20 weeks. This indicates that raising the soil to this high pH level slowed down the activity of those heterotrophic organisms concerned with the decomposition of organic materials and immobilization of P.

The extent to which the organic P fraction in the two added materials (straw and sewage sludge) mineralized over the 20 weeks incubation period was calculated from the differences between the control and treated soils initially and after 20 weeks of incubation. It was found that there was no significant net mineralization of organic P where straw was added, but there was a net mineralization of organic P with the sewage sludge treatment ranging from 39 to 80 ppm, with the highest value occurring at pH 6.5. Since sewage sludge increased the organic P content of the soil by only 17 ppm, it appears that the addition of sewage sludge also stimulated the mineralization of soil organic P. It is also interesting to note that the increased mineralized phosphate due to sewage sludge addition was accounted for entirely as Al- and Fe-P at pH 5.3 but mainly as Ca-P at pH 7.7, whilst at pH 6.5 it was accounted for equally by Ca-P and (Al+Fe)-P. This ability of sewage sludge to

mineralize its own organic P and to stimulate the mineralization of soil organic P indicates that it may be a useful source of phosphorus for plants.

SUMMARY

Dacca soils of pH 5.3 (original pH), 6.5 and 7.7 were treated with 200 ppm water-soluble phosphate-P and the effects of addition of 1% straw, sewage sludge and cellulose (plus 100 ppm NH_4NO_3-N) on inorganic and organic P forms were determined during incubation (50% mwhc, 30°C) for up to 20 weeks.

Early in incubation there were considerable changes in the proportions of Ca- and Fe-P but lesser changes in the proportion of Al-P irrespective of the organic material treatment. At all pH levels Ca-P decreased early in incubation accompanied by increases in Fe- and Al-P. Microbial activity involving immobilization of phosphate was generally greater in soil at its original pH than at higher pH levels.

At pH 5.3 P-immobilizing organisms utilized only Ca-P and not Al- or Fe-P; the immobilizing effects were predominent during the 0-6 week period with all treatments. At pH 6.5 cellulose caused immobilization whilst straw and sewage sludge caused mineralization of phosphorus during 0-6 weeks. With further incubation mineralization occurred with the cellulose treatment and immobilization with the straw treatment. At pH 7.7 the immobilization phase of phosphate occurred over the whole 20 weeks period.

After 20 weeks there was no net mineralization of organic P of straw, but there was a fair mineralization of organic P of sewage sludge at all pH levels, particularly at pH 6.5. Sewage sludge also increased the mineralization of soil organic P.

EXPERIMENT 2

CHANGES IN Al-, Fe-, Ca- AND ORGANIC-P DURING INCUBATION, AFTER ADDITION OF 400 PPM P AS MONOCALCIUM PHOSPHATE, OF DACCA SOIL PREVIOUSLY HELD MOIST FOR 8 MONTHS AFTER TREATMENT WITH 2% STRAW AND COMPOST (PLUS 100 ppm UREA-N).

Since Dacca soil is low in organic matter compared with temperate region soils, the purpose of this experiment was to determine the effect of previously raising the soil organic matter content (by holding the soil moist for 8 months after treatment with straw and compost) on the mode of fixation of added water-soluble phosphate during subsequent incubation. It is seen that this experiment differs from the previous one (Expt. 1) where organic materials and water-soluble phosphate were added just before incubation. This experiment was done only on the Dacca soil at its original pH of 5.3.

METHODS

A 2 kg portion of the air-dry 1 mm sieved Dacca soil of original pH 5.3 was mixed with finely ground urea to supply 100 ppm N on the dry soil basis. 500 g portions of this soil were treated as follows - (1) mixed with 2% w/w finely ground oat straw, (2) mixed with 2% w/w finely ground compost (this had been prepared by allowing a mixture of chopped grass and straw of initial C/N ratio of 40 to decompose for 6 months by which time the C/N ratio had fallen to 20 (Cornfield, 1958)) and (3) no organic material added (control). The three 500 g portions were placed in separate glass pots and

and wetted to 50% mwhc. The pots were held at room temperature (18-22°C) for 8 months and water added when necessary to maintain soil moisture content at 40-50% mwhc. The soils were then dried and ground to pass a 1 mm sieve.

All soils were then treated with finely ground monocalcium phosphate, $Ca(H_2PO_4)_2.H_2O$, to supply 400 ppm P on the dry soil basis. Sufficient 10 g portions of each soil were set up to allow for analysis in duplicate initially (zero incubation) and after 3, 6, and 12 weeks of incubation at 30°C and 50% mwhc. The zero incubation samples were actually analysed 24 hours after addition of water as described in the previous experiment. Analyses for fractionation of P were also as described in the previous experiment.

RESULTS

EFFECTS OF STRAW AND COMPOST TREATMENTS ON ORGANIC AND INORGANIC P FORMS AFTER 8 MONTHS MOIST CONTACT

Before describing the main part of this experiment, namely, the effects of the previous straw and compost treatments on the mode of fixation of added water-soluble phosphate, the effects of these treatments on changes in the organic and inorganic P forms will be considered. These results are shown in Table 6.

Where straw was added, the increase in total P after 8 months was due mainly (91%) to an increase in organic P. In the case of compost 66% of the increase was due to an increase in organic P and 34% due to inorganic P. The straw treatment increased Al- and Fe-P, but decreased Ca-P, after 8 months, whilst the compost treatment increased all three forms of inorganic P.

TABLE 6

Effect of 2% straw and compost on organic P and inorganic P fractions after 8 months moist contact with Dacca soil.
(Results are in ppm P on dry soil basis)

Treatment	Total P	Inorg.P	Org. P	Al-P	Fe-P	Ca-P
Control	175	20.6	154.4	0.6	10.0	10.0
Straw	196	22.1	173.9	2.3	14.4	5.4
Compost	220	35.9	184.1	4.6	17.7	13.6
L. S. D. at Prob. <0.05	2.2	1.2		0.8	1.9	0.3

TABLE 7

Levels of Al-, Fe- and Ca-P over 12 weeks of incubation after addition of 400 ppm P as $Ca(H_2PO_4)_2.H_2O$ to Dacca soil previously treated with 2% straw and compost plus 100 ppm urea-N. (Results are given (a) in ppm P on dry soil basis and (b) as percentage of total inorganic P)

Weeks of incubation – Treatment		Al-P				Fe-P				Ca-P			
		0	3	6	12	0	3	6	12	0	3	6	12
Control	(a)	73	130	120	118	54	88	95	99	151	153	118	106
	(b)	27	35	37	36	19	24	28	31	54	41	35	33
Straw	(a)	60	143	131	108	51	87	81	76	98	141	107	97
	(b)	29	39	41	38	24	23	25	27	47	38	34	35
Compost	(a)	65	130	140	138	51	85	90	90	112	140	142	131
	(b)	29	37	38	39	22	24	24	25	49	39	38	36

L.S.D. for P levels at Prob. <0.05 Al-P = 7.7, Fe-P = 3.2, Ca-P = 11.8

CHANGES IN Al-, Fe- AND Ca-P DURING INCUBATION

Table 7 and Figure 4 shows these results expressed in ppm P and as percentages of total inorganic P ((Al + Fe + Ca)-P).

Changes in Al-P

In the control soil the Al-P level increased considerably to 3 weeks, decreased slightly to 6 weeks, but was not further affected to 12 weeks. With the straw treatment Al-P increased considerably to 3 weeks and then declined somewhat to 12 weeks. With the compost treatment Al-P increased considerably to 3 weeks and then slightly to 6 weeks, but was not further affected to 12 weeks.

When expressed as a percentage of total inorganic P, Al-P% increased to 3 weeks but was little affected with further incubation in the control and treated soils.

Changes in Fe-P

In the control soil the Fe-P level increased to a fair extent to 3 weeks and then to a moderate extent to 6 and 12 weeks. With the straw treatment Fe-P increased to a fair extent to 3 weeks and then decreased to a moderate extent to 6 and 12 weeks. With the compost treatment Fe-P increased to a fair extent to 3 weeks and to a small extent to 6 weeks, but did not change further to 12 weeks.

When expressed as a percentage of total inorganic P, Fe-P% in the control increased to 6 weeks but showed little change to 12 weeks. With the straw and compost treatments, Fe-P% showed little change due to incubation.

Changes in Ca-P

In the control soil the Ca-P level showed no change to 3 weeks, decreased to a moderate extent to 6 weeks and to a further small

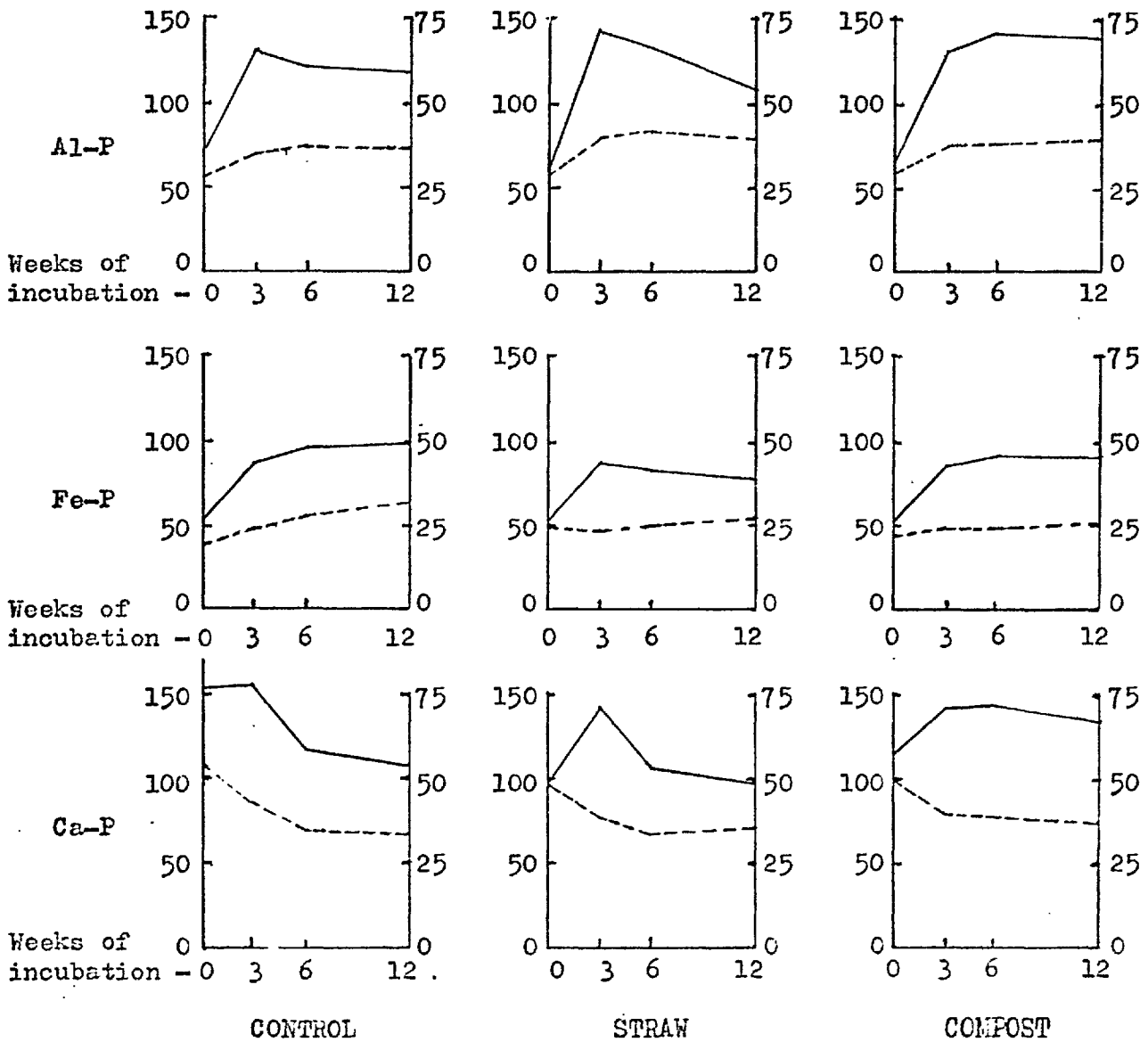
FIGURE 4

Levels of Al-, Fe- and Ca-P over 12 weeks of incubation after addition of 400 ppm P as $Ca(H_2PO_4)_2.H_2O$ to Dacca soil previously treated with 2% straw and compost plus 100 ppm urea-N.

——— P as ppm P on soil basis (Left hand 'y' axis)

- - - - P as % of total inorganic P (Right hand 'y' axis)

L.S.D. for P levels at Prob. < 0.05 Al-P I Fe-P I Ca-P I



extent to 12 weeks. With the straw treatment Ca-P increased to a fair extent to 3 weeks, then decreased to a fair extent to 6 weeks but showed no further change to 12 weeks. With the compost treatment Ca-P increased to a fair extent to 3 weeks, but showed no further change to 6 and 12 weeks.

When expressed as a percentage of total inorganic P, Ca-P% decreased to 3 weeks but showed little further change to 6 or 12 weeks in the control and treated soils.

CHANGES IN INORGANIC P ((Al+Fe+Ca)-P) AND ORGANIC P DURING INCUBATION.

Results are shown in Table 8 expressed as ppm P and as percentage of total P. Figure 5 shows results in ppm P.

In the control soil organic P decreased to 3 weeks and then increased again to 12 weeks. With the straw treatment organic P decreased to 3 weeks to a greater extent than in the control soil and increased again to 12 weeks. In both soils organic P after 12 weeks were less than initial values. With the compost treatment organic P decreased mainly to 3 weeks and slightly to 6 weeks, but showed little further change to 12 weeks.

DISCUSSION

Initially in the control soil 52% of the total P was accounted for as organic P, indicating that 143 ppm of the added water-soluble phosphate had been converted to organic form. This conversion is probably due to adsorption by soil organic matter, since the 24 hour holding period after addition of water-soluble phosphate would hardly be sufficient to cause microbial immobilization of P.

TABLE 8

Levels of inorganic P ((Al + Fe + Ca)-P) and organic P during 12 weeks of incubation (see Table 7).

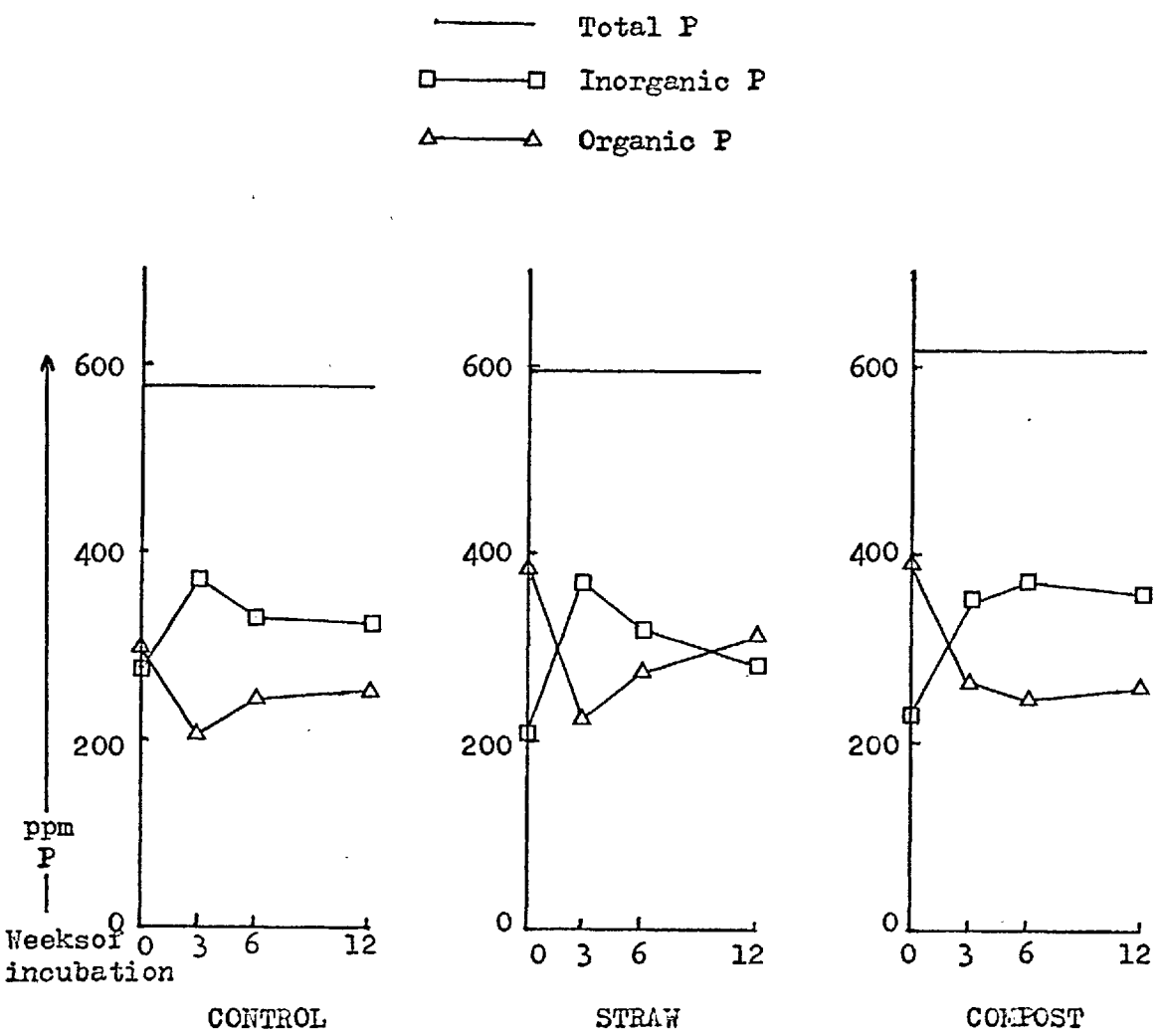
(Results are on dry soil basis)

Treatment	Weeks	Total P (ppm)	Inorg.P (ppm)	Inorg.P as % of total P	Org. P (ppm)	Org. P as % of total P
Control	0	575	278	48	297	52
	3		371	65	204	35
	6		333	58	242	42
	12		323	56	252	44
Straw	0	595	209	35	386	65
	3		371	62	224	38
	6		319	54	276	46
	12		281	47	314	53
Compost	0	619	228	37	391	63
	3		355	57	264	43
	6		372	60	247	40
	12		359	58	260	42

FIGURE 5

Levels of inorganic and organic P during 12 weeks of incubation.

(Results are in ppm P on soil basis)



It seems that 8 months moist contact of the control soil with added urea resulted in microbial activity which generated organic material which had the ability to adsorb phosphate. The higher proportions of organic P (65% and 63%) due to the straw and compost treatments respectively indicate that the residues of these added organic materials caused further adsorption of water-soluble phosphate.

During the first 3 weeks of incubation there was considerable mineralization of P in all soils, particularly due to the straw treatment. The mode of fixation of mineralized P was altered by the straw and compost treatments. In the control soil Al-P accounted for two-thirds and Fe-P accounted for the rest of the mineralized P fixation. However, the straw and compost treatments altered the mode of fixation of mineralized P in that about a quarter was fixed as Ca-P and the rest mainly as Al-P. Thus it is seen that during the predominently mineralization phase which occurred during the first three weeks of incubation the presence of residues of the added organic materials favoured to some extent the formation of Ca-P.

During the 3-12 week incubation period there were general increases in organic P in the control and straw treatments, but little change in compost treatment. This indicates that another immobilization phase occurred in the control and, in particular, in the straw treated soil, in view of greater increases in organic P in the later soil. It is probable that straw residues were decomposing further during the 3-12 week period, since phosphate was not limiting the decomposition of straw as it may have been doing during the 8 months preincubation period. (It is worth noting (Table 6) that Ca-P was decreased by the straw treatment during

this 8 month period). During the incubation immobilization phase the decrease in inorganic P was accounted for to about the same extent by decreases in Al-P and Ca-P in the straw treatment, in contrast to a decrease mainly of Ca-P in the control soil. With the compost treatment the absence of change in organic P during the 3-12 weeks period indicates that the residues of this material had come to equilibrium with the soil after the first three weeks of incubation.

In spite of changes which usually occurred in actual levels of Al-, Fe- and Ca-P during incubation due to the straw and compost treatments, the proportions of these three forms of P (expressed as % of total inorganic P) were not affected to a great extent. The main effects were : (a) both organic treatments reduced the trend for the proportion of Ca-P to decrease and that of Fe-P to increase during incubation but had little effect on the proportion of Al-P ; (b) by the end of incubation the proportion of Ca-P was little affected by both treatments ; the proportion of Al-P was increased while that of Fe-P was decreased by both treatments.

The results in the present experiment can be compared with those of the previous experiment (Expt. 1). The main general effect was the high initial adsorptive fixation of added water-soluble phosphate which occurred after the soils were allowed to react for 8 months with added urea without or with organic materials; there were no adsorptive fixation when the soils did not recieve the preliminary treatment. The application of a higher level of water-soluble phosphate in the present compared with the previous experi-

ment may also have contributed to the high adsorptive fixation which occurred in this experiment.

SUMMARY

Dacca soil at its original pH (5.3) was held moist for 8 months at room temperature after treatment with 2% straw and compost (plus 100 ppm urea-N). The treated and control soils were then incubated (at 50% mwhc, 30°C) for 12 weeks after addition of 400 ppm water-soluble phosphate-P.

Within 24 hours of application of soluble phosphate about 50% of this was converted to adsorbed forms in the control soil and about 66% where straw and compost were added. During the first 3 weeks of incubation there was considerable mineralization of P in all soils, but particularly when straw was added. During this mineralization phase the addition of organic materials favoured the formation of Ca-P over Fe- or Al-P.

During the 3-12 weeks incubation period, organic P increased in the control and straw treatments but changed little in the compost treatment. During this phase Ca-P was mainly immobilized in the control soil whilst both Ca-P and Al-P were immobilized in the straw-treated soil.

In spite of the changes which usually occurred in the actual levels of Al-, Fe- and Ca-P during incubation due to the straw and compost treatments the proportions of the three forms of P were affected to a lesser extent.

C H A P T E R V

MODE OF FIXATION OF ADDED WATER-SOLUBLE PHOSPHATE IN RELATION TO SIZE OF SOIL SEPARATES AND AS AFFECTED BY REMOVAL OF ORGANIC MATTER AND IRON OXIDES FROM SOIL.

Experiment 3 :

Fractionation of phosphorus in mechanical separates of Dacca soil before and after treatment with 1,000 ppm P as KH_2PO_4.

Experiment 4 :

Effect of removal of organic matter and/or iron oxides from Dacca soil on the mode of fixation of added water-soluble phosphate.

Experiment 5 :

Effect of alternate wetting and drying of Dacca soil on the mode of fixation of added water-soluble phosphate.

CHAPTER V

EXPERIMENT 3

FRACTIONATION OF PHOSPHORUS IN MECHANICAL SEPARATES OF DACCA SOIL BEFORE AND AFTER TREATMENT WITH 1,000 PPM P AS KH_2PO_4.

A number of workers have reported on the distribution of inorganic P forms in mechanical separates of soils, i.e., the clay, silt and sand fractions (Williams & Saunders, 1965a & b; Sheffer et al., 1960; Kaila, 1965; Halstead, 1967; Juo & Ellis, 1968; and Hanley & Murphy, 1970). In general it was found that the inorganic P in the clay and silt separates was mainly Fe-P and Al-P whilst Ca-P was the dominant form in the sand separate.

In this experiment, Dacca soil was separated into clay, silt and sand fractions and each fraction was analysed for Al-, Fe- and Ca-P before and after reaction with water-soluble phosphate.

METHODS

100 g soil was placed in a 1½ litre bottle and 1 litre of water was added. The top of the liquid level was marked. The bottle was shaken for 48 hours and then allowed to stand for 6 hours. The clay suspension was siphoned off. The residue was diluted to the mark, shaken vigorously for 5 minute, set aside for 6 hours and supernatant suspension was again siphoned off. This process was repeated (6 more times) until the supernatant liquid was clear. The same process was repeated to separate silt from sand, except

that the bottle was allowed to stand for 47 seconds after shaking. The combined suspensions of clay were concentrated to a low volume on a slow waterbath, completely dried over silica gel in a dessiccator and ground to pass through a 0.5 mm sieve. The combined silt suspensions were allowed to stand overnight. The clear supernatant liquid was siphoned off and the residue treated in the same way as the clay. The wet sand fraction was dried at 40°C and rubbed through a 1 mm sieve. This separation resulted in the following particle-size dimensions : sand, 1mm-0.05mm; silt, 0.05mm-0.002mm; and clay <0.002mm.

One gram portions in duplicate of the soil separates were fractionated for inorganic P forms using the Modified method described in Chapter III. Further 1 g portions in duplicate of the separates were shaken for 48 hours with 20 ml of solution containing potassium dihydrogen phosphate, KH_2PO_4, so as to supply 1,000 ppm P on the soil separate basis. After centrifuging, the supernatant liquid was poured off and the residue shaken with 20 ml water and again centrifuged to remove soluble phosphate. The residues were fractionated for inorganic P as described above.

RESULTS

THE PROPORTIONS OF SAND, SILT AND CLAY OBTAINED BY MECHANICAL ANALYSIS (CHAPTER II) AND BY MECHANICAL SEPARATION.

This is shown in Table 9 (overleaf) where losses due to organic matter removal and materials going into solution during analysis have been allowed for.

TABLE 9

	Mechanical analysis	Mechanical separation
% sand	8	25
% silt	60	56
% clay	32	19

It is seen that although the proportions of silt obtained by the two processes are approximately the same, the proportion of sand was lower and that of clay was higher by mechanical analysis than by mechanical separation.

Table 10(i) shows the levels of Al-, Fe-, Ca- and total inorganic-P and also the three forms expressed as percentage of total inorganic P for the separates not treated with phosphate. Table 10(ii) presents the results for soil separates treated with 1,000 ppm water-soluble PO_4-P before fractionation. Figure 6a shows the levels of Al-, Fe- and Ca-P in the soil separates where no P was added and Figure 6b shows these levels where the materials were pretreated with phosphate.

LEVELS OF INORGANIC P FORMS BEFORE TREATMENT WITH PHOSPHATE

Level of total inorganic P was higher in clay than in silt and sand.

Levels of Al-P and Fe-P in clay were higher than in sand and silt. The level of Ca-P in silt was slightly lower than those in sand and clay. The proportion of Ca-P increased, that of Fe-P decreased, whilst that of Al-P did not change with increasing particle size of the separates.

TABLE 10

Fractionation of phosphorus in mechanical separates of Dacca soil before and after treatment with 1,000 ppm P as KH_2PO_4.
(Results are given (a) in ppm P on dry separate basis and (b) as percentage of total inorganic phosphorus)

i) Before treatment with phosphate

Separates		Al-P	Fe-P	Ca-P	Inorganic P
Sand	(a)	12	20	10	42
	(b)	29	48	23	
Silt	(a)	12	21	8	41
	(b)	29	51	20	
Clay	(a)	22	40	11	73
	(b)	30	55	15	
L.S.D. for P levels at Prob. <0.05		1.9	3.0	2.2	3.8

ii) After treatment with water-soluble phosphate

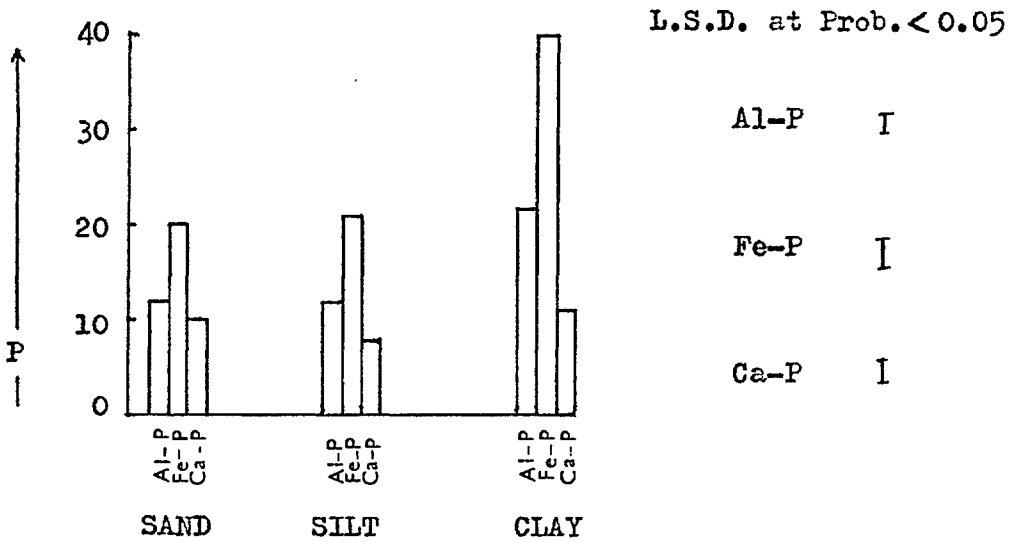
Separates		Al-P	Fe-P	Ca-P	Inorganic P
Sand	(a)	166	150	202	518
	(b)	32	29	39	
Silt	(a)	164	94	212	470
	(b)	35	20	45	
Clay	(a)	302	211	314	827
	(b)	37	25	38	
L.S.D. for P levels at Prob. <0.05		27	23	39	45

FIGURE 6

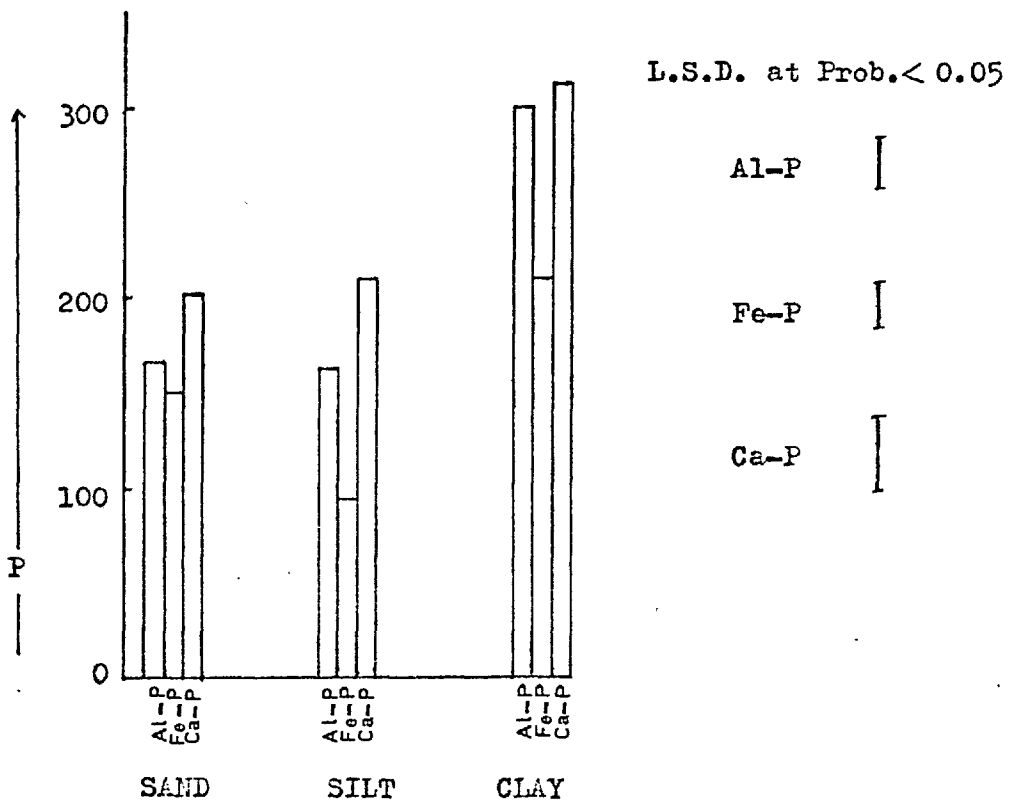
Fractionation of phosphorus in mechanical separates of Dacca soil before and after treatment with 1,000 ppm P as KH_2PO_4.

(Results are in ppm P on dry deparate basis)

(a) Before treatment with phosphate



(b) After treatment with water-soluble phosphate



LEVELS OF INORGANIC P FORMS AFTER TREATMENT WITH WATER-SOLUBLE PHOSPHATE.

Levels of Al-, Fe- and Ca-P were higher in clay than in silt or sand. The Fe-P level was lower in silt than in sand with no differences in Al- or Ca-P. The proportion of Al-P declined slightly with increasing particle size of the separates. The proportion of Fe-P was at a minimum and that of Ca-P at a maximum in the silt fraction. The percentages of water-soluble phosphate fixed by the separates were 75, 43 and 48 for clay, silt and sand respectively (allowances were made for the amount of native organic P present).

DISCUSSION

The higher proportion of sand and the lower proportion of clay obtained by mechanical separation compared to mechanical analysis is probably due to the presence of clay aggregates of "sand" size in the separated sand and/or to clay strongly cemented to sand particles. It must be borne in mind that during mechanical analysis organic matter is destroyed and its binding effect in forming clay aggregates is removed. In mechanical separation, on the other hand, organic matter is not destroyed and even the long period of dispersion in water (48 hours of shaking) was not able to disperse 41% of the clay aggregates or clay-sand aggregates, and these appeared as "sand" size particles.

It is seen in Fig. 6a that the pattern and levels of the three inorganic P forms were very similar in the silt and sand separates. This indicates that the sand separate is behaving very similarly to the silt separate with respect to the nature of the forms of the

inorganically bound phosphates. The fact that Fe-P accounted for more phosphate than did Al-P or Ca-P might indicate that iron oxides, containing iron-bound P, are in firm combination with sand. On the other hand, the high Fe-P in sand may be due to the presence of sand size aggregates mentioned above. The latter seems more likely since in the clay separate Fe-P was higher than Al-P or Ca-P compared with the sand and silt separates.

Where the separates were treated with water-soluble phosphate, the pattern of distribution of the inorganically bound phosphorus (Fig. 6b) differed from the results obtained with the untreated separates. The main difference was that the added phosphate was fixed to a lesser extent as Fe-P than as Al-P or Ca-P in all, but particularly, in silt and clay separates. This indicates a preferential fixation in Al-P and Ca-P forms in silt and clay but not in sand. This again was most likely due to the presence of sand-size clay aggregates in the sand separate, but not of the silt-size clay aggregates in the silt separate. This is supported to some extent by the higher Fe-P value in clay and sand than in silt.

The greater fixation (75%) of the added phosphate by clay compared with that of silt (43%) or sand (48%) would be expected because of the greater number of fixing sites in clay. However, the fair amount of fixation of added phosphate by sand indicates that the sand separate may contribute to a fair extent to the fixation of added phosphate. This agrees with results obtained for two of the Irish soils studied by Hanley and Murphy (1970) who found that sand contributed more to the overall phosphate fixation than did either silt or clay.

SUMMARY

Dacca soil was shaken with water for 48 hours and then separated by sedimentation into clay, silt and sand-sized separates. The forms of inorganic P (Al-, Fe- and Ca-P) present were determined before and after treatment of each separate with 1,000 ppm water-soluble phosphate-P.

Where no phosphate was added before fractionation, the pattern and levels of the three inorganic P forms were very similar in sand and silt separates, more of the total inorganic P being accounted for as Fe-P than as Al- and Ca-P. The high Fe-P in the sand-sized separate was due to the presence of Fe-bound P in firm combination with sand and/or to the presence in the sand separate of stable sand-sized clay aggregates.

In the clay separate Al- and Fe-P was higher whilst Ca-P was the same as in the sand and silt separates.

Where the separates were treated with water-soluble phosphate before fractionation, less of the total inorganic P was fixed as Fe-P than as Al- or Ca-P, particularly in the silt and clay separates. The clay, silt and sand separates fixed 75%, 43% and 48% respectively of the added water-soluble phosphate.

EXPERIMENT 4

EFFECT OF REMOVAL OF ORGANIC MATTER AND/OR IRON OXIDES FROM DACCA SOIL ON THE MODE OF FIXATION OF ADDED WATER-SOLUBLE PHOSPHATE.

This experiment was carried out to determine the contribution of organic matter and iron oxides present in the soil on the mode of fixation of added water-soluble phosphate. This was done by determining fixation on the original soil and comparing the results with those obtained after removal of either organic matter or iron oxides and removal of both these constituents.

METHODS

For the removal of organic matter (O.M.) 100 g soil was boiled with 200 ml of 6% hydrogen peroxide until frothing ceased. After cooling somewhat, 50 ml of 30% hydrogen peroxide was added and the mixture again boiled. This process was repeated once again and the suspension was boiled till all peroxide have been destroyed. The soil residue was then filtered off under suction in a Buchner funnel, washed five times with water and then allowed to air-dry.

A further 100 g of the original soil was treated by the dithionite-citrate method (Aguilera & Jackson, 1953) to remove iron oxides (Fe_2O_3) and the residual soil was air-dried after washing with water.

For the removal of both O.M. and Fe_2O_3, the O.M. was first removed before subjecting the soil to the treatment for the removal of Fe_2O_3.

Removal of O.M. did not alter soil pH, but the two samples

subjected to Fe_2O_3 removal had pH levels of about 7. This was due to sodium residues from the dithionite-citrate treatment. These samples were washed 5 times, with centrifuging, with 100 ml portions of 0.1N acetic acid and then with 5 portions of water to remove excess acetic acid. After drying the soils had pH within 0.1 unit of the original soil.

1 g portions,in duplicate, of the original and treated soils were shaken for 48 hours in centrifuge tubes with 20 ml of a solution containing monocalcium phosphate, $Ca(H_2PO_4)_2.H_2O$, to supply 200 ppm P on soil basis. The suspensions were centrifuged and the residual liquid (water-soluble phosphate) poured off for analysis. The residual soils were then shaken with 40 ml of N NH_4Cl for 30 minutes, centrifuged, and the residual liquid poured off and combined with the water-soluble phosphate fraction for analysis as NH_4Cl-extractable P. The residual soils were then subjected to fractionation for Al-, Fe- and Ca-P forms as described in Modified method (Chap. III).

RESULTS

Results are shown in Table 11 for NH_4Cl-extractable P and Al-, Fe-, Ca- and total inorganically fixed -P; the three forms of P are also shown as percentages of total inorganically fixed P. Fig. 7 shows results for Al-, Fe- and Ca-P in ppm P on dry soil basis.

The removal of O.M. increased whilst the removal of Fe_2O_3 decreased the extent of fixation of added water-soluble phosphate to a moderate extent. The removal of both O.M. and Fe_2O_3 decreased inorganic P fixation to a slight extent. The changes in inorganic P fixation were negatively correlated with the levels of NH_4Cl-

TABLE 11

Effects of removal of organic matter (O.M.), iron oxides (Fe_2O_3) and O.M. & Fe_2O_3 from Dacca soil on the mode of fixation of added water-soluble phosphate (200 ppm P as $Ca(H_2PO_4)_2.H_2O$ on soil basis).

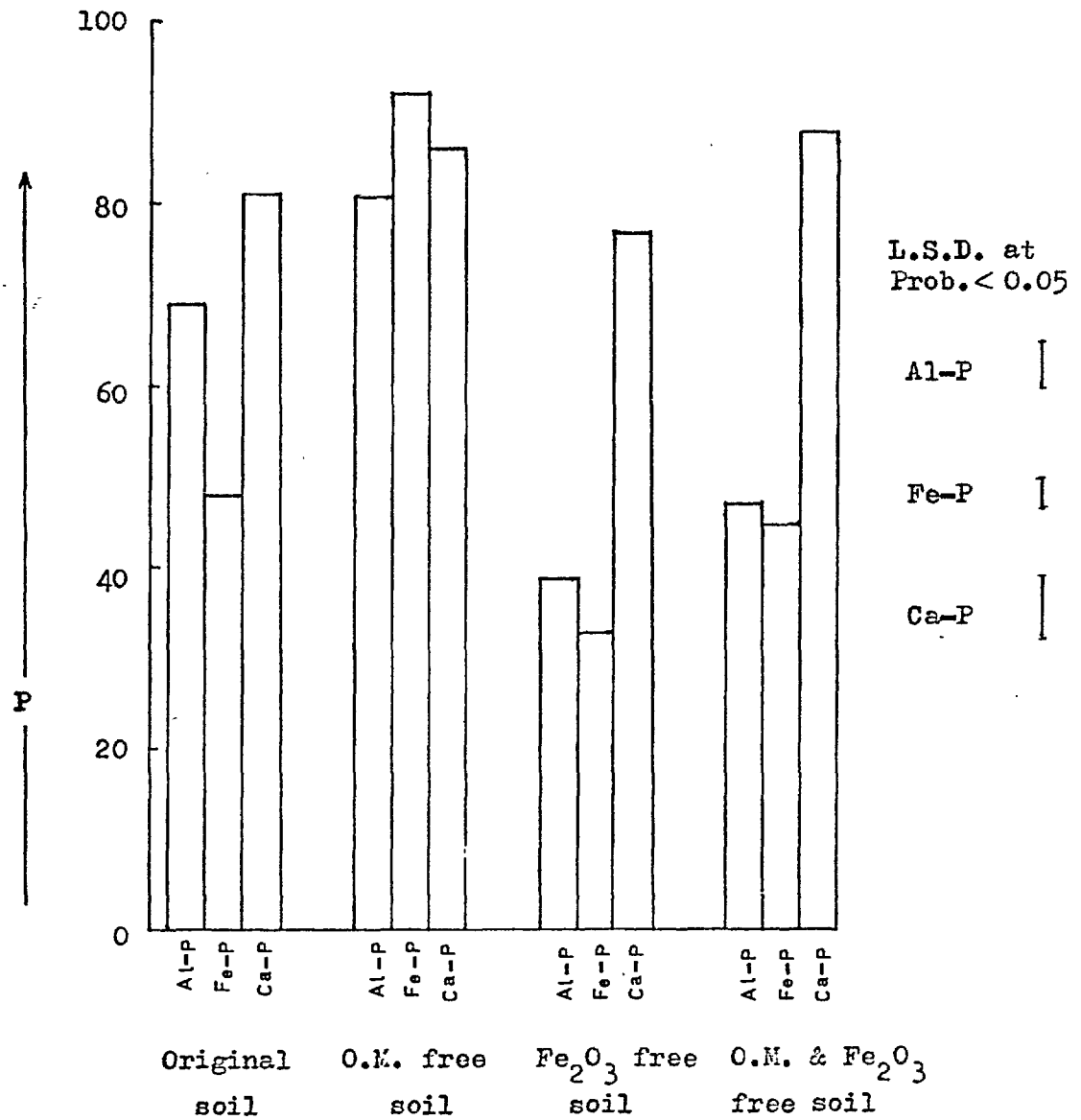
(Results are given (a) in ppm P on dry soil basis and (b) as percentage of total fixed inorganic phosphorus)

Treatment		NH_4Cl-extractable P	Al-P	Fe-P	Ca-P	Total fixed Inorganic P
Original soil	(a)	15	69	48	81	198
	(b)		35	24	41	
O.M. free soil	(a)	8	81	92	86	259
	(b)		31	36	33	
Fe_2O_3 free soil	(a)	48	39	33	77	149
	(b)		26	22	52	
O.M. & Fe_2O_3 free soil	(a)	34	47	45	88	180
	(b)		26	25	49	
L.S.D for P levels at Prob. <0.05		2.1	5.0	3.1	7.1	6.1

FIGURE 7

Effects of removal of organic matter (O.M.), iron oxides (Fe_2O_3) and O.M. & Fe_2O_3 from Dacca soil on the mode of fixation of added water-soluble phosphate (200 ppm P, on soil basis, of $Ca(H_2PO_4)_2.H_2O$).

(Results are in ppm P on dry soil basis)



extractable P.

The removal of O.M. and/or Fe_2O_3 had no effect on Ca-P levels. The removal of O.M. increased Al-P slightly and Fe-P to a fair extent. The removal of Fe_2O_3 decreased Al-P to a fair extent and Fe-P to a moderate extent. The removal of both O.M. and Fe_2O_3 decreased Al-P somewhat but had no effect on Fe-P.

The removal of O.M. decreased the proportion of Ca-P, increased that of Fe-P and had little effect on that of Al-P. The removal of Fe_2O_3 or both O.M. and Fe_2O_3 increased the proportion of Ca-P, decreased that of Al-P but had little effect on the proportion of Fe-P.

DISCUSSION

The fact that the removal of O.M. increased the extent of fixation of inorganic P forms indicates that in the original soil the O.M. had some protective effect against fixation of P in inorganic forms. The O.M. removal treatment was the only one in which the native and added inorganic phosphate was completely accounted for as NH_4Cl-extractable and fixed inorganic P forms. In the original soil the 85% recovery of phosphate was probably due to some adsorption of added phosphate on soil organic matter. The fact that the removal of O.M. increased mainly the Fe-P level, with relatively small effects on Al-P and Ca-P levels, indicates that in the original soil there was a close association between O.M. and Fe_2O_3 with some of the active iron sites complexed by O.M..

The treatment given to remove Fe_2O_3 had almost as great an effect in decreasing inorganic P fixation as did the removal of

O.M. in increasing the fixation. Whereas there was little change in Ca-P fixation due to Fe_2O_3 removal, this removal resulted in a greater decrease in Al-P than in Fe-P fixation. It appears therefore that the dithionite-citrate method used was more effective in removing active Al- than active Fe-fixing sites. In addition the fact that only 31% of the active iron sites were removed by the dithionite-citrate treatment suggests that for this soil this treatment was relatively inefficient in removing active iron. It may be, as suggested by Chang and Jackson (1957b), that aluminium-iron-phosphate (barrandite-like) is formed in this soil.

The removal of both O.M. and Fe_2O_3 gave results for inorganic P fixation which were nearer to the removal of Fe_2O_3 alone than to the removal of O.M. alone. This applied particularly to Al-P and Fe-P levels. However, the small increases in all three forms of inorganic P due to both O.M. and Fe_2O_3 removal compared with the removal of Fe_2O_3 alone indicates that O.M. had a small protective effect against fixation in all three forms.

SUMMARY

The effects of removal of organic matter and iron oxides from Dacca soil on the mode of fixation of P after treatment with 200 ppm water-soluble phosphate P were determined.

The removal of organic matter increased the fixation of added phosphate mainly as the Fe-P form. The removal of iron oxides did not affect Ca-P fixation but decreased Al-P fixation, in particular, and Fe-P fixation. The removal of both organic matter and iron oxides gave results of inorganic P fixation which were nearer to

the removal of iron oxides alone than to the removal of organic matter alone.

EXPERIMENT 5

EFFECT OF ALTERNATE WETTING AND DRYING OF DACCA SOIL ON THE MODE OF FIXATION OF ADDED WATER-SOLUBLE PHOSPHATE.

Field soils are usually subjected to variable moisture contents ranging from a moist condition after rainfall or irrigation to a dry condition due to evaporation. During the summer season in Pakistan the top few inches of soil can approach an almost air-dry condition and this can occur several times where irrigation water is applied every few days. The purpose of this experiment was to simulate this process by using varying cycles of wetting and drying and determining the mode of fixation of water-soluble phosphate added initially.

METHODS

The original Dacca soil (pH 5.3) was used. Six 1 g samples in centrifuge tubes were treated with 1 ml solution of monocalcium phosphate, $Ca(H_2PO_4)_2.H_2O$, to supply 200 ppm P on soil basis. The tubes were placed in an oven at 50°C until dry (3 days). This will be referred to as the 1-cycle treatment. The contents of the two tubes were used for fractionation of inorganic P forms. The other four tubes were subjected to 5 further cycles of wetting (to 50% mwhc) and drying every three days (5-cycle treatment) and the contents of 2 further tubes were analysed. The remaining two tubes were subjected to a further 5 cycles of wetting and drying and their contents analysed (10-cycle treatment). The wetting and drying treatments took 30 days.

RESULTS

Results are shown in Table 12a and Fig 8a for inorganic P forms and Table 12b and Figure 8b for total inorganic and organic P.

Al-P increased somewhat after 5 cycles of wetting and drying and decreased slightly after 10 cycles. Fe-P decreased after 5 cycles and increased to a fair extent after 10 cycles. Ca-P decreased after 5 cycles and increased slightly after 10 cycles. The proportions of the three inorganic fomrs after the varying cycles more or less parallelled the levels of the three forms except that the proportion of Ca-P declined during the last 5 cycles.

The decrease in total inorganic P after 5 cycles was accounted for by decreases in both Fe- and Ca-P. The increase in total inorganic P between the 5-cycle and 10-cycle treatments was due almost entirely to increase in Fe-P.

DISCUSSION

The increased organic P between 1- and 5-cycle treatments indicates that immobilization of phosphate occurred during this period. The immobilizing organisms utilized Fe- and Ca-P but not Al-P, which in fact increased during this period. Immobilization presumably occurred during the period just after the soil had been wetted and continued until the soil became too dry for any further microbial activity. Somewhat greater utilization of Fe-P than of Ca-P under the present conditions of varying moisture content is in contrast with the results obtained in Expt. 1 where under constant moisture condition (50% mwhc) Ca-P was the preferred form which was immobilized. From the differences in results between the experiments

TABLE 12

Effects of varying cycles of wetting and drying on the mode of fixation of P in Dacca soil treated initially with water-soluble phosphate (200 ppm P on dry soil basis as $Ca(H_2PO_4)_2.H_2O$).

(Results in ppm P on dry soil basis)

(a) Inorganic P forms expressed as (i) levels and as (ii) percentage of total inorganic P.

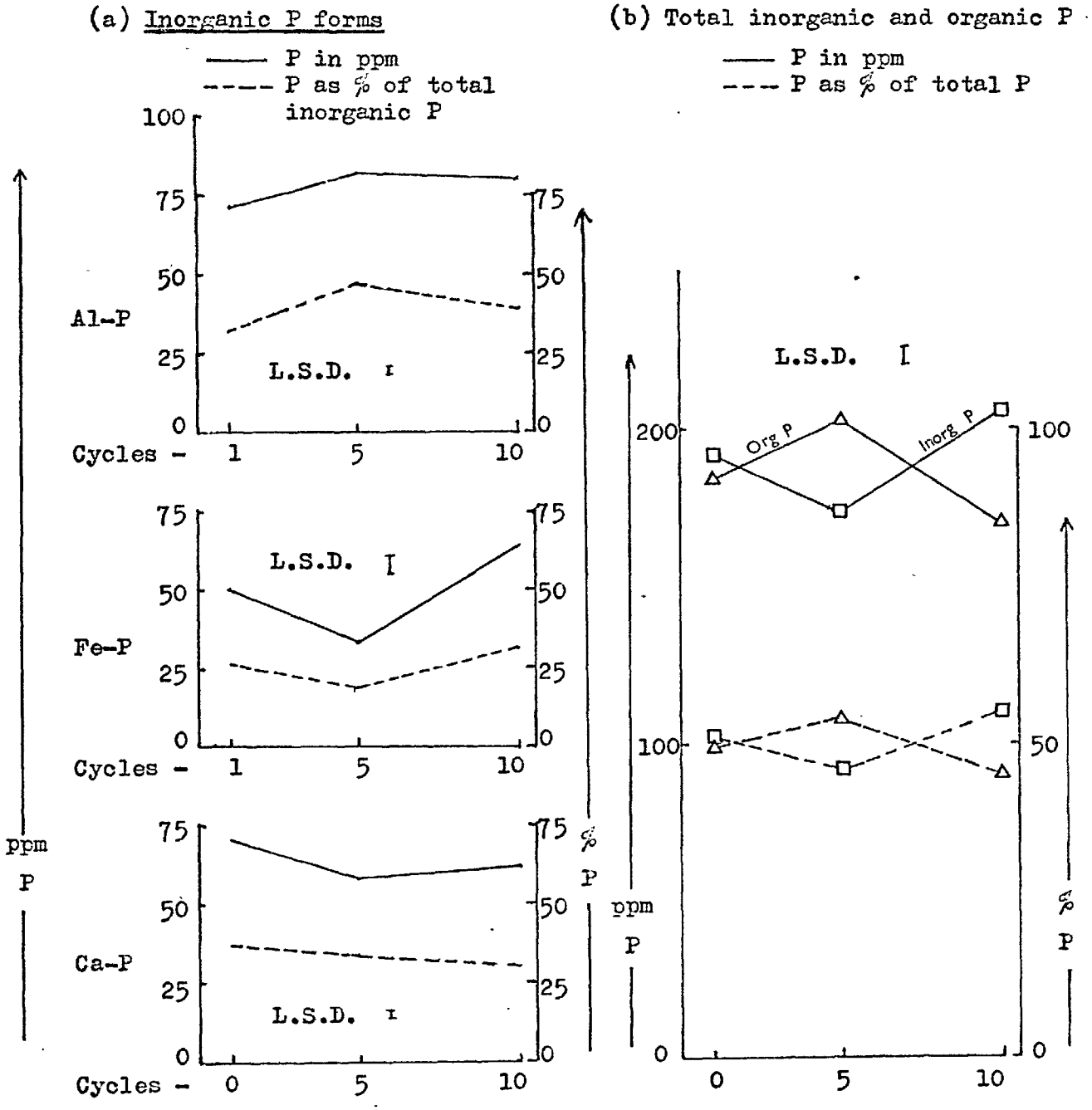
Cycles		Al-P	Fe-P	Ca-P
1	(i)	71	50	70
	(ii)	32	26	37
5	(i)	82	33	58
	(ii)	47	19	34
10	(i)	80	64	61
	(ii)	39	31	30
L.S.D. for P levels at Prob. < 0.05		1.8	5.3	1.8

(b) Total inorganic and organic P expressed as (i) levels and as (ii) percentage of total P.

Cycles		Total P	Inorg. P	Org. P
1	(i)	375	191	184
	(ii)		51	49
5	(i)	375	173	202
	(ii)		46	54
10	(i)	375	205	170
	(ii)		55	45
L.S.D. for P levels at Prob. < 0.05			6.4	6.4

FIGURE 8

Effects of varying cycles of wetting and drying on the mode of fixation of P in Dacca soil treated initially with water-soluble phosphate (200 ppm P, on the dry soil basis, as $Ca(H_2PO_4)_2.H_2O$).
(Results in ppm P on dry soil basis; L.S.D. at Prob. < 0.05)



it is suggested that in the present experiment Ca-P was immobilized when soil moisture content was relatively high whilst Fe-P was immobilized during the middle stages of the drying cycle when the moisture content was relatively low.

During the mineralization phase which occurred during the last 5 cycles of wetting and drying the mineralized P accumulated virtually entirely as Fe-P. This is in contrast to the results obtained in Expt. 1 where mineralized P occurred mainly as Ca-P and to a lesser extent as Al- and Fe-P. The difference in the forms of mineralized P between the two experiments indicates that where soil moisture content falls to low levels, as in the present experiment, the Fe-fixing sites are more active than the Ca- or Al-fixing sites for phosphates.

The greater tendency for mineralized phosphate to be fixed as Fe-P in this experiment compared with the other experiment may also have been due to the higher temperature used in this experiment ($50^{\circ}C$ compared with $30^{\circ}C$ in Expt. 1).

SUMMARY

Original Dacca soil (pH 5.3) was treated with 200 ppm water-soluble phosphate P and the mode of fixation of added phosphate was determined after 1, 5 and 10 cycles of wetting (50% mwhc) and drying ($50^{\circ}C$).

During the first 5 cycles of wetting and drying there was a decrease in inorganic P accounted for as Fe- and Ca-P whilst Al-P increased slightly. During the last 5 cycles there was an increase in total inorganic P accounted for almost entirely by an increase in Fe-P.

CHAPTER VI

COMPARISON OF DIFFERENT "AVAILABILITY" EXTRACTANTS FOR ASSESSING THE P STATUS OF DACCA SOIL, AND THE EFFECTS OF INCUBATION WITH ORGANIC MATERIALS.

Experiment 6 :

Effects of addition of compost and grass on changes in P levels, as determined by four "availability" extractants, during incubation of Dacca soil.

Experiment 7 :

Changes in P levels (as determined by three "availability" extractants) during incubation, after addition of water-soluble phosphate, of Dacca soil previously held moist for eight months after treatment with straw and compost.

Experiment 8 :

Effect of pH of Dacca soil on the extent of inorganic P fixation and the proportions of fixed inorganic P removed by three "availability" extractants.

CHAPTER VI

EXPERIMENT 6

EFFECTS OF ADDITION OF COMPOST AND GRASS ON CHANGES IN P LEVELS, AS DETERMINED BY FOUR "AVAILABILITY" EXTRACTANTS, DURING INCUBATION OF DACCA SOIL.

The main purpose of this experiment was to compare the levels of phosphorus obtained by four "availability" extractants during incubation of Dacca soil. The superimposed treatments were the addition of compost and grass to the soil followed by an equilibration period before incubation started.

METHODS

Bulk samples of Dacca soil were treated with 2% w/w levels of finely ground compost and grass (see Chap. II). 10 g portions of treated and control soils were placed in incubation tubes and wetted to 50% mwhc. Sufficient tubes of each treatment were set up to allow for analysis in duplicate after being held for 4 weeks (this equilibration period represents zero incubation) and also after further 4 and 8 weeks of incubation at 30°C.

The barium peroxide method was used for aeration and adsorption of CO_2. After each period the soils were air-dried and suitable aliquots of each were extracted with (i) 0.2N H_2SO_4, (ii) Morgan's reagent, (iii) Truog's reagent and (iv) 0.5M $NaHCO_3$ (pH 8.5). The reagents and the methods of analysing the extracts for phosphorus are described in Chapter II.

RESULTS

Results are shown in Table 13 for extractable P levels (ppm P on soil basis) in the control and treated soils, the effects of compost and grass initially and after 4 and 8 weeks of incubation, and the net effects of compost and grass after 4 and 8 weeks of incubation (zero incubation values subtracted from 4- and 8-week incubation values). The net effects of compost and grass are also shown in Figure 9.

When the soil was incubated without addition of organic materials, there was no change in 0.2N H_2SO_4-P levels; Morgan-P levels decreased slightly with time, whilst Truog-P and 0.5M $NaHCO_3$-P levels increased to 4 weeks and decreased to approximately the original values after 8 weeks.

The net effects of compost was to increase 0.2N H_2SO_4-P after 4 weeks but this effect disappeared after 8 weeks. Grass had no effect up to 4 weeks but increased 0.2N H_2SO_4-P up to 8 weeks.

Both compost and grass increased Morgan-P up to 4 weeks and there was a further increase due to grass, but not due to compost, up to 8 weeks.

After 4 weeks Truog-P was decreased to a greater extent by grass than by compost. During 4 to 8 weeks Truog-P increased due to both treatments; the 8-week P value due to compost was greater, whilst that due to grass was less, than the initial value.

After 4 weeks of incubation 0.5M $NaHCO_3$-P was increased to the same extent by grass and compost. After 8 weeks the P level due to grass decreased slightly whilst that due to compost decreased to a somewhat greater extent.

TABLE 13

Effects of compost and grass on P levels, as determined by four "availability" extractants, during incubation (30°C, 50% mwhc) of Dacca soil.

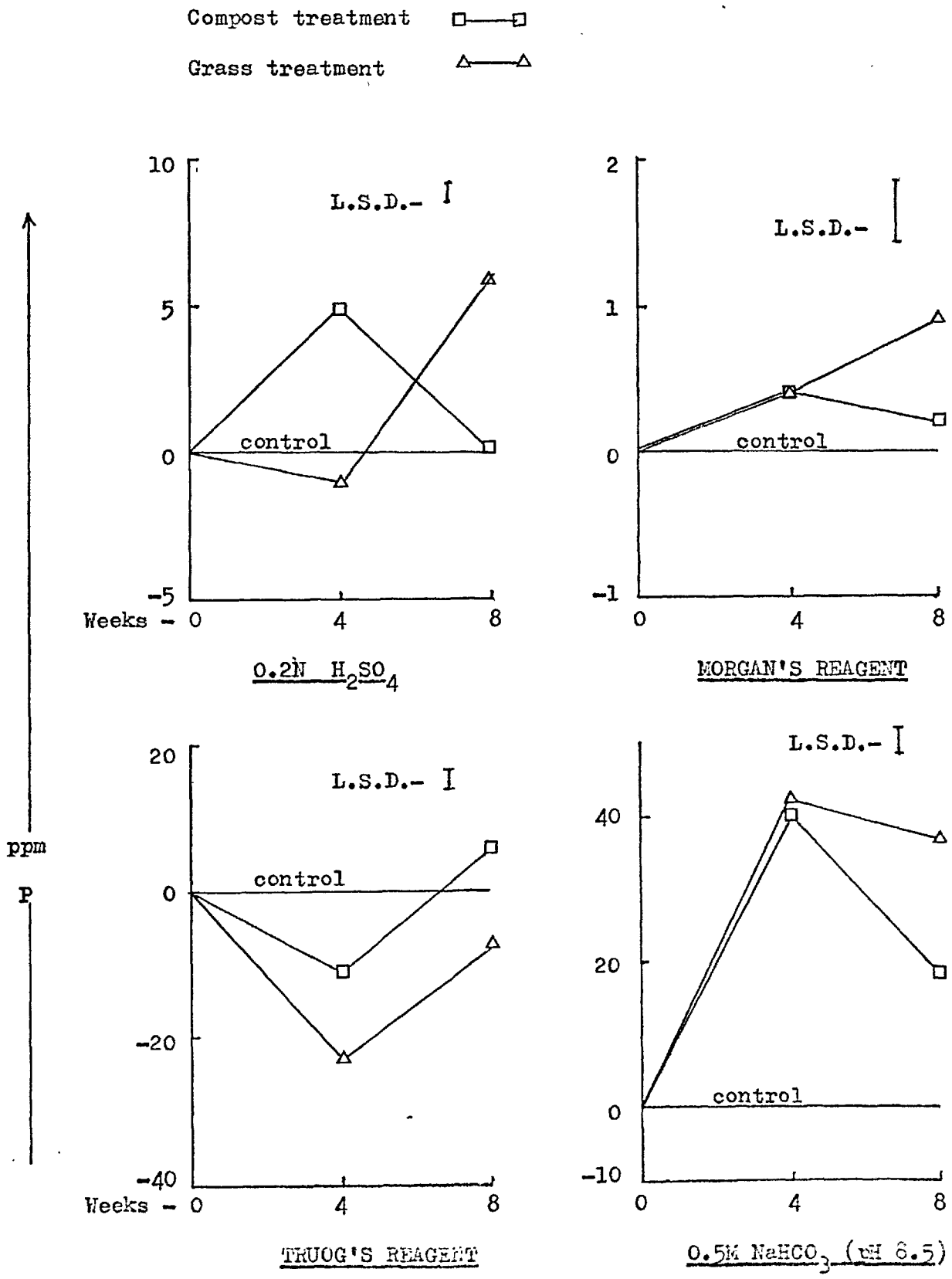
(Results in ppm P on dry soil basis)

Treatment	Weeks of incubation 0	4	8	L.S.D. at Prob.<0.05
0.2N H_2SO_4				
Soil only	12.0	11.5	12.6	
Soil + compost	21.5	25.9	22.2	
Effect of compost	9.5	14.4	9.6	
Net effect of compost *	-	4.9	0.1	2.1
Soil + grass	31.5	30.0	38.0	
Effect of grass	19.5	18.5	25.4	
Net effect of grass *	-	-1.0	5.0	
Morgan's reagent				
Soil only	2.5	2.0	1.8	
Soil + compost	1.6	1.5	1.1	
Effect of compost	-0.9	-0.5	-0.7	
Net effect of compost *	-	0.4	0.2	0.4
Soil + grass	2.1	2.0	2.3	
Effect of grass	-0.4	0.0	0.5	
Net effect of grass *	-	0.4	0.9	
Truog's reagent				
Soil only	12.0	20.0	8.0	
Soil + compost	10.0	7.0	12.0	
Effect of compost	-2.0	-13.0	4.0	
Net effect of compost *	-	-11.0	6.0	2.5
Soil + grass	20.0	5.0	8.8	
Effect of grass	8.0	-15.0	0.8	
Net effect of grass *	-	-23.0	-7.2	
0.5M $NaHCO_3$ (pH 8.5)				
Soil only	26.0	47.0	28.7	
Soil + compost	9.0	70.0	30.0	
Effect of compost	-17.0	23.0	1.3	
Net effect of compost *	-	40.0	18.3	3.6
Soil + grass	6.4	69.5	46.0	
Effect of grass	-19.6	22.5	17.3	
Net effect of grass *	-	42.1	36.9	

* Zero incubation values subtracted from 4- and 8-week incubation values.

FIGURE 9

Net effects of compost and grass on P levels, as determined by four "availability" extractants, during incubation (30°C, 50% mwhc) of Dacca soil. (Results are in ppm P on dry soil basis; L.S.D. at Prob.<0.05



DISCUSSION

It is seen that the net effect of compost on extractable P levels during incubation showed a similar pattern for 0.2N H_2SO_4, Morgan's reagent and 0.5M $NaHCO_3$; there was an increase to 4 weeks followed by decrease to 8 weeks. The Truog reagent, however, showed a decreased effect to 4 weeks followed by an increase to 8 weeks.

The main similarity among the four extractants with respect to the net effects of grass on extractable P was that these were higher after 8 weeks than initially for all extractants except Truog's reagent. The Truog reagent showed a net depressing effect of grass on extractable P.

Compost is a relatively stable material and probably underwent little microbial decomposition during incubation. Cornfield (1959) found that a similar type of compost caused relatively small changes in nitrogen levels during incubation after addition to soil. Grass, on the other hand, contains decomposable carbohydrate materials and during its decomposition phosphate could be immobilized. After decomposition of carbohydrate remineralization of phosphate could take place. Cornfield (1959) noted similar effects with nitrogen due to grass decomposition in soil. The immobilization of phosphate during the first 4 weeks of incubation with grass followed by remobilization during the last 4 weeks was noted only where 0.2N H_2SO_4 and Truog's reagent were used.

The differences among the reagents with respect to the pattern of extractable phosphate is probably due to differences in forms and amounts of phosphate extracted by the different reagents. 0.5M $NaHCO_3$ on average extracted more P from the treated and untreated

soils than did the other reagents whislt Morgan's reagent extracted the least P. 0.2N H_2SO_4 and Truog's reagent extracted intermediate amounts, except that 0.2N H_2SO_4 tended to extract more P than did Truog's reagent from the treated soils. The nature of the inorganic P forms will be considered in the next experiment.

SUMMARY

The effects of addition of 2% ground compost and grass to Dacca soil (pH 5.3) on changes in P levels, as determined by four "availability" extractants, were studied over 8 weeks of incubation (30°C, 50% mwhc) following a 4-week equilibration period.

The net effects of compost on extractable P after 4 and 8 weeks of incubation were similar for 0.2N H_2SO_4, Morgan's reagent and 0.5M $NaHCO_3$ (pH 8.5), although the magnitude of the effects differed among the three reagents; extractable P increased to 4 weeks and decreased to 8 weeks. The Truog reagent showed a net depressing effect of compost on availiable P to 4 weeks followed by slight increases to 8 weeks.

The net effects of grass on extractable P differed among the four reagents. 0.2N H_2SO_4-P increased only during the last 4 weeks. Morgan-P increased to 4 weeks and further to 8 weeks. Truog-P decreased to 4 weeks, and although it increased again to 8 weeks, there was still a slight negative effect. 0.5M $NaHCO_3$-P increased to 4 weeks and decreased slightly to 8 weeks.

EXPERIMENT 7

CHANGES IN P LEVELS (AS DETERMINED BY THREE "AVAILABILITY" EXTRACTANTS) DURING INCUBATION, AFTER ADDITION OF WATER-SOLUBLE PHOSPHATE, OF DACCA SOIL PREVIOUSLY HELD MOIST FOR EIGHT MONTHS AFTER TREATMENT WITH STRAW AND COMPOST.

The present experiment [redacted] differed from the previous one (Expt. 6) in that the organic materials added were allowed to decompose under moist aerobic conditions for 8 months before the samples were set up for incubation. In addition, water-soluble phosphate was added immediately before incubation. This experiment was concerned with the residual effects of previous organic material treatments on subsequent changes in "available" levels of added phosphate. The soil samples from Experiment 2, where inorganic P forms (Al-, Fe- and Ca-P) were determined, were used in the present experiment, so that it was possible to asses the forms of inorganic phosphorus removed by the "availability" extractants.

METHODS

The materials used in this experiment were the same as those used in Expt. 2, in which changes in inorganic and organic P forms were determined during incubation of Dacca soil which had been treated with 2% w/w straw and compost (plus 100 ppm urea-N) and held moist for 8 months before being subjected to incubation immediately after addition of 400 ppm P as $Ca(H_2PO_4)_2.H_2O$. Suitable portions of the same samples, which in Expt. 2 were analysed for inorganic and organic P forms initially and after each incubation period, were used in the present experiment for determining P levels as

assessed by three "availability" extractants (Truog's reagent, Morgan's reagent and 0.5M $NaHCO_3$ (pH 8.5)).

RESULTS

Results are shown in Table 14 for extractable P levels (ppm P on soil basis) in the control and treated soils, the effects of straw and compost after 0, 3, 6 and 12 weeks of incubation after addition of water-soluble phosphate, and the net effects of straw and compost after 3, 6 and 12 weeks of incubation (zero incubation values subtracted from 3-, 6- and 12-week incubation values). The net effects of straw and compost are also shown in Figure 10.

IMMEDIATE EFFECTS OF ORGANIC MATTER TREATMENTS ON P LEVELS

The immediate effects of previous organic material treatments, it must be remembered (Expt. 2), were in fact determined after a period of 24 hours of moist contact in order to allow the main chemical changes to occur. The effect of straw treatment was to decrease and of compost treatment to increase Truog-P. Straw had no effect on, whilst compost slightly increased, 0.5M $NaHCO_3$-P. Both straw and compost increased Morgan-P.

NET EFFECTS OF ORGANIC MATTER TREATMENTS AFTER VARIOUS PERIODS OF INCUBATION.

The net effect of straw was to increase Truog-P with incubation up to 6 weeks, with little further change to 12 weeks. The net effects of compost was to decrease Truog-P to 3 weeks, increase it to 6 weeks and to have no further effect to 12 weeks. Straw had a considerably greater net effect in increasing Truog-P than did compost.

TABLE 14

Effect of previous treatments with straw and compost on P levels, as determined by three "availability" extractants, of Dacca soil, recieving 400 ppm water-soluble phosphate just before incubation (30°C, 50% mwhc).

(Results in ppm P on dry soil basis)

Treatment	Weeks of incubation 0	3	6	12
Truog's reagent				
Soil only	307	125	80	44
Soil + straw	265	146	140	96
Effect of straw	-42	21	60	52
Net effect of straw *	—	63	102	94
Soil + compost	341	136	150	120
Effect of compost	33	11	70	76
Net effect of compost *	—	-22	37	43
L.S.D. at Prob. < 0.05 = 14				
Morgan's reagent				
Soil only	48	8	5	3
Soil + straw	72	12	8	5
Effect of straw	24	4	3	2
Net effect of straw *	—	-20	-21	-22
Soil + compost	79	9	10	6
Effect of compost	31	1	5	3
Net effect of compost *	—	-30	-26	-28
L.S.D. at Prob. < 0.05 = 2				
0.5M $NaHCO_3$ (pH 8.5)				
Soil only	182	107	100	51
Soil + straw	186	132	142	77
Effect of straw	4	25	42	26
Net effect of straw *	—	21	38	22
Soil + compost	194	140	165	98
Effect of compost	12	33	65	47
Net effect of compost *	—	21	53	35
L.S.D. at Prob. < 0.05 = 6				

* Zero incubation values subtracted from 3-, 6- and 12-week incubation values.

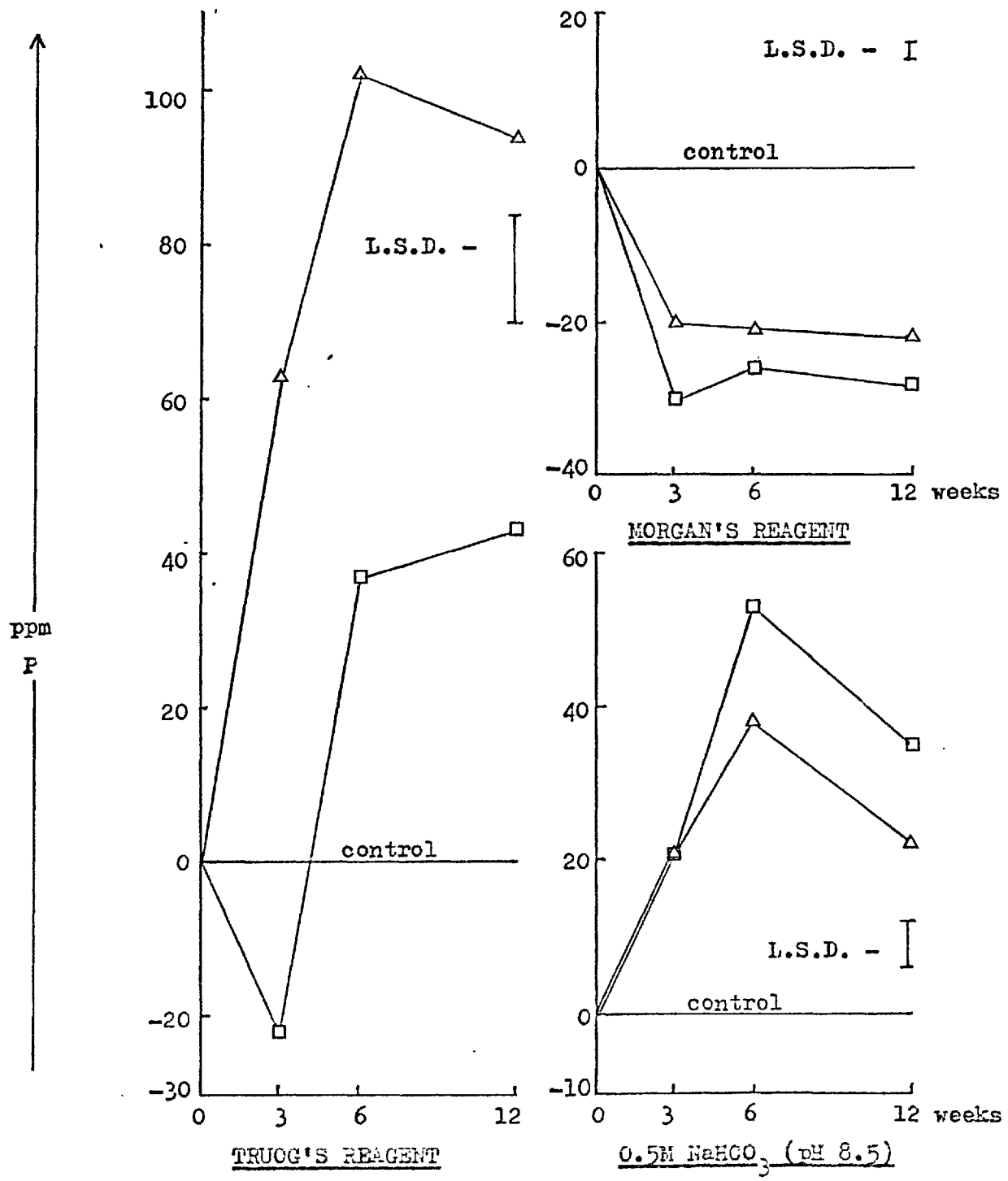
FIGURE 10

Net effects of previous treatments with straw and compost on P levels, as determined by three "availability" extractants, of Dacca soil recieving 400 ppm water-soluble phosphate-P just before incubation.

(Results in ppm P on dry soil basis; L.S.D. at Prob. <0.05)

Straw treatment - △——△

Compost treatment - □——□



The net effect of straw was to decrease Morgan-P to 3 weeks with little further change up to 12 weeks. The net effect of compost was to decrease Morgan-P to a slightly greater extent after 3 than after 6 or 12 weeks. Compost had a slightly greater effect in decreasing Morgan-P than did straw.

Both straw and compost had a greater net effect in increasing 0.5M $NaHCO_3$-P after 6 than after 12 weeks. The effects of compost after 6 and 12 weeks were somewhat greater than those of straw.

RELATIONSHIPS BETWEEN "AVAILABLE" P LEVELS AND INORGANIC P FORMS

Linear correlation coefficients (r) were calculated between the P levels obtained with each of the "availability" extractants and the levels of Ca-, Fe- and Al-P obtained from Expt. 2 (Chap. IV). Zero incubation values were excluded from these calculations since it is seen from the results mentioned above (Table 14) that these values were usually so much higher than those obtained after the three incubation periods that inclusion of these would obscure the more important relationships occurring during incubation.

Correlation coefficients (r) are shown below in Table 15.

TABLE 15

	Truog-P vs.	Morgan-P vs.	0.5M $NaHCO_3$-P vs.
Ca-P	0.609	0.551	0.517
Fe-P	-0.500	-0.236	-0.305
Al-P	0.755*	0.632	0.706*

"r" required for significance at Prob. $< 0.05 = 0.666$*

It is seen that highest correlation coefficients with all three available forms of P were obtained with Al-P. The correlations

of Truog- and 0.5M $NaHCO_3$-P with Al-P was significant at Prob. <0.05. The correlation between Morgan-P and Al-P was almost significant at Prob. <0.05. The correlations with Ca-P were all positive and although of reasonable magnitude were not significant. All correlations with Fe-P were negative and nonsignificant and only the Fe-P correlation with Troug-P was of reasonable magnitude.

DISCUSSION

A comparison of the effects of straw and compost on available P levels using the three extractants (Table 14) with their effects on inorganic P forms (Table 7 or Fig. 4 of Expt. 2) initially (zero incubation) shows that, in general, the changes in available P forms due to the organic material treatments were not reflected in the changes in the three forms of inorganic P. This indicates that the use of these "availability" extractants very soon after the application of water-soluble phosphate could give inconsistent indications of the inorganic forms of P present. This is also shown up in the considerable decreases during the first three weeks of incubation in all available forms of P, but particularly in Truog- and Morgan-P, in the control and treated soils. In distinct contrast to this, all inorganic P forms increased during the first three weeks of incubation. During this early stage of incubation a complex series of chemical and microbiological changes, involving mineralization and immobilization processes, are occurring. The overall changes occurring in the inorganic P forms were not reflected in the P levels as determined by any of the availability extractants. A practical implication of this is that the available P levels as

determined by chemical extractants should not be used for the soil until time has been given for some measure of chemical and microbiological equilibrium to be attained.

A comparison of the net effects of straw and compost on P levels after each incubation period as determined by the three "availability" extractants showed very considerable differences due to the type of extractant. The Morgan reagent indicated that both straw and compost decreased P levels after all periods of incubation. Truog's reagent and 0.5M $NaHCO_3$ increased P levels, except after 3 weeks with the compost treatment with Truog's reagent. In addition, whereas Truog's reagent indicated a higher net effect of straw than of compost in increasing P levels, the reverse applied to 0.5M $NaHCO_3$.

The significant or almost significant correlations obtained between Al-P and the three forms of "available" P indicates that Al-P is the main form extracted by the three reagents. The somewhat lower correlations with Ca-P were, however, of sufficient magnitude to indicate that this form of P was also being extracted to some extent by the three reagents. On the other hand, the negative and generally low correlations with Fe-P suggest that this form of P is not being extracted by the three "availability" reagents.

The above results indicate that the available forms of P in this soil are determined mainly by the Al-P content and to a lesser extent by the Ca-P content, but were not affected by the Fe-P content. The only suitable indicator of P availability is that which is absorbed by plants. When this particular soil is brought into cultivation, it will be necessary to compare the results obtained

for P uptake in field trials in response to various levels of applied phosphate fertilizers with the levels of P obtained by various availability extractants. In this way it would be possible to determine which would be the most siutable extractant for general use in the area for indicating the phosphate status of the soil.

A comparison of the net effects of compost in the present and the previous experiments(this was the only organic material treatment common to both experiments) show that 0.5M $NaHCO_3$ was the only extractant which indicated similar positive net effects on extractable P. The Morgan and Truog reagents indicate net positive effects in one and net negative effects in the other experiment. This suggests that 0.5M $NaHCO_3$ is likely to be the most suitable indicator of P availability in Dacca soil.

SUMMARY

Dacca soil was treated with 2% ground straw and compost and the treated and control soils were held moist for 8 months after addition of 100 ppm urea-N. After air-drying the soils were incubated for up to 12 weeks after addition of 400 ppm P as $Ca(H_2PO_4)_2.H_2O$ and P determined using three "availability" extractants.

There were net increases in Truog- and 0.5M $NaHCO_3$-P to 6 weeks due to the previous straw treatment, follwed by slight decreases to 12 weeks. The net effect of straw on Morgan-P was to decrease it to same extent after all periods of incubation.

Compost decreased Truog-P to 3 weeks, but increased it

considerably to 6 weeks and slightly more to 12 weeks. Compost decreased Morgan-P to about the same extent after all periods of incubation. Compost increased 0.5M $NaHCO_3$-P after 6 weeks, but decreased it somewhat after 12 weeks.

Linear correlation coefficients were calculated between P levels obtained for each of the three availability extractants and the levels of Ca-, Fe- and Al-P obtained in Expt. 2 (Chap. IV) using the values obtained after all incubation periods. Al-P was significantly correlated (Prob. <0.05) with Truog-P and 0.5M $NaHCO_3$-P and almost significantly correlated with Morgan-P. Ca-P was positively, though not significantly, correlated, whilst Fe-P was negatively, but not significantly, correlated with the three forms of available P.

EXPERIMENT 8

EFFECT OF pH OF DACCA SOIL ON THE EXTENT OF INORGANIC P FIXATION AND THE PROPORTIONS OF FIXED INORGANIC P REMOVED BY THREE "AVAILABILITY" EXTRACTANTS.

METHODS

10 g portions of soil were shaken with 0.2, 0.5 and 1.0% $CaCO_3$ and 20 ml of water for 24 hours. A control soil without $CaCO_3$ was treated in the same way. After centrifuging and pouring off the supernatant liquid the residual soils were allowed to air-dry. All soils were then shaken for 48 hours with 20 ml of a solution containing monocalcium phosphate to supply 10,000 ppm P on the soil basis. pH was determined, the suspensions were then centrifuged and the supernatant liquid poured off. The soils were then washed once, with centrifuging, with 20ml of water and were then air-dried and ground to pass through a 2 mm sieve. Each soil was analysed for total inorganic P by extraction with 0.5N H_2SO_4 (2 hour extraction) and for "available" P by the Truog and Morgan reagents and 0.5M $NaHCO_3$ (pH 8.5).

RESULTS AND DISCUSSION

Table 16 (overleaf) shows results for (a) ppm P levels on dry soil basis as determined by the four extractants and (b) "available" P as percentage of total inorganic P for the three "availability" extractants.

The extent of inorganic P fixation by the soil increased slightly with pH. The proportion of the applied inorganic P which

TABLE 16

% $CaCO_3$ (w/w)	pH		Total inorganic P	Truog's reagent	Morgan's reagent	0.5M $NaHCO_3$ (pH 8.5)
0.0	5.0*	(a)**	2,000	274	11.2	330
		(b)**		13.7	0.56	16.6
0.2	5.9	(a)	2,100	360	14.3	330
		(b)		17.6	0.67	15.7
0.5	6.5	(a)	2,400	390	33.3	360
		(b)		16.3	1.40	15.0
1.0	6.6	(a)	2,440	404	39.0	380
		(b)		16.5	1.60	15.5

* Original soil; ** See text.

was fixed by the soil ranged from 20.0% at pH 5.0 to 24.4% at pH 6.6. Morgan-P levels were very much lower than Truog-P and 0.5M $NaHCO_3$-P levels. Morgan-P levels increased with pH and showed a 3.5-fold increase from pH 5.0 to 6.6. Truog- and 0.5M $NaHCO_3$-P levels also increased with pH, but the extent of increase was much less compared with Morgan-P (1.47-fold for Truog-P and 1.15-fold for 0.5M $NaHCO_3$-P). Morgan-P as a percentage of total inorganic P increased 2.9-fold over the whole pH range. Truog-P as a percentage of total inorganic P increased slightly from pH 5.0 to 5.9 but changed little at higher pH levels. o.5M $NaHCO_3$-P as a percentage of total inorganic P was similar at all pH levels.

It is seen that the capacity of Dacca soil to fix applied phosphate in inorganic forms was increased only slightly by raising the pH of the soil. This is in agreement with the results obtained in Chap. III (Table 2), where increasing pH of Dacca soil to 6.5 had no effect on the proportion of inorganic P fixed when the soil was treated with 1,000 ppm phosphate-P. It is seen that the

proportion of inorganic P extracted by Morgan's reagent was much less than those extracted by the other two availability extractants. This is no reflection on the suitability of Morgan's reagent for determining the P-status of soils. Workers in temperate regions, where Morgan's reagent has been widely used as a measure of soil P availability, have shown that it is satisfactory in spite of its ability to remove only a small proportion of the available P. The usual practice to allow for this was to apply some correction factor.

Both Truog's reagent and 0.5M $NaHCO_3$ extracted approximately the same proportions of inorganic P. These proportions were little affected by pH, indicating that the nature of the inorganic P forms extracted by these reagents were similar at all pH levels. On the other hand, the increased proportion of total inorganic P extracted by Morgan's reagent with increasing soil pH indicates that this reagent extracts different forms of P in relation to pH.

SUMMARY

Dacca soil of original pH and at higher pH levels, obtained by shaking with water and varying amounts of $CaCO_3$, was shaken for 48 hours with 10,000 ppm P as $Ca(H_2PO_4)_2.H_2O$ and the residual soils were then extracted with 0.5N H_2SO_4 (to determine the total inorganic P fixation) and also with three "availability" reagents.

The proportions of applied water-soluble inorganic P fixed as total inorganic P by the soils increased with pH (5.0 to 6.6) and ranged from 20.0 to 24.4%. Morgan-P levels increased with pH, showing a 3.5-fold increase. Morgan-P as a percentage of total

inorganic P increased 2.9-fold with pH, whilst Truog- and 0.5M $NaHCO_3$-P as percentages of total inorganic P showed relatively small changes with pH.

CHAPTER VII

Experiment 9 :

Changes in available P (0.5M $NaHCO_3$ (pH 8.5) extraction) during incubation of Dacca soil of different pH levels treated initially with monocalcium phosphate (200 ppm P) and the effects of addition of 1% straw, sewage sludge and cellulose.

CHAPTER VII

EXPERIMENT 9

CHANGES IN AVAILABLE P (0.5M $NaHCO_3$ (pH 8.5) EXTRACTION) DURING INCUBATION OF DACCA SOIL OF DIFFERENT pH LEVELS TREATED INITIALLY WITH MONOCALCIUM PHOSPHATE (200 PPM P) AND THE EFFECTS OF ADDITION OF 1% STRAW, SEWAGE SLUDGE AND CELLULOSE.

This experiment reports on changes occurring in levels of 0.5M $NaHCO_3$-extractable P (available P) over 20 weeks of aerobic incubation of Dacca soil (at its original pH of 5.3 as well as after previous adjustment to pH 6.5 and 7.7) treated with $Ca(H_2PO_4)_2.H_2O$ at 200 ppm P just before incubation. The methods and materials used were the same as those in Expt. 1 (Chap. 1) so that it was possible to determine the relationship between available P and each inorganic P form (Al-, Fe- and Ca-P) after each incubation period. In addition, the effects of addition of 1% levels of straw, sewage sludge and cellulose were also determined.

METHODS

Details of materials and methods used are described in Expt. 1 (Chap. IV). Initially and after each incubation period suitable portions of soils were extracted with 0.5M $NaHCO_3$ (pH 8.5).

RESULTS

In this experiment the expression "available" P will be used to refer to 0.5M $NaHCO_3$-extractable P. Results are given on the air-dry soil basis.

Table 17 shows, for soils of each pH, results for available P levels in the control and treated soils, the effects of organic materials after 0, 6, 12 and 20 weeks of incubation, and the net effects of organic materials after 6, 12 and 20 weeks (zero incubation values subtracted from 6-, 12- and 20-week incubation values). The net effects of organic materials are also shown in Figure 11.

CONTROL SOILS (SOILS NOT TREATED WITH ORGANIC MATERIALS)

Available P at zero incubation was higher at pH 6.5 and 7.7 than at pH 5.3.

At pH 5.3 available P decreased considerably to 6 weeks, increased slightly to 12 weeks and showed little change to 20 weeks. At pH 6.5 and 7.7 available P decreased considerably to 6 weeks, increased slightly to 12 weeks and decreased again to 20 weeks. The decrease in available P during incubation were greater at pH 6.5 and 7.7 than at pH 5.3.

NET EFFECTS OF ORGANIC MATERIAL TREATMENTS AFTER VARIOUS PERIODS OF INCUBATION

Net effect of straw

At pH 5.3 the net effect of straw was to decrease available P to 6 weeks, but there was no further change to 12 or 20 weeks. At pH 6.5 straw decreased available P to 6 weeks, had no further effect to 12 weeks, but decreased it even more to 20 weeks. At pH 7.7 straw increased available P to 6 weeks, decreased it to less than its initial value at 12 weeks and increased it again to somewhat more than its initial value to 20 weeks.

Net effect of sewage sludge

At pH 5.3 the net effect of sewage sludge was to increase

TABLE 17

Changes in available P (0.5M $NaHCO_3$ (pH 8.5) extraction) during incubation of Dacca soil of different pH treated initially with monocalcium phosphate (200 ppm P) and the effects of addition of 1% straw, sewage sludge and cellulose.

(Results in ppm P on dry soil basis)

Treatment	Weeks of incubation 0	6	12	20
pH 5.3				
Soil only	106	25	42	45
Net effect *	-	-81	-64	-61
Soil + straw	120	25	43	46
Effect of straw	14	0	1	1
Net effect of straw *	-	-14	-13	-13
Soil + sewage sludge	114	47	70	75
Effect of sewage sludge	8	22	28	30
Net effect of sewage sludge *	-	14	20	22
Soil + cellulose	114	34	57	39
Effect of cellulose	8	9	15	-6
Net effect of cellulose *	-	1	7	-14
pH 6.5				
Soil only	160	45	54	43
Net effect *	-	-115	-106	-117
Soil + straw	175	46	54	35
Effect of straw	15	1	0	-8
Net effect of straw *	-	-14	-15	-23
Soil + sewage sludge	125	45	63	36
Effect of sewage sludge	-35	0	9	-7
Net effect of sewage sludge *	-	35	43	28
Soil + cellulose	116	22	44	20
Effect of cellulose	-44	-23	-10	-23
Net effect of cellulose *	-	21	34	21
pH 7.7				
Soil only	164	36	57	51
Net effect *	-	-128	-107	-113
Soil + straw	152	40	35	47
Effect of straw	-12	4	-22	-4
Net effect of straw *	-	16	-10	8
Soil + sewage sludge	201	52	73	75
Effect of sewage sludge	37	16	16	24
Net effect of sewage sludge *	-	-21	-21	-13
Soil + cellulose	169	18	45	36
Effect of cellulose	5	-18	-12	-15
Net effect of cellulose *	-	-23	-17	-20

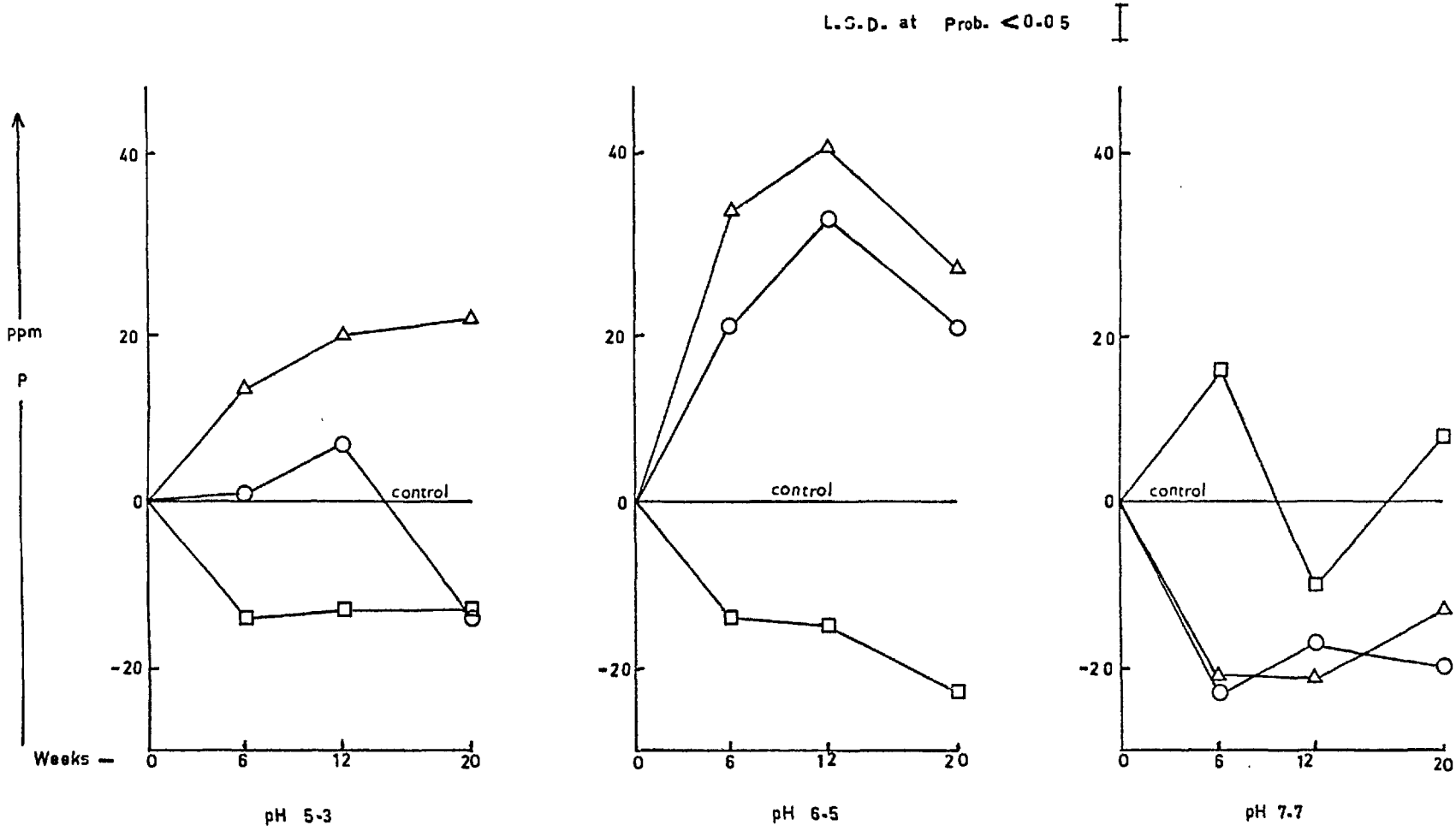
L.S.D. at Prob. <0.05 = 4.5 ppm P

* Zero incubation values subtracted from 6-, 12- and 20-week incubation values.

FIGURE 11

Net effects of organic materials during incubation of Dacca soil of varying pH, treated with 200 ppm P as monocalcium phosphate. (Results are in ppm P on dry soil basis)

Straw □——□ ; Sewage sludge △——△ ; Cellulose ○——○ .



available P up to 12 weeks, with no further change to 20 weeks. At pH 6.5 sewage sludge increased available P after all periods of incubation with the maximum effect occurring at 12 weeks. At pH 7.7 sewage sludge decreased available P after all periods of incubation with slightly greater effects occurring after 6 and 12 weeks.

Net effect of cellulose

At pH 5.3 cellulose had no effect on available P up to 6 weeks, increased it slightly to 12 weeks and decreased it somewhat to 20 weeks. At pH 6.5 cellulose increased available P after all periods of incubation, with the maximum effect after 12 weeks. At pH 7.7 cellulose decreased available P to 6 weeks and there were only slight further changes to 12 or 20 weeks.

RELATIONSHIP BETWEEN AVAILABLE P AND INORGANIC P FORMS

Linear correlation coefficients (r) were calculated between available P and levels of Al-, Fe- and Ca-P obtained in Expt. 1 (Chap. IV). Zero incubation values were excluded from these calculations since it was seen from the results mentioned above (Table 17) that these values were usually so much higher than those obtained after three incubation periods that inclusion of these would obscure the relationships occurring during incubation.

Correlation coefficients (r) at each pH level are shown below in Table 18.

TABLE 18

	pH 5.3	pH 6.5	pH 7.7
Al-P	0.844**	0.415	0.584*
Fe-P	0.369	-0.126	0.550
Ca-P	0.927**	0.377	0.638*

'r' required for significance at Prob.$<$0.01 = 0.708**
Prob.$<$0.05 = 0.576*

It is seen that at pH 5.3 very high correlations (significant at Prob.$<$0.01) were obtained between available P and both Al- and Ca-P, whilst Fe-P was poorly correlated with available P. At pH 6.5 there were generally poor correlations between available P and all three inorganic P forms. At pH 7.7 available P was significantly (Prob.$<$ 0.05) correlated with both Al- and Ca-P but not with Fe-P, although this correlation was slightly lower than that with Al-P.

DISCUSSION

CONTROL SOILS (SOILS NOT TREATED WITH ORGANIC MATERIALS)

It must be remembered that zero incubation values were determined 24 hours after moist contact of soil with added water-soluble phosphate. It is seen that available P at zero incubation was considerably lower at pH 5.3 than at pH 6.5 and 7.7. This is in contrast to the levels of total inorganic P ((Al + Fe + Ca)-P) obtained during fractionation (Table 5, Expt. 1), which at zero incubation was slightly higher at pH 5.3 than at the two higher pH levels. It is worth noting that at pH 6.5 and 7.7 the available P levels were very nearly equal to the sum of the Al- and Ca-P levels, whereas at pH 5.3 available P was less than the sum of the two forms.

The greater decrease in available P during the first 6 weeks of incubation at pH 6.5 and 7.7 than at pH 5.3 indicated greater fixation at the two higher pH levels. This is in contrast to changes in the three inorganic forms of P (Fig. 3, Expt. 1) where the greatest decrease in Ca-P during this period occurred at pH 5.3 and there were little differences due to pH in the changes in Al- and Fe-P. With incubation beyond 6 weeks the relatively small changes

in available P at all pH levels were not related to any particular inorganic form of P.

NET EFFECTS OF ORGANIC MATERIALS

The net effects of the added organic materials on available P at each pH during incubation can be considered in relation to the main types of changes which can occur during decomposition of these materials in the soil. These include (1) their effects on chemical fixation of added water-soluble inorganic phosphate, (2) immobilization, which would tend to occur early in incubation, and (3) mineralization, which would tend to occur later in incubation. The net effects of these materials would depend on their total P content; cellulose (containing no P) and straw (containing only 0.1% P) would be expected to have net negative effects on available P, whilst sewage sludge containing 0.81% P would be expected to have a net positive effect. Fuller et al. (1956) found that the critical level of P in carbonaceous materials which determine whether mineralization or immobilization would occur was approximately 0.2%.

Considering the net effects of the added organic materials obtained in this experiment (Fig. 11) the main point to note is the general similarity at pH 5.3 and 6.5, whilst at pH 7.7 considerably different results were obtained.

The net negative effects of straw on available P at pH 5.3 and 6.5 is what would be expected since the P content of straw (0.10%) is less than the critical value of 0.2% and immobilization should occur. At pH 7.7, however, the rather erratic effects of straw (a net positive effect to 6 weeks followed by a net negative effect to 12 weeks and a net positive effect again after 20 weeks)

is difficult to explain. It may be that early in incubation the easily decomposable (soluble) constituents of straw were being decomposed rapidly resulting in the production of carbonic acid and organic acids which had a solubilizing effect on native inorganic P which was in excess of the immobilizing effect on P of the micro-organisms responsible. During the 6-12 week period, by which time the cellulose constituents of straw were decomposing, immobilization exceeded solubilization resulting in a net negative effect in P availability. By 12 weeks most of the straw had probably decomposed and during the 12-20 week period initially immobilized P was mineralizing again, resulting in a net positive effect. It is seen that there was no tendency for remineralization of phosphorus during the later period of incubation where straw was added at pH 5.3 and 6.5. This is possibly the reflection of the higher microbial activity at pH 7.7 than at the lower pH levels.

Sewage sludge had a positve net effect on available P after all periods of incubation at pH 5.3 and 6.5, but had a negative effect after all periods at pH 7.7. The results obtained at the lower pH levels are what might be expected since the P content of sewage sludge is well above the critical level of 0.2% and a net mineralization would be expected. The net negative effect of sewage sludge at pH 7.7 is probably due to the fixation of phosphate as highly insoluble and hence unavailable hydroxyapatite and/or chloroapatite.

The generally small net effect of cellulose on available P at pH 5.3 compared with relatively large positive effects at pH 6.5 and negative effects at pH 7.7 can be explained on the basis of a

number of opposing effects. Premi (1968) found that the same purified cellulose powder as used in this experiment decomposed rather slowly when incubated with soil, as measured by the rate of which mineral N was immobilized. In the Dacca soil of pH 5.3 this also appears to be the case as shown by the relatively small effects of cellulose during the first 12 weeks of incubation, whilst cellulose decomposed more rapidly during the 12-20 week period, resulting in immobilization of P which was reflected in a net negative effect on available P. The net positive effects on available P at pH 6.5 are probably due to earlier and higher microbial activity at this pH compared with that at pH 5.3. Solubilizing effects exceeded any immobilizing effect after all periods of incubation, although the tendency for the net positive effect to decrease somewhat during 12-20 weeks indicated that immobilization was prominent over this period. At pH 7.7 microbial activity was probably greater than at lower pH levels but resulted in net negative effects on available P after all periods of incubation; this presumably arose from an excess of immobilization over solubilization and mineralization.

The results obtained with both straw and cellulose, whose P content would indicate that immobilization would be expected, show how pH variation may alter these expected effects as a result of altering the balance of immobilization processes in relation to solubilizing and mineralizing processes.

RELATIONSHIP BETWEEN AVAILABLE P AND INORGANIC P FORMS

The very high correlation (Prob. < 0.01) between available P and both Al- and Ca-P at pH 5.3, in contrast to the low correlation with Fe-P, indicates that both Al- and Ca-P are the predominent

forms of P extracted by 0.5M $NaHCO_3$ at this pH. In contrast to this, the relatively low correlations of available P with all three forms of inorganic P at pH 6.5 indicate that no one particular form of P was being extracted. At pH 7.7 the moderately high correlation coefficients with all inorganic forms of P (significant at Prob. <0.05 for Al- and Ca-P and just nonsignificant for Fe-P) indicates that all three forms of P are concerned with availability.

SUMMARY

The effect of pH of Dacca soil (original pH 5.3 and pH 6.5 and 7.7 obtained by previous treatments with $CaCO_3$) and addition of 1% straw, sewage sludge and cellulose on changes in available P (0.5M $NaHCO_3$ (pH 8.5) extractable) during 20 weeks of incubation (30°C and 50% mwhc) were determined.

In the control soil of pH 5.3 available P decreased considerably to 6 weeks of incubation, but showed relatively little further change up to 20 weeks. At pH 6.5 and 7.7 available P decreased considerably (to a greater extent than at pH 5.3) to 6 weeks, increased slightly to 12 weeks and decreased again to 20 weeks.

At pH 5.3 and 6.5 there were net negative effects of straw on P availability to 6 weeks, followed by no further change to 20 weeks at pH 5.3, with a further net negative effect at pH 6.5. At pH 7.7 straw had a net positive effect on available P after 6 and 20 weeks with a net negative effect after 12 weeks.

At pH 5.3 sewage sludge showed a net positive effect on available P with increase in time of incubation. At pH 6.5 sewage sludge showed a net positive effect up to 12 weeks, but this declined

somewhat to 20 weeks. At pH 7.7 sewage sludge showed a net negative effect to 6 and 12 weeks and a small decrease in this negative effect to 20 weeks.

At pH 5.3 cellulose showed no effect to 6 weeks, a slight positive effect to 12 weeks and a moderate negative effect to 20 weeks. At pH 6.5 cellulose showed a net positive effect to 6 and 12 weeks and a decline to 20 weeks. At pH 7.7 cellulose showed a net negative effect to 6 weeks with no further change to 20 weeks.

At pH 5.3 available P was highly correlated (Prob. <0.01) with Al- and Ca-P, but not with Fe-P. At pH 6.5 available P was not significantly correlated (Prob. <0.05) with any inorganic form of P. At pH 7.7 available P was significantly (Prob. <0.05) correlated with Al- and Ca-P and almost significantly with Fe-P.

Results are described in relation to the opposing effects of immobilization of phosphorus by decomposing organic materials on one hand and mineralizing and solubilizing processes on the other hand.

CHAPTER VIII

EFFECTS OF VARYING MOISTURE CONTENTS ON AVAILABILITY OF PHOSPHATE DURING INCUBATION OF DACCA SOIL.

Experiment 10 :

Effects of varying static moisture contents during incubation (28 days) of Dacca soil on availability (0.5M $NaHCO_3$ (pH 8.5) extraction) of native soil phosphorus.

Experiment 11 :

Effects of varying static and changing moisture contents during incubation (12 weeks) on availability (0.5M $NaHCO_3$ (pH 8.5) extraction) of native soil phosphorus of Dacca soil and the effect of addition of straw.

Experiment 12 :

Effects of varying static moisture contents during incubation (6 weeks) on availability (Morgan's reagent) of phosphate of Dacca soil which had been initially saturated with phosphate.

CHAPTER VIII

The three experiments in this chapter describe the effects of varying static and changing moisture contents during incubation of Dacca soil of original pH on availability of phosphorus. Experiment 10 reports on the effects of varying static moisture contents on the soil without any previous treatment. Experiment 11 reports on the effects of varying static and changing moisture contents during incubation on the original and straw-treated soils. Experiment 12 reports on the effects of varying static moisture contents on the soil after saturation with inorganic phosphate.

EXPERIMENT 10

EFFECTS OF VARYING STATIC MOISTURE CONTENTS DURING INCUBATION (28 DAYS) OF DACCA SOIL ON AVAILABILITY (0.5M $NaHCO_3$ (pH 8.5) EXTRACTION) OF NATIVE SOIL PHOSPHORUS.

METHODS

1 g portions of the original Dacca soil were set up for incubation at moisture contents of 20, 50, 75 and 100% mwhc. Sufficient replicates for each treatment were prepared to allow for analysis in duplicate after 2, 14 and 28 days of incubation (at 30°C). The soils were extracted with 0.5M $NaHCO_3$ (pH 8.5) without drying.

RESULTS

Results after incubation, in ppm P on dry soil basis, are shown in Table 19 below and in Figure 12. Initial extractable P (before incubation) was 7.5 ppm.

TABLE 19

% mwhc	2-day	14-day	28-day
20	5.4	9.9	2.9
50	4.4	6.7	2.4
75	2.9	5.5	2.9
100	4.2	5.4	2.1

L.S.D. at Prob. $< 0.05 = 0.5$ ppm P.

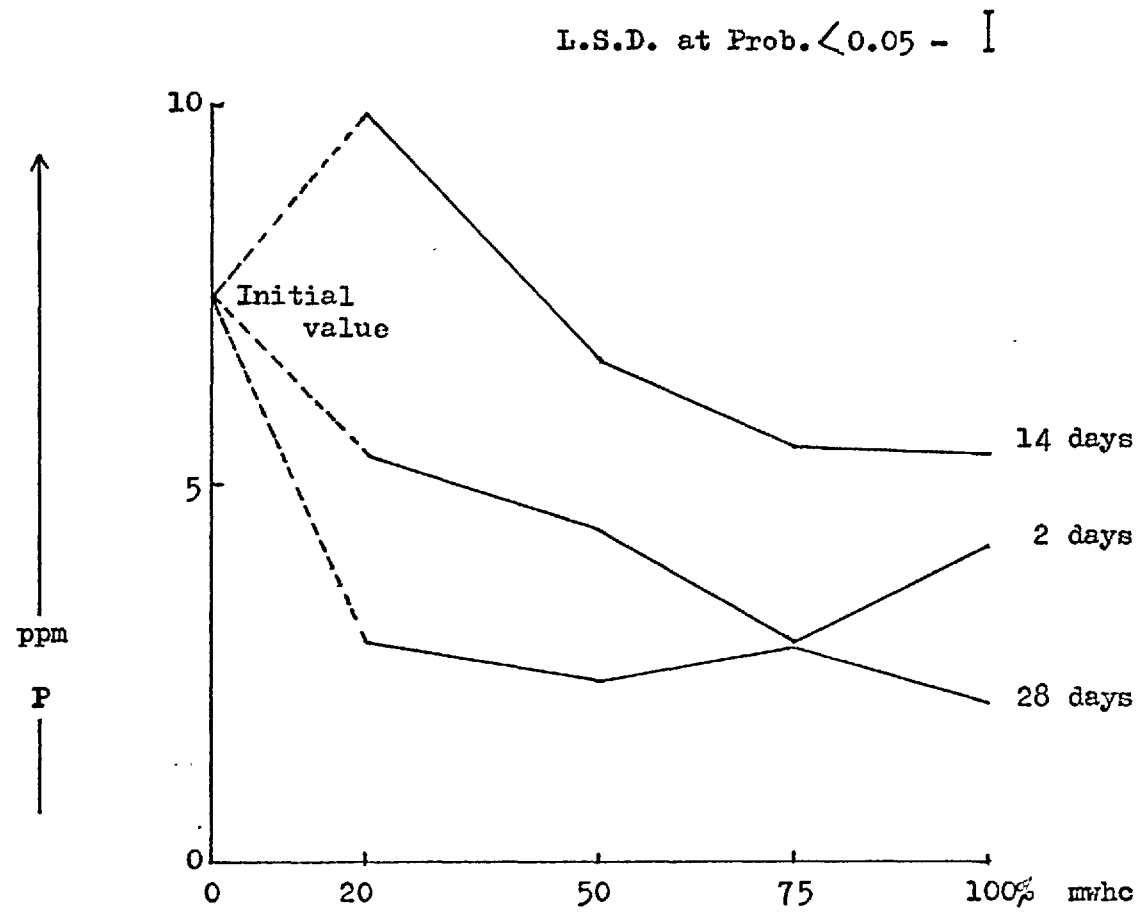
After 2 days of incubation extractable P decreased with increasing moisture content up to 75% mwhc and increased again at 100% mwhc. After 14 days of incubation extractable P decreased with increasing moisture content up to 75-100% mwhc. After 28 days extractable P levels were very similar at all moisture contents although the level at 100% mwhc was significantly less than at 20 and 50% mwhc.

At each moisture level extractable P increased during the 2-14 day period and decreased during the 14-28 day period to values less than the 2-day value. The changes in P levels due to incubation were greater at 20 and 50% mwhc than at 75 and 100% mwhc. Extractable P levels after all incubation periods at all moisture contents were less than the initial values except after 14 days incubation at 20% mwhc.

FIGURE 12

Effect of varying static moisture contents on availability (0.5M $NaHCO_3$ (pH 8.5) extraction) of native P of Dacca soil.

(Results are in ppm P on dry soil basis)



DISCUSSION

The generally decreasing extractable P with increasing soil moisture content up to 14 days indicates that phosphorus immobilization and fixation processes increased with moisture content. During this period extractable P increased only at 20%mwhc after 14 days although this was preceded by a decrease over 2 days incubation. The generally increasing extractable P from 2 to 14 days followed by an overall decrease to 28 days indicates that mineralization processes were exceeding immobilization processes early in incubation with the opposite being true later in the incubation. The decrease in extractable P to about the same extent at all moisture contents after 28 days of incubation indicates that the opposing effects mentioned above had balanced each other.

The results obtained with this acid Dacca soil differed from those reported from temperate region soils (Bromfield, 1954; Gasser & Bloomfield, 1955; and Ekpete & Cornfield, 1966) where it was usually found that extractable P increased somewhat near anaerobic moisture content of 75% mwhc and to an even greater extent at virtually anaerobic moisture content of 100% mwhc. These increases are suggested as being due to the reduction of insoluble ferric phosphate to soluble ferrous phosphate or to the increased solubility of Al-, Fe- and Ca-phosphate in organic acids produced during anaerobic microbial activity. The lack of any effect of higher moisture content in increasing extractable P in Dacca soil is probably due to the low organic carbon content of the soil and its resistence to attack by microorganisms. This would exclude the formation of organic acids which are responsible for the solubiliza-

tion of inorganically bound P forms. In addition, the very low Fe-P content (10 ppm) of Dacca soil would hardly permit much increase in soluble ferrous phosphate under anaerobic conditions.

SUMMARY

The effects of varying static moisture contents (20, 50, 75 and 100% mwhc) on available P (0.5M $NaHCO_3$ (pH 8.5) extraction) were determined after 2, 14 and 28 days of incubation of the original Dacca soil.

At 20% mwhc available P decreased to 2 days, increased to 14 days and decreased again to its lowest value after 28 days. At higher moisture contents available P decreased after all periods of incubation with the least decrease after 14 days and the greatest in general after 28 days.

EXPERIMENT 11

EFFECTS OF VARYING STATIC AND CHANGING MOISTURE CONTENTS DURING INCUBATION (12 WEEKS) ON AVAILABILITY (0.5M $NaHCO_3$ (pH 8.5) EXTRACTION) OF NATIVE SOIL PHOSPHORUS OF DACCA SOIL AND THE EFFECT OF ADDITION OF STRAW.

This experiment is comparable with Experiment 10 except that (1) longer static incubation periods were used (6 and 12 weeks), (2) a further moisture treatment was imposed, namely, 6 weeks of varying static moisture contents ranging from 20 to 133% mwhc followed by a further 6 weeks after changing the moisture contents of all soils to 50% mwhc, and (3) the effect of addition of 1% straw were also determined.

METHODS

Sufficient 1 g portions of Dacca soil and Dacca soil treated with 1% w/w finely ground straw (1,000 ppm total P) were set up at moisture contents of 20, 50, 75, 100 and 133% mwhc to allow for analysis in duplicate after 6 and 12 weeks of incubation (30°C). A further treatment, using both original and straw-treated soils, involved incubation for 6 weeks at the moisture contents mentioned above followed by a further 6 weeks of incubation after the soils had their moisture contents changed to 50% mwhc. This was done by addition of water or by placing the tubes in vacuum desiccator with periodic weighing until the moisture contents had been reduced to 50% mwhc (this took 2 days). The extractant used after incubation was 0.5M $NaHCO_3$ (pH 8.5).

RESULTS

Results (in ppm P on dry soil basis) are shown in Table 20 and Figure 13. In addition, Table 20 shows the net effects of straw, obtained by subtracting results from the soil alone from the corresponding results for the straw-treated soils.

Soil alone

After 6 weeks of static moisture incubation available P was unaffected at 133% mwhc but was increased at all other moisture contents with a maximum at 50% mwhc. With further incubation up to 12 weeks available P decreased at all moisture contents with a slight trend for the decrease to be greater at 75 to 133% mwhc than at lower moisture contents. With changing moisture incubations (over 12 weeks) available P increased with 20→50% mwhc change, decreased with the 133→50% mwhc change, but was not affected by the other changing treatments.

Straw-treated soil

After 6 weeks of static moisture incubation available P decreased at 20% mwhc, but increased at all other moisture contents, with maximum increases at 50 and 75% mwhc. After 12 weeks available P decreased at all moisture contents but to the greatest extent at 20% mwhc. With changing moisture incubation available P decreased with the 20→50% mwhc change and 100→50% mwhc change, increased with the 75→50% mwhc change but was not affected by the 133→50% mwhc changing treatment.

Net effect of straw

The general net effect of straw was to decrease available P at 20% mwhc static and 20→50% mwhc changing moisture contents and

TABLE 20

Effects of varying static and changing moisture contents during incubation of original and straw-treated Dacca soil on available P (0.5M $NaHCO_3$ (pH 8.5) extraction).

(Results in ppm P on dry soil basis)

	% mwhc	Weeks of incubation – 0	6	12 static	12 changing
Soil alone	20	8.6	12.6	5.7	10.3
	50	"	13.3	5.4	(5.4)*
	75	"	11.0	4.4	8.3
	100	"	10.0	4.9	8.7
	133	"	7.9	4.0	6.3
Soil + straw	20	11.4	8.4	4.2	7.9
	50	"	17.6	7.4	(7.4)*
	75	"	16.8	6.6	13.4
	100	"	13.4	7.4	9.1
	133	"	13.4	6.6	11.2
Net effect of straw	20	2.8	-3.5	-1.5	-2.4
	50	"	4.3	2.0	(2.0)*
	75	"	5.8	2.2	5.1
	100	"	3.4	2.5	0.4
	133	"	5.5	2.6	4.9

L.S.D. at Prob. < 0.05 = 0.89 ppm P.

* Since no change in moisture occurred at 50% mwhc these values are the same as the 12-week static values.

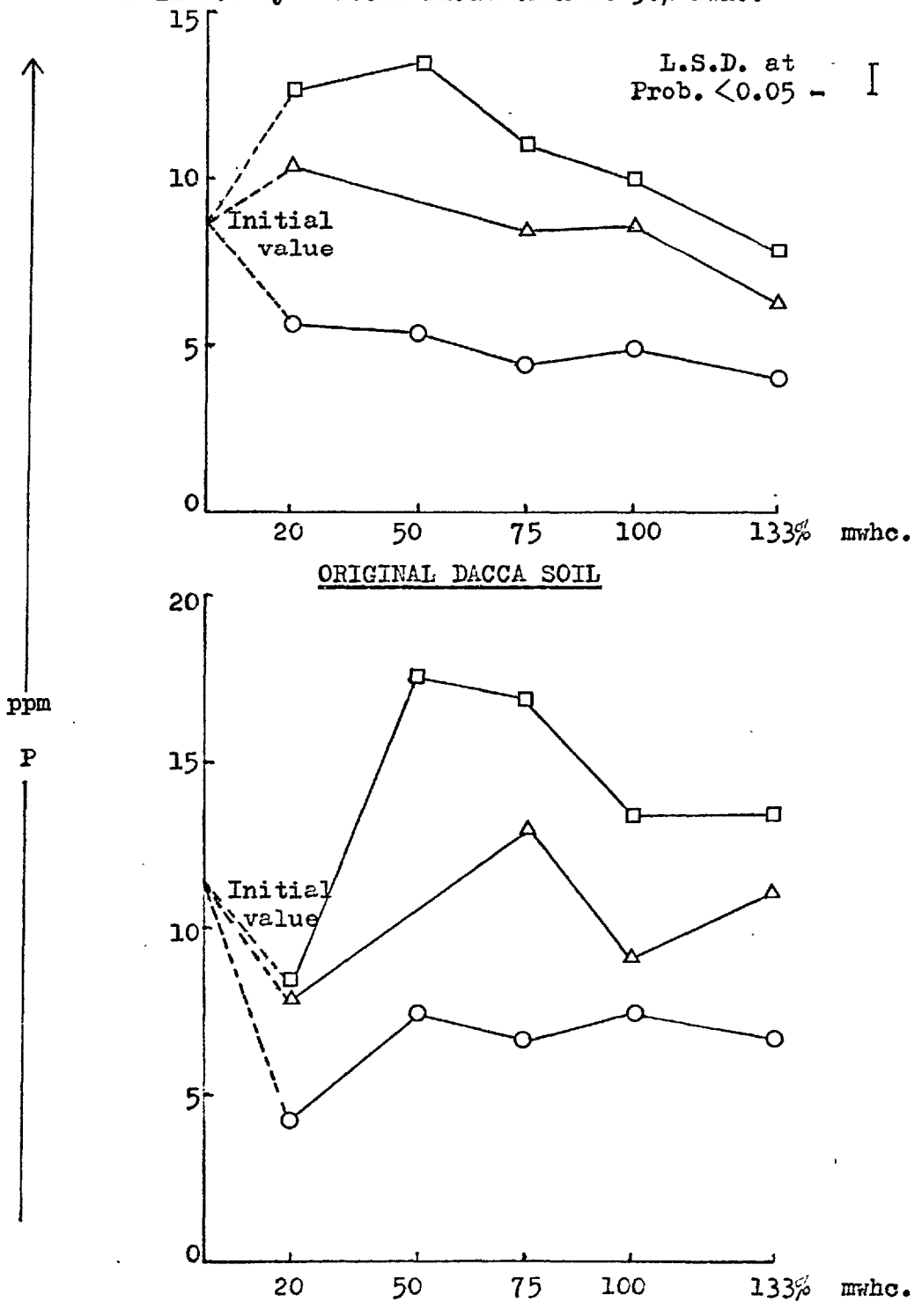
FIGURE 13

Effects of varying static and changing moisture contents during incubation of original and straw-treated Dacca soil on available P ($0.5M\ NaHCO_3$ (pH 8.5) extraction). (Results in ppm P on dry soil basis)

□—□ 6 weeks incubation at various static moisture levels.

○—○ 12 weeks incubation at various static moisture levels.

△—△ 6 weeks incubation at various static moisture levels followed by 6 weeks incubation at 50% mwhc.



to increase it at all (except 100→50% mwhc changing treatment) other moisture treatments. After 6 weeks of static incubation and the changing moisture treatments the effects of straw on available P was greater at 75 and 133% mwhc than at the other moisture contents. After 12 weeks of static moisture incubation the positive effects were no different over the moisture range of 50 to 133% mwhc.

DISCUSSION

In the original soil the relatively small effects of the anaerobic static moisture contents (100 and 133% mwhc) on available P over 6 weeks compared with the increases at lower moisture contents indicate that mineralization processes exceeded immobilization processes only at the lower moisture contents. During the last 6 weeks of incubation the decrease in available P at all moisture contents indicated that immobilization and fixation processes exceeded mineralization.

The decrease in available P which occurred only at 133% mwhc where changing moisture contents were used may be due to : (1) iron mobilized as Fe(II) under anaerobic condition of the first 6 weeks would be oxidised to Fe(III) during the second 6 weeks aerobic period, thus causing precipitation of ferric phosphate (Gasser & Bloomfield, 1955), (2) active hydrated oxides of aluminium and iron produced during the initial high moisture period could have formed insoluble potassium and ammonium aluminium phosphate during the later low moisture period (Haseman, et al., 1950).

The net negative effect of straw on available P at 20% mwhc indicates that immobilization and fixation processes exceeded mineral-

ization. In contrast, the net positive effects of straw at all higher moisture contents indicate the opposite effects. It is likely that at 20% mwhc straw decomposition was limited by low moisture content and fixation processes were being favoured. At higher moisture contents moisture was not limiting straw decomposition and conditions were less favourable to fixation. In addition, the greater decomposition of straw at the higher moisture contents implies more release of CO_2 which could result in a greater solubilization effect on the fixed forms of phosphorus. The greater net effect of straw at 75 and 133% mwhc than at 100% mwhc after 6 weeks and after the changing moisture contents is more difficult to explain. The only explanation that can be given is that at 75% mwhc, where conditions were predominently aerobic, solubilizing effect of carbonic acid produced was mainly responsible for increasing available P. Under the completely anaerobic condition of 133% mwhc the solubilizing effect of the organic acids produced was the main mechanism responsible for increasing available P. At the intermediate 100% mwhc conditions were such that both carbonic acid production and organic acid production were low.

SUMMARY

The effects of varying static moisture contents (20, 50, 75, 100 and 133% mwhc) over 6 and 12 weeks and changing moisture contents (6 weeks at various static moisture contents followed by further 6 weeks after changing all moisture contents to 50% mwhc) on available P (0.5M $NaHCO_3$ (pH 8.5) extraction) were determined during incubation of Dacca soil alone or treated with 1% straw.

After 6 weeks static incubation of the soil alone available P was increased at 20 to 100% mwhc, with a maximum at 50% mwhc, but was not affected at 133% mwhc. After 12 weeks static incubation available P decreased at all moisture contents. With changing moisture contents available P increased with the 20→50% mwhc change and decreased with the 133→50% mwhc change, but was unaffected by other changing moisture treatments.

During incubation with straw the net effect of straw was to decrease available P at 20% mwhc with static and changing moisture treatments. At higher static moisture contents the net effect of straw was to increase available P at all moisture contents with maximum effects at 75 and 133% mwhc after 6 weeks, but with somewhat lower positive effects after 12 weeks. With changing moisture treatments straw had no net effect on available P with the 100→50% mwhc change but had positive effects with the 75→50% and 133→50% mwhc changes.

EXPERIMENT 12

EFFECTS OF VARYING STATIC MOISTURE CONTENTS DURING INCUBATION (6 WEEKS) ON AVAILABILITY (MORGAN'S REAGENT) OF PHOSPHATE OF DACCA SOIL WHICH HAD BEEN INITIALLY SATURATED WITH PHOSPHATE.

This experiment differed from the previous one in that the soil was first treated with an excess of water-soluble phosphate in order to saturate the inorganic phosphate-fixing positions of the soil before being set up for incubation at varying static moisture contents.

METHODS

200 g of the original Dacca soil was shaken for 48 hours with 1 L of water containing sufficient dissolved monocalcium phosphate to supply 10,000 ppm P on the dry soil basis. The soil was then filtered off in a Buchner funnel and washed with five 200 ml portions of water to remove water-soluble phosphate. The residual soil was then air-dried and ground to pass a 2 mm sieve.

Duplicate 10 g portions of soil were set up for incubation ($30^{\circ}C$) for 6 weeks at moisture contents of 20, 40, 60, 80, 100 and 133% mwhc. Morgan's reagent was used for extraction of P at the end of incubation so that the results could be compared with those obtained by Ekpete and Cornfield (1966) for an English soil of similar texture, who used the same experimental conditions described here (with the exception that the English soil was not pretreated with phosphate since the Morgan-P level was already very high as a result of many years of previous treatment in the field with high levels of superphosphate).

RESULTS

Results for Morgan-P levels (ppm P on dry soil basis) after 6 weeks of incubation are shown in Table 21 below and Figure 14 for both the Dacca and English soils. The Dacca soil contained initially 2,120 ppm total inorganic P (0.5N H_2SO_4 extraction) and the English soil 2,417 ppm inorganic P.

TABLE 21

Soil	% mwhc – 0	20	40	60	80	100	133	L.S.D.*
Dacca soil	86	80	69	28	54	77	92	7
English soil	115	101	100	102	123	179	244	10

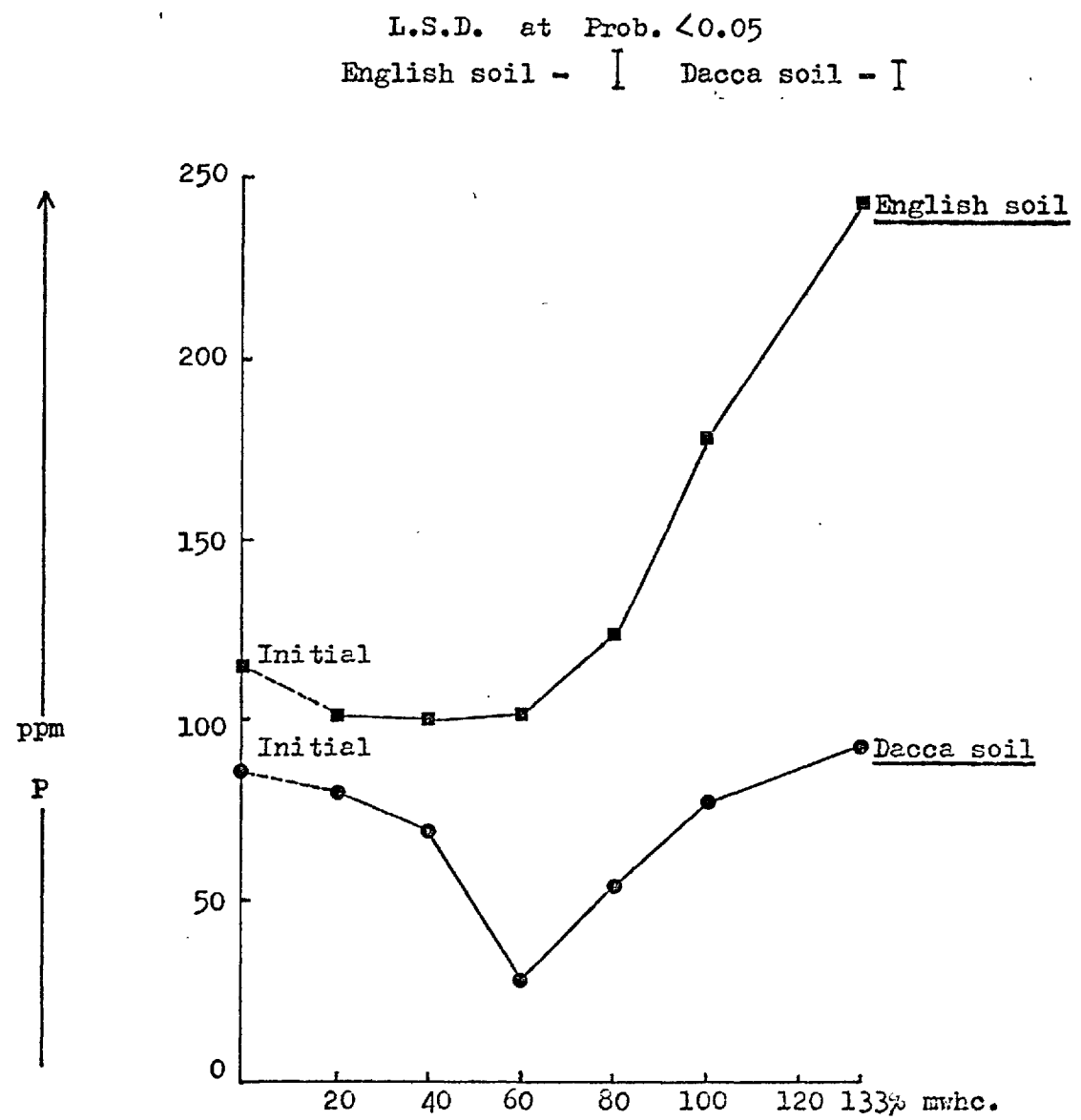
* at Prob. < 0.05.

The main difference between the two soils in Morgan-P levels at the various moisture contents occurred at 20 to 60% mwhc. The English soil showed a slight decrease in Morgan-P after incubation at moisture contents of 20, 40 and 60% mwhc with no difference due to moisture whilst the Dacca soil showed a continuing significant decrease with increasing moisture up to 60% mwhc. Both soils showed increasing Morgan-P with increasing moisture content of 80 to 133% mwhc, but the rate of increase was greater in the English soil than in the Dacca soil. In the English soil Morgan-P values at 100 and 133% mwhc were greater than initial value. In the Dacca soil, on the other hand, the highest Morgan-P value (at 133% mwhc) was similar to the initial value.

FIGURE 14

Effects of varying static moisture contents after 6 weeks of incubation on available P (Morgan's reagent) of Dacca soil and an English soil.

(Results are in ppm P on dry soil basis)



DISCUSSION

The decrease in available P in Dacca soil with increasing moisture content from 20 to 60% mwhc is probably due to increasing fixation under these aerobic conditions. At moisture contents of 80% mwhc or higher both aerobic and anaerobic effects were probably operative. Bremner and Shaw (1958) and Ekpete and Cornfield (1966) found that anaerobic effects occurred with respect to nitrogen changes at moisture contents greater than 60% mwhc and the extent of these effects increased with moisture content after waterlogging. With regard to phosphorus in Dacca soil it appears that at 80% mwhc fixation processes exceeded those processes (reduction of Fe(III) to Fe(II) (Broomfield, 1954) and increased solubilization of iron, aluminium and calcium phosphates by organic acids (Gasser and Bloomfield, 1955)) so that available P was still less than the initial value. With increasing moisture contents beyond 80% mwhc anaerobic effects became greater than aerobic effects, until at 133% mwhc (waterlogging) the effects balanced each other.

The English soil, on the other hand, showed only slight decreases with moisture contents up to 60% mwhc. This soil had a pH of 6.5 and there was presumably no fixation of iron and aluminium phosphates as occurred in Dacca soil (pH 5.3). The English soil also showed considerable increases in available P at moisture contents of 100% mwhc and, particularly, of 133% mwhc. This is probably due to the higher organic matter content of the English soil (3.5% organic C compared with 1.0% organic C in Dacca soil). This would result in a greater production of organic acids under anaerobic conditions causing greater solubilization of inorganic phosphate forms.

SUMMARY

The effects of varying static moisture contents (20, 40, 60, 80, 100 and 133% mwhc) on available P (Morgan's reagent extraction) were determined after 6 weeks of incubation of Dacca soil which had been saturated with phosphate before incubation.

Available P was not affected at 20 and 133% mwhc, but was decreased to a moderate extent at 40, 80 and 100% mwhc, and to the greatest extent at 60% mwhc.

Results were compared with those obtained (from the literature) for an English soil of similar texture which had been used for the same type of experiment.

CHAPTER IX

EFFECT OF TEMPERATURE OF INCUBATION AND OF ALTERNATE WETTING AND DRYING ON AVAILABILITY OF PHOSPHATE (0.5M $NaHCO_3$ (pH 8.5) EXTRACTION) OF DACCA SOIL ALONE AND AFTER PRETREATMENT WITH ORGANIC MATERIALS.

Experiment 13 :

Effect of incubation temperature (at 30°C and 50°C) on available P (0.5M $NaHCO_3$ (pH 8.5) extraction) during incubation of Dacca soil alone and after pretreatment with straw and compost.

Experiment 14 :

Effects of various cycles of wetting and drying (at 30°C and 50°C) on availability (0.5M $NaHCO_3$ (pH 8.5) extraction) of native and added P of Dacca soil alone and after pretreatment with straw and compost.

CHAPTER IX

EXPERIMENT 13

EFFECT OF INCUBATION TEMPERATURE (AT 30°C AND 50°C) ON AVAILABLE P (0.5M $NaHCO_3$ (pH 8.5) EXTRACTION) DURING INCUBATION OF DACCA SOIL ALONE AND AFTER PRETREATMENT WITH STRAW AND COMPOST.

METHODS

The organic material treatments used in this experiment are described in detail in Expt. 2 (Chap. IV). Briefly, they involved holding bulk portions of original Dacca soil and Dacca soil treated with 2% w/w finely ground oat straw and compost for 8 months at 18-22°C and 40-50% mwhc; 100 ppm urea-N was supplied to all soils. The soils were then air-dried and ground to pass a 2 mm sieve.

1 g portions of soils were set up for incubation at 30°C and 50°C, with sufficiet replicates to allow for analysis in duplicate after 3 and 6 weeks of incubation at 50% mwhc. 0.5M $NaHCO_3$ (pH 8.5) was used for extraction of P.

RESULTS

Results for available P levels and net effects of organic materials are shown in Table 22. Available P levels are also shown in Figure 15.

The zero incubation values represent the effect of 8 months moist holding of soils after addition of organic materials. It is seen that compost had a greater net effect than straw in increasing available P.

TABLE 22

Effect of temperature on available P levels during incubation of Dacca soil alone and after pretreatment with straw and compost, and the net effects of organic materials.

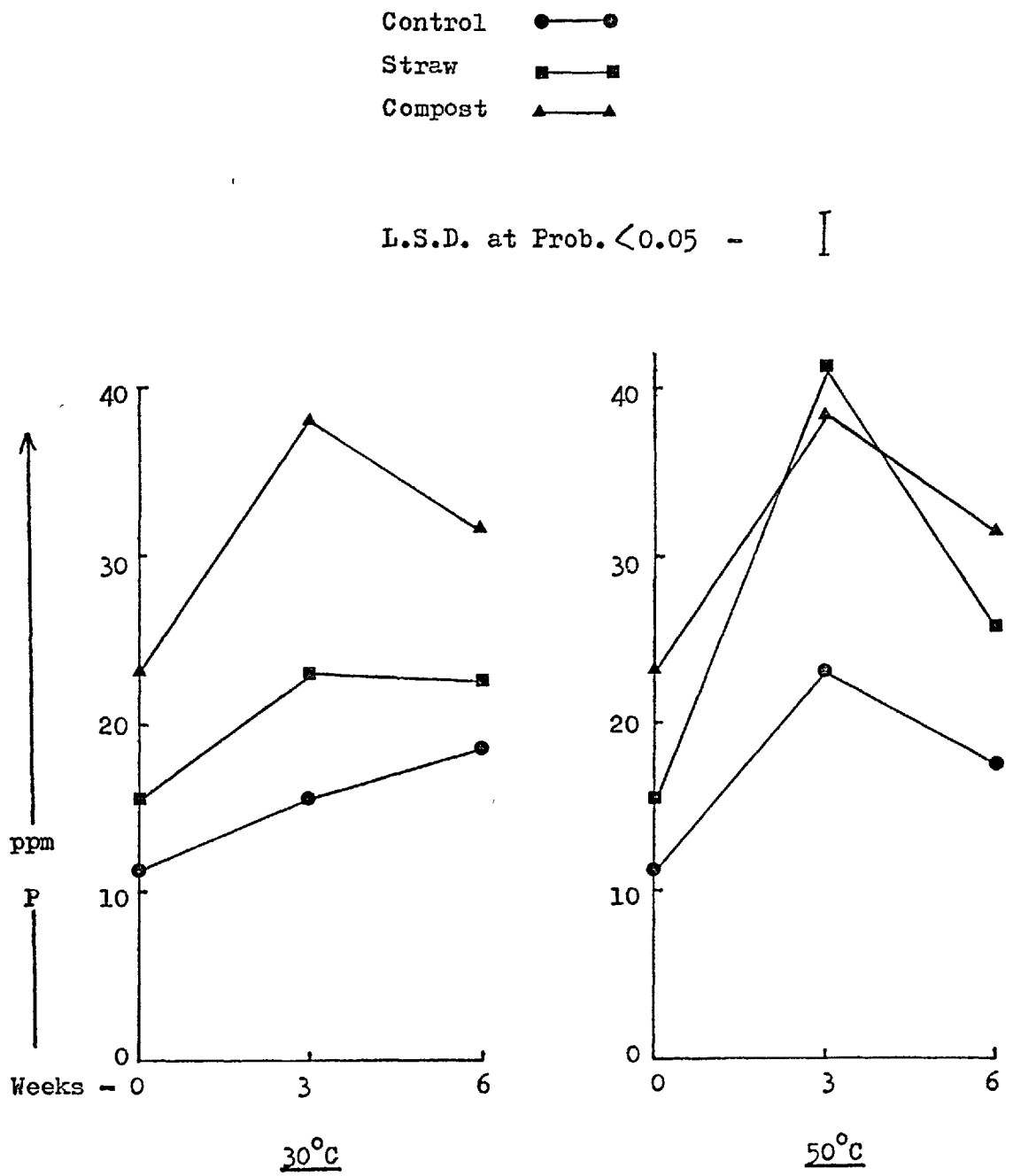
(Results in ppm P on dry soil basis)

Temp.	Treatment	Weeks of incubation 0	3	6
30°C	Soil alone	11.2	15.7	18.5
	Soil + straw	15.4	23.0	22.5
	Soil + compost	23.2	38.0	31.8
50°C	Soil alone	11.2	23.0	17.5
	Soil + straw	15.4	41.2	25.8
	Soil + compost	23.2	38.3	31.6
	Net effects			
30°C	Straw	4.2	7.3	4.0
	Compost	12.0	22.3	13.3
50°C	Straw	4.2	18.2	8.3
	Compost	12.0	15.3	14.1

L.S.D for P levels at Prob. $< 0.05 = 2.3$

FIGURE 15

Effect of temperature on available P (0.5M $NaHCO_3$ (pH 8.5) extraction) levels during incubation of Dacca soil alone and after pretreatment with straw and compost. (Results are in ppm P on dry soil basis).



During incubation of the control soil at 30°C available P increased to 3 weeks and increased further to 6 weeks. At 50°C available P increased to 3 weeks to a greater extent than at 30°C, but then decreased to 6 weeks to the same levels as at 30°C.

In the straw-treated soil at 30°C available P increased to 3 weeks, but showed no further change to 6 weeks. At 50°C available P increased considerably to 3 weeks and then declined to a moderate extent to 6 weeks. Available P at 50°C was considerably higher after 3 weeks and slightly higher after 6 weeks than after the corresponding period at 30°C.

In the compost-treated soil changes in available P were very similar at both temperatures of incubation. Available P increased somewhat to 3 weeks and then decreased to 6 weeks, but the levels were still higher after 6 weeks than initially.

At 30°C the net effect of compost in increasing available P was greater than the net effect of straw. At 50°C both materials had similar net effects in increasing available P after 3 weeks but compost had somewhat greater net effect after 6 weeks.

DISCUSSION

In the control soil greater increase in available P after 3 weeks at 50°C than at 30°C suggests that the thermophilic organisms operating at the higher temperature were more active than the mesophilic organisms operating at lower temperature. However, with further incubation to 6 weeks immobilization and fixation processes at the higher temperature were greater than mineralization resulting in a decrease in available P during the 3-6 week period.

During the 8 month moist ~~moist~~ preincubation period added organic materials would have decomposed as far as they could, and their effects on available P during incubation would be due to their relatively stable residues.

A comparison of the shape of the curve in Fig. 15 (or the net effects of straw and compost in Table 22) shows that the effects of the two organic materials on available P during incubation differed with temperature. At 30°C the straw-treatment curve paralleled the control curve with no or little increase in available P during 3-6 weeks, whilst the compost-treatment curve showed a maximum after 3 weeks. At 50°C the control and compost-treatment curves were parallel whilst the straw-treatment curve showed a much steeper increase in available P to 3 weeks followed by a steeper decrease to 6 weeks. This suggests difference due to temperature on the nature of microorganisms attacking the residues of the applied organic materials. It appears that mesophilic organisms were able to mineralize the organic P from the compost residues but not from the straw residues, whilst thermophilic organisms had the reverse effect.

It is also seen that, at both temperatures, where available P was increased to the greatest extent after 3 weeks this was followed by the greatest decrease over the 3-6 week period. This implies that the higher levels of phosphorus mobilized early in incubation were in such a form as to be susceptible to greater immobilization and/or fixation during the later period of incubation.

SUMMARY

Available P (0.5M $NaHCO_3$ (pH 8.5) extraction) was determined after 3 and 6 weeks of incubation (at 50% mwhc) at 30°C and 50°C of Dacca soil alone and after 8 months moist pretreatment with addition of 2% w/w straw and compost plus 100 ppm urea-N.

In the control soil (no organic material treatment) at 30°C available P increased with incubation time up to 6 weeks. At 50°C available P increased to 3 weeks but declined somewhat to 6 weeks so that the effect after 6 weeks was same as at 30°C.

Straw had a greater net effect in increasing available P at 50°C than at 30°C after 3 weeks of incubation. After 6 weeks the net effect of straw on available P decreased at both temperature but particularly at 50°C.

Compost had a greater net effect in increasing available P at 30°C than at 50°C after 3 weeks. After 6 weeks the effect of compost decreased at 30°C but not at 50°C and the net effect of compost was the same at both temperatures.

EXPERIMENT 14

EFFECTS OF VARIOUS CYCLES OF WETTING AND DRYING (AT 30°C AND 50°C) ON AVAILABILITY (0.5M $NaHCO_3$ (pH 8.5) EXTRACTION) OF NATIVE AND ADDED P OF DACCA SOIL ALONE AND AFTER PRETREATMENT WITH STRAW AND COMPOST.

Tropical field soils may be subjected to alternate moist and dry conditions as a result of intermittent rainfall and irrigation. The temperature of drying of soils may also vary depending on atmospheric temperature and intensity of sunshine. The purpose of this experiment was to compare the effects of a varying number of cycles of wetting and drying at temperatures of 30°C and 50°C on available P levels in original Dacca soil and after pretreatment with straw and compost.

METHODS

The pretreatments used were as described in the previous experiment, namely, the original Dacca soil and soil after treatment with 2% finely ground oat straw and compost and kept moist at aerobic conditions of 8 months; 100 ppm urea-N was added to all soils initially. After air-drying and grinding 1 g samples were placed in incubation tubes. Half the incubation tubes were treated with water to bring the moisture content to 50% mwhc. The other half were treated with water (to give 50% mwhc) containing sufficient monocalcium phosphate to supply 200 ppm P on dry soil basis. Sufficient replicates of each nil-P and P-treated soil were set up to allow for analysis after 1, 5 and 10 cycles of wetting and drying (of the unstoppered tubes) at temperature of 30°C and 50°C. Each cycle took 5 days and this was determined by the drying rate at 30°C.

RESULTS

Results are shown in Table 23 and Figure 16 for available P levels, whilst Table 23 also shows the net effects of organic materials. The initial values were actually obtained after one wetting and drying cycle in order to allow the added inorganic phosphate to react chemically with the soil.

There were increases in available P after the first 5 cycles (of wetting and drying) with all treatments except for the control soil at 50°C with inorganic P addition, whilst during the last 5 cycles there were increases in available P with all treatments.

The initial values represent the effects of 8 months moist pretreatment with organic materials. The straw pretreatment had no effect on available P at 30°C where no inorganic P was added and at 50°C where inorganic P was added. The other straw pretreatments and all the compost treatments increased initial available P.

In the control soils (no organic material pretreatment) where no inorganic P was added available P increased to the same extent at both temperatures after 10 cycles. Where inorganic P was added, available P after 10 cycles increased to a greater extent at 30°C than at 50°C.

The net effect of the compost pretreatment in increasing available P was always greater at both temperatures and with and without inorganic P treatment than was the net effect of straw pretreatment, although the differences were sometimes not significant.

The net effects of both organic materials in increasing available P after 10 cycles were greater at 30°C than at 50°C whether or not inorganic P was added.

TABLE 23

Availability of native and added inorganic P levels after various cycles of wetting and drying at 30°C and 50°C of Dacca soil alone and after pretreatment with 2% straw and compost, and the net effects of the organic materials.(Results in ppm P on dry soil basis).

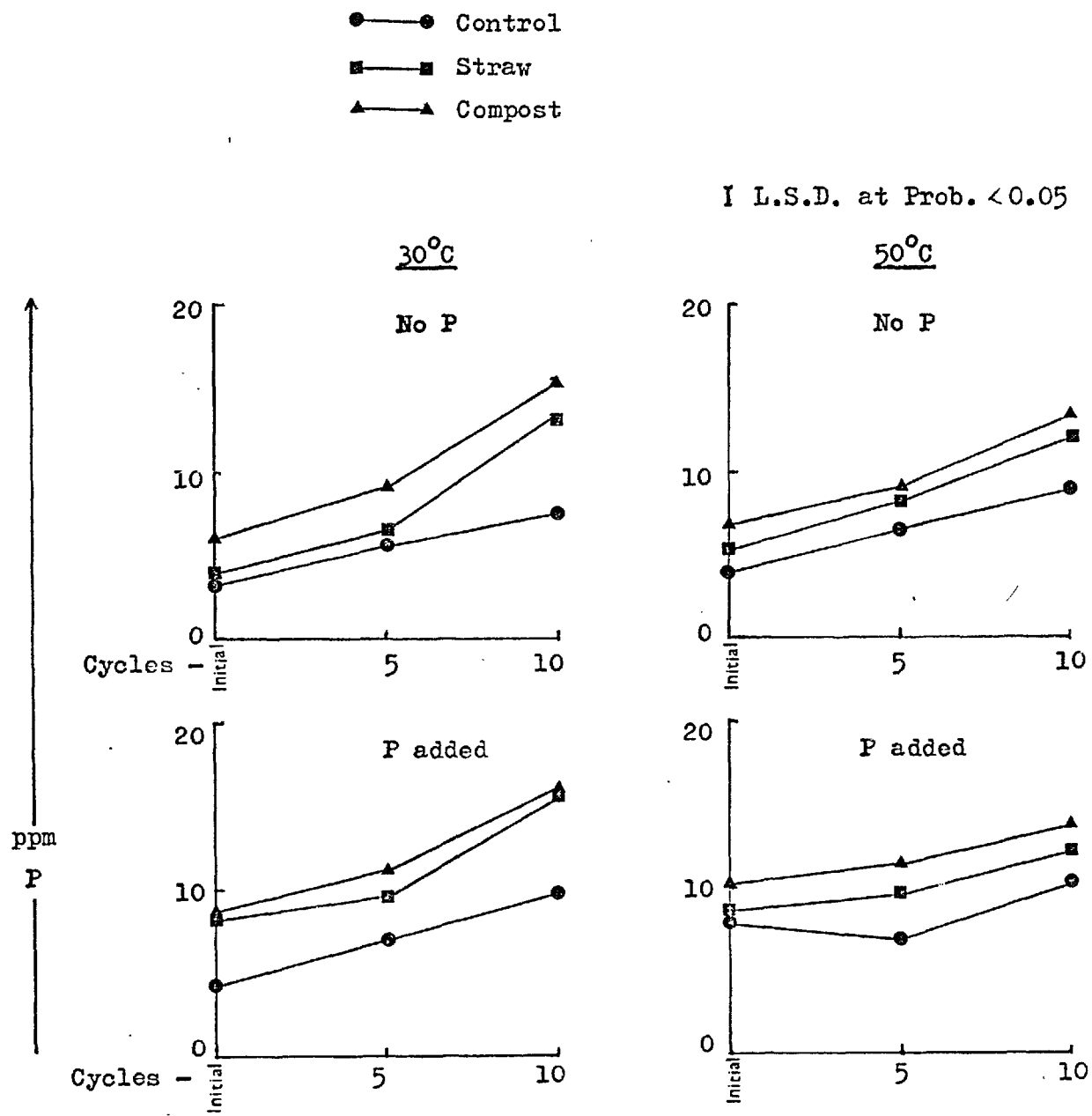
Temp.	Treatment	Number of cycles 0	5	10
30°C	Without P			
	Soil alone	3.3	5.8	7.5
	Soil + straw	4.0	6.9	13.1
	Soil + compost	6.0	9.1	15.2
	With P			
	Soil alone	4.2	7.0	9.7
	Soil + straw	8.1	9.6	15.4
	Soil + compost	8.6	11.2	16.0
50°C	Without P			
	Soil alone	4.0	6.6	9.0
	Soil + straw	5.4	8.2	12.8
	Soil + compost	6.8	9.0	13.4
	With P			
	Soil only	7.9	7.0	10.4
	Soil + straw	8.6	9.7	11.3
	Soil + compost	10.2	11.6	13.9
	Net effects			
30°C	Without P			
	Straw	0.7	1.1	5.6
	Compost	2.7	3.3	7.7
	With P			
	Straw	3.9	2.6	5.7
	Compost	4.4	4.2	6.3
50°C	Without P			
	Straw	1.4	1.6	3.8
	Compost	2.8	2.4	4.4
	With P			
	Straw	0.7	2.7	0.9
	Compost	2.3	4.6	3.5

L.S.D. at Prob. <0.05 = 1.0 ppm P

FIGURE 16

Effects of various cycles of wetting and drying (at 30°C and 50°C) on availability (0.5M $NaHCO_3$ (pH 8.5) extraction) of native and added P of Dacca soil alone and after pretreatment with straw and compost.

(Results are in ppm P on dry soil basis)



At 30°C the net effect of compost after 10 cycles in increasing available P was slightly greater where no P was added than where inorganic P was added, whilst there was no difference in the effect of straw. At 50°C after 10 cycles compost increased available P to the same extent without or with added inorganic P, whereas straw increased available P only when no inorganic P was added.

Comparison of 5 and 10 cycles showed that at 30°C the net effects of both organic materials in increasing available P was greater after 10 than after 5 cycles whether or not inorganic P was added. At 50°C the same applied where no P was added; where P was added compost had the same effect after 5 and 10 cycles, whilst straw had a positive net effect after 5 cycles but no effect after 10 cycles.

DISCUSSION

During incubation under conditions where moisture content decreases with time, such as in this experiment, it is possible for microbial reaction to occur during the short period following wetting, although towards the end of each period soils would probably be too dry for microbial reaction to occur. During the drier phases of the cycles fixation processes would be operative, resulting in decreases in available P.

The consistently lower available P levels after 10 cycles at 50°C compared with 30°C, when the organic material pretreatment had been given, is probably due to the fact that at the high temperature there were longer periods of dryness in each cycle giving more chance for fixation processes to occur. The fact that this difference due to temperature occurred only when the residues

of organic materials were present suggests that these residues were stimulating fixation at the higher temperature compared with the lower temperature. Alternatively, mineralization processes were stimulated by the organic residues to a greater extent at 30°C than at 50°C. This applied partioularly during the last 5 cycles, during which period available P increased to a greater extent at the lower temperature.

The results obtained in this experiment (where no inorganic P was added) can be compared with those obtained in the previous experiment. The main difference between the two experiments was for available P to first increase and then decrease where moisture did not alter during incubation compared with the continuous increases where periods of dryness occurred during each cycle. However, the overall effects of time on available P were similar with the constant and changing moisture treatments. This implies that available P levels may fluctuate more under constant than under changing moisture contents.

SUMMARY

Available P (0.5M $NaHCO_3$ (pH 8.5) extraction) was determined after 5 and 10 cycles of wetting and drying (at 30°C and at 50°C) of Dacca soil alone or after 8 months moist pretreatment with addition of 2% w/w straw and compost plus 100 ppm urea-N. The effect of addition of 200 ppm P as monocalcium phosphate just before the wetting and drying treatments was also determined.

The addition of inorganic P had virtually no effect on available P. In the control soil (no organic material pretreatment)

available P increased to a greater extent at 30°C than at 50°C where inorganic P was added but increased to about the same extent where no P was added.

At both temperatures the compost pretreatment had greater net effect in increasing available P than did the straw pretreatment after 5 cycles, in particular, and also after 10 cycles.

The net effects of both organic materials in increasing available P were similar at both temperatures after 5 cycles, but were greater at 30°C than at 50°C after 10 cycles.

CHAPTER X

GENERAL DISCUSSION AND SUMMARY

CHAPTER X

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In temperate-region soils added water-soluble phosphate is usually fixed in Al- and Fe-bound forms (Al- and Fe-P) whilst at higher pH levels it tends to be fixed as Ca-P. Acid soils are usually limed so as to encourage fixation of added phosphate as Ca-P, which is considered to be the most available form of P to plants. However, the lateritic Dacca soil used in this study did not behave in this way. In fact, the Ca-P level and its proportion of the total inorganic P was highest at the lowest pH and decreased slightly with increasing pH.

During incubation there were changes in the proportion of the three inorganic forms of P, particularly Ca- and Fe-P (Expt. 1, Chap. IV). Early in incubation the decreases in Ca-P were generally accompanied by concomitant increases in the two other forms of P. These changes, as well as immobilization effects, were generally greater in the soil at its original pH of 5.3 than at the higher pH levels. In addition, at pH 5.3 immobilizing organisms were utilizing only Ca-P.

There was also a trend for overall microbial activity to decrease with increasing soil pH in that the immobilizing effects continued to 20 weeks at pH 7.7, but were generally completed after 6 weeks at pH 5.3. Of the two organic materials containing P (straw and sewage sludge) only sewage sludge showed a net mineralization of its organic P and in addition stimulated the

mineralization of soil organic P. This relatively cheap form of organic fertilizer may be a useful source of P for the Dacca soil.

Whether or not this lateritic soil should be limed when it is brought into cultivation depends on the type of crops to be grown. Insofar as the effects on P availability are concerned this study on the mode of fixation of added water-soluble phosphate has shown that the proportion of Ca-P is not increased by liming, indicating tentatively that P availability is not likely to be increased by liming. Except for the effect of sewage sludge in increasing Ca-P, and hence possibly P availability, at all pH levels, the added organic materials generally had little overall effects by the end of incubation, although changes in inorganic P forms occurred during incubation.

Dacca soil, in common with most tropical soils, is relatively low in organic matter compared with temperate region soils. An experiment (Expt. 2, Chap. IV) was set up to determine the effects of artificially raising the organic matter content of the soil (by holding the soil moist for 8 months after treatment with straw and compost plus urea added to all, including control, soils) on the subsequent mode of fixation of water-soluble phosphate added just before incubation.

The inability to account for all the added water-soluble phosphate as inorganic forms within 24 hours of application indicates that there was considerable adsorptive fixation of phosphate on organic matter. This occurred even in the control soil and indicated that the presence of urea over the 8 months preincubation period resulted in microbial activity which generated organic

matter which had the ability to adsorb phosphate. Residues of both organic materials resulted in even more adsorptive fixation. Early in incubation there was fair mineralization in all soils, but particularly where straw was added, and during this phase the organic residues favoured the formation of Ca-P over Fe- or Al-P. With further incubation an immobilization phase occurred in the control and straw-treated soils, but not in the compost-treated soil; in the control soil mainly Ca-P, whilst in the straw-treated soil both Ca- and Al-P were immobilized. By the end of incubation the straw residues decreased and compost residues increased total inorganic P. The increase in inorganic P due to compost was accounted for by increases in both Ca- and Al-P.

When Dacca soil was separated by sedimentation in water into clay-, silt- and sand-sized particles before fractionation, the predominent form of inorganic P in all separates was Fe-P (Expt. 3, Chap. V). However, when the separates were treated with water-soluble phosphate before fractionation, Fe-P was lower than Al- and Ca-P, particularly in the silt and clay separates. A comparison of mechanical analysis (where aggregates were destroyed by alkali) and mechanical separation in water indicated that the sand separate contained clay aggregates and/or clay-sand aggregates of sand size. These results are of interest if erosion by wind or water should occur and indicate that the strong association between clay and sand would reduce the loss of clay. It was noted that the clay separate was higher in total inorganic P than the other two separates in the original and phosphate-treated samples.

The effects of organic matter and iron oxides in Dacca soil

on the mode of fixation of added water-soluble phosphate were determined (Expt. 3, Chap. V) by comparing fixation in the original soil with that obtained after removal of either organic matter (O.M.) or iron oxides (Fe_2O_3) and removal of both these constituents. The fact that the removal of O.M. increased Fe-P fixation much more than Al- and Ca-P fixation indicates that in the original soil there was a close association between O.M. and Fe_2O_3 with some of the active iron sites complexed by O.M.. Removal of Fe_2O_3 had almost as great an effect in decreasing inorganic P fixation as did the removal of O.M. in increasing fixation. The removal of Fe_2O_3 resulted mainly in decreasing Al- and Fe-P fixation. When both the constituents were removed, the extent of inorganic P fixation was nearer to the removal of Fe_2O_3 alone than to the removal of O.M. alone indicating that the effect of Fe_2O_3 in increasing inorganic P fixation was greater than the effect of O.M. in decreasing fixation. There were indications that the dithionite-citrate method used was more effective in removing active Al- than active Fe-fixing sites.

Since Dacca soil in the field may be subjected to widely varying moisture contents depending on rainfall and irrigation on one hand and the tendency of the soil to reach almost air-dry condition under intense sunshine, an experiment (Expt. 5, Chap. V) was done to simulate this process by subjecting the soil to varying cycles of wetting (to 50% mwhc) and drying (at 50°C) and determining the mode of fixation of water-soluble phosphate added initially. During the first 5 cycles of wetting and drying (15 days) there was a decrease in total inorganic P, accounted for as Fe- and Ca-P,

whislt Al-P increased slightly. During a further 5 cycles there was an increase in total inorganic P, accounted for entirely by increases in Fe-P. The results indicate that the P-fixing iron sites become more active than Al- or Ca-sites as moisture disappears.

A comparison of several chemical extractants used for assessing "available" P showed (Expt. 6, Chap. VI) that during incubation of Dacca soil after addition of compost or grass 0.2N H_2SO_4, Morgan's reagent and 0.5M $NaHCO_3$ (pH 8.5) showed generally increased net effects and similar changes in availability with time. The Truog reagent showed generally decreased net effects. However, the magnitude of the effects differed among the three reagents and this was due to the varying proportions of available P extracted by them.

Where water-soluble phosphate was added after 8 months moist pretreatment of soil with straw and compost, Truog's reagent and 0.5M $NaHCO_3$ (pH 8.5) showed (Expt. 7, Chap. VI) generally similar net positive effects on available P during subsequent incubation. However, the Morgan reagent showed net negative effects due to both organic materials.

The differences in apparent available P and changes in time among the extractants suggest that when this Dacca soil is brought into cultivation, pot and field tests will be needed to compare the different extractants to determine which is most suitable for indicating likely responses to application of P fertilizers.

Correlation coefficients between available P, as determined by three extractants, and inorganic P forms showed that Al-P was significantly correlated (Prob. < 0.05) with both Truog- and 0.5M

$NaHCO_3$-P and was also well correlated with Morgan-P. However, Ca-P was fairly well correlated with these two available forms as well as with Morgan-P. Fe-P was negatively correlated with all three available forms.

The phosphate-fixing capacity of Dacca soil increased with pH from 2,000 ppm at pH 5.0 to 2,440 ppm at pH 6.6 (Expt. 8, Chap. VI). The Truog reagent and 0.5M $NaHCO_3$ (pH 8.5) extracted approximately the same proportions of fixed phosphate. These proportions were little affected by pH, indicating that the inorganic P forms extracted by these reagents were similar at all pH levels. On the other hand, the increased proportion of fixed phosphate extracted by Morgan's reagent with increasing soil pH indicates that this reagent extracts different forms of phosphate in relation to pH.

The effects of addition of straw, sewage sludge and cellulose on availability of P during incubation (Expt. 9, Chap. VII), as measured by 0.5M $NaHCO_3$ (pH 8.5) extraction, was determined in Dacca soil of pH 5.3, 6.5 and 7.7 treated with water-soluble phosphate. The net effect of sewage sludge was to increase available P at pH 5.3 and 6.5 but to decrease it at pH 7.7. Cellulose increased available P at pH 6.5 and decreased it at pH 7.7, whilst at pH 5.3 it was increased early and decreased by the end of incubation. Straw decreased available P at pH 5.3 and 6.5 and generally increased it at pH 7.7. The results are discussed in relation to the expected effects of the organic materials (based on their total P contents) and the results actually obtained. At pH 5.3 Al- and Ca-P were the predominent forms of P extracted by 0.5M $NaHCO_3$ (pH 8.5) whilst at pH 7.7 Al-, Fe- and Ca-P forms were

extracted. At pH 6.5 the relatively low correlations of available P with all three inorganic forms indicated that no particular form of P was contributing to availability as determined by 0.5M $NaHCO_3$ (pH 8.5).

During incubation for up to 28 days of Dacca soil at varying static moisture contents (20 to 100% mwhc) available P (0.5M $NaHCO_3$ (pH 8.5) extraction) increased only at 20% mwhc but then only early in incubation (Expt. 10, Chap. VIII). By the end of incubation available P decreased to about the same extent at all moisture contents.

With incubation for 6 and 12 weeks at varying static moisture contents (Expt. 11, Chap. VIII) available P increased at 20 to 100% mwhc, with a maximum at 50% mwhc, but was not affected at 133% mwhc. By 12 weeks available P decreased to about the same extent at all moisture contents. When the soil was incubated at various static moisture contents for 6 weeks followed by further 6 weeks after changing the moisture content to 50% mwhc, available P increased with the 20→50% mwhc change and decreased to 133→50% mwhc change, but was unaffected by other moisture changes. The net effect of adding straw before incubation was to decrease available P at 20% mwhc with static and changing moisture treatments. Straw increased available P at all higher moisture contents with maximum effects at 75 and 133% mwhc after 6 weeks, but with lower positive effects after 12 weeks. With changing moisture treatments straw had no net effect on available P with the 100→50% mwhc change, but had positive effects with the 75→50% and 133→50% mwhc changes.

When Dacca soil was saturated with phosphate before incubation at various static moisture contents (Expt. 12, Chap. VIII), available P (Morgan's reagent) was not affected at 20% and 133% mwhc, but was decreased at intermediate moisture contents, particularly at 60% mwhc. The results differed considerably from those obtained (from the literature) with an English soil of comparable texture. Results are discussed in relation to differences in pH and organic matter content between the soils.

The effects of incubation temperature of 30°C and 50°C (both at 50% mwhc) on available P (0.5M $NaHCO_3$ (pH 8.5) extraction) were determined in native Dacca soil as well as after pretreatment with straw and compost (Expt. 13, Chap. IX). Straw had a greater, whilst compost had a lesser, net effect in increasing available P at 50°C than at 30°C after 3 weeks of incubation. After 6 weeks the net effects of straw on available P decreased at both temperatures, but particularly at 50°C. The net effect of compost decreased only at 30°C. The results suggest differences due to temperature on the nature of microorganisms acting on the added organic materials. It appears that mesophilic organisms are able to mineralize the organic P from compost but not from straw residues, whilst thermophilic organisms had the reverse effects. There was also a greater trend at 50°C than at 30°C for phosphorus mobilized early in incubation to be immobilized and/or fixed later in incubation.

The effects of 5 and 10 cycles of wetting (to 50% mwhc) and drying at 30°C and 50°C on availability (0.5M $NaHCO_3$ (pH 8.5) extraction) of native and added P of Dacca soil alone and after

8 months moist pretreatment with straw and compost were studied (Expt. 14, Chap. IX). The addition of water-soluble phosphate had virtually no effect on available P. At both temperatures the compost pretreatment had greater net effects in increasing available P than the straw pretreatment after 5 cycles, in particular, and also after 10 cycles. The net effects of both organic materials in increasing available P were similar at both temperatures after 5 cycles, but were greater at 30°C than at 50°C after 10 cycles. Results are discussed in relation to differences in mobilization and immobilization effects between the wet and dry periods of the drying cycles. A comparison of changes in available P under constant moisture conditions and under alternate wetting and drying conditions showed that although the ultimate effects were similar, there were greater fluctuations in available P under alternate wetting and drying treatments.

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