ORGANIC PHOSPHORUS STUDIES IN SOME SOILS OF MALAWI

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ABSTRACT

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In the present study, organic phosphorus studies were made in four soils from Malawi, of which two were selected for studying mineralization of organic P.

The four soils were found to differ widely in their chemical, physical and mineralogical properties. A relative degree of weathering could be assigned to the soils based on gibbsite content, phosphorus adsorption capacity, per cent base saturation, pH, and reactive SiO_2/Al_2O_3 ratio. The mineralogical analyses were carried out by X-ray diffraction (XRD), differential thermal analysis (DTA), and selective dissolution analysis (SDA).

A comparative study of four procedures for estimation of soil organic phosphorus showed that ignition procedures were superior to extraction procedures. Thus, an ignition procedure (550°C followed by 2N H_2SO_4 extraction) was selected for evaluation of organic phosphorus mineralization during laboratory incubation.

Continuously moist incubation studies were made on the Mulanje and Dedza soils at 22°C and 35°C, and 0% and 2% organic residue. Soil samples were taken at 3 week intervals to observe organic P mineralization. Finally, wet and dry incubation studies were done as in continuously moist incubation studies,

except that the 22°C treatment was excluded, and also that soil samples were taken at one week intervals. In continuously moist incubation, there was generally an initial immobilization of P in both soils followed by net mineralization, except in Dedza samples where 2% organic residue was added. The wet and dry incubation results, on the other hand, showed an initial mineralization of P in both soils, but that subsequent incubation resulted in immobilization of P, except in the Mulanje sample where 2% organic residue was added.

BIOGRAPHICAL SKETCH

The author was born in Gamba Village, Chitipa District, Malawi on September 24, 1941. He attended primary school at Roan School, Luanshya, Zambia and at Nthalire Full Primary School in Chitipa District, Malawi and secondary school at Karonga, Nkhata Bay and Dedza Secondary Schools, Malawi. He also attended one year at the University of Malawi after which he was awarded a scholarship by U.S. Agency for International Development in 1966. In February, 1970, he obtained a Bachelor of Science degree in Plants and Soils at the University of Massachusetts, and studied at Cornell University during the spring semester of 1970 as a special graduate student.

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The Author is a member of the Soil Science Society of America, the American Society of Agronomy and the International Society of Soil Science.

To the memory of Elisa Kanyimbo who
never saw the end of her son's studies.

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INTRODUCTION

Phosphorus in Highly Weathered Soils

Many of the soils in the tropics have been subjected to weathering for much longer than the soils in the temperate regions. These highly weathered soils are strongly leached and are deep; the plant nutrients are concentrated in surface layers of the soil which arises due to the recycling of nutrient by vegetation (Enwezor and Moore, 1966; Greenland, 1973; Nye and Bertheux, 1957; Russell, 1968). Although the measurement of total phosphorus may be a useful indicator of probable P deficiency , it is less useful than other methods. In most of these soils, the level may be as low as 200 ppm. Enwezor and Moore (1966a), for example, showed that total P averaged 211 and 170 ppm for 0-15 and 15-30 cm layers of five forest-soil profiles, and 110 ppm for the corresponding layers of 14 savanna profiles, of which the organic P constituted 43 and 28 per cent of total P in the 0-15 and 15-30 cm layers of the forest soils, and 18 and 10 per cent in the corresponding layers of the savanna soils. Similar findings were reported by other workers who report that forest soils have a higher concentration of total phosphorus than savanna soils (Greenland, 1973; Nye and Bertheux, 1957). Although the organic P compounds may be in soil solution, they are largely unavailable for plant use. The organic form of phosphorus does, however, represent a potential source of phosphorus which can be available upon mineralization into inorganic forms.

Fixation or immobilization of phosphorus is also a common feature of the highly weatherd soils of the tropics. In most of these soils, fixation can be extremely rapid and strong as a result of the relatively large contents of free iron and aluminum oxides. The extent of the fixation reaction per unit mass of soil is largely dependent on the crystallinity of the iron and aluminum oxides. Generally, the amorphous or noncrystalline forms are more active in phosphorus retention than are crystalline, well-ordered forms (Greenland, 1973).

In most of the highly weathered soils of the tropics, organic may represent a greater proportion of the total phosphorus than in less weathered soils of the temperate regions and the tropics. Friend and Birch (1960) reported that the organic fraction accounted for about 86 per cent of the total soil phosphorus for some soils of East Africa. Acquaye (1963) found the organic P content of some Ghanaian soils ranged from 46.0 to 69.5 per cent of the total. This quantity varied with depth. The greater amounts of total P in the top soil was attributed to the presence of organic P (Bates and Baker, 1960). Cunningham (1963) found that in the tropical soils of Ghana in cacao experiments, organic P was in the order of 75 and 55 per cent of the total in 0.5 cm and 5-15 cm horizons respectively. Bornemisza and Igue (1967) found the proportion of organic P to be in the same order for Costa Rican soils.

Relationship of Organic Phosphorus to Fertility of Highly Weathered Soil.

Field studies have shown that soil organic phosphorus content is correlated with crop yields. Omotoso (1971) working on some cocoa growing acid soils of southern Nigeria found that for the majority of the soils, there was little response to phosphate fertilizer application where the organic P content was above 30 mg/100 g soil. That is, where the organic P comprised a greater percentage of the total P, there is likely to be very little response to fertilizer P. The correlation was in line with the findings of Friend and Birch (1960) and Acquaye (1963) and Smith and Acquaye (1963).

In the humid tropics, the rapid rate of production and decomposition of organic matter, should cause the mineralization of organic phosphorus to be more significant than in the less weathered soils. For most of the low income countries, where the cost of fertilizer is very high and the price of the produce is relatively low, most of the farmers at subsistence level do and will have to depend on the use of manure, plant residues, and management practices that enhance organic phosphorus mineralization, although this might not be adequate for continued high production of annual crops.

Origin and Form of Organic Phosphorus.

In general the soil organic phosphorus is part of the organic matter which in turn originates from decaying natural vegetation, although some is accumulated as a result of microbial activity (Anderson, 1967; Birch, 1961; Cosgrove, 1967).

Cosgrove (1967) considered that the organic P compounds in plant and animal remains probably decompose at a rapid rate which prevents their becoming more than a very small proportion of the total organic phosphorus of the soil, and this may be true if one considers some of the information on the possible origins of some phosphate esters known to be present in the soil.

The chemical nature of soil organic phosphorus is not exactly known, but the organic phosphorus compounds in soils are generally considered to fall into three main groups, and these are: phospholipids, nucleic acids and the inositol phosphates. The phospholipids comprise a small proportion of soil phosphorus, and most values reported do not exceed 3 ppm of phosphorus (Anderson, 1967).

The nucleic acids (ribonucleic and deoxyribonucleic) reach the soil from decomposing microbial, plant, and animal remains. Anderson (1967) points out that it is unlikely that they account for more than 5 to 10 per cent of the ester phosphates in soils. The third group consists of the inositol phosphates which are the esters of inositol, a saturated cyclic, six-carbon alcohol with a phosphate group on each carbon. Four isomers have been discovered of which only one is found in the inositol of plants, which clearly indicates that the inositol phosphates of the soil are not only residual from plants, but also that they may be produced in soils from microorganisms (Cosgrove, 1967). Wide variations have been reported with regard to the absolute amounts of the esters, but Anderson (1967)

points out that the inositol phosphates may account for more than 50 per cent of the total organic phosphorus, although the average may be put at 30-35 per cent. In a thorough review of organic P, Roberts and Weaver (1973) pointed out that over half of the organic phosphates have not been identified.

Mineralization of Organic Phosphorus.

Organic phosphorus is not directly available for plant nutrition, and must first be mineralized since the plant takes up phosphorus in the inorganic form. The problem is that the soil, being a dynamic system, is not in a state of equilibrium so that the mineralization of organic P will depend not only on the presence of microbial populations, but also on whether the dynamic state favors mineralization or re-immobilization of the mineralized phosphorus.

In his studies of P transformation during plant decomposition, Birch (1961) found that during the first two days, there was a small rise in the amount of organic phosphorus followed by a decline as a result of dephosphorylation to inorganic P. This is in agreement with other workers (Enwezor, 1966, 1967); Jackman, 1955) who report similar results. Enwezor (1967) found that there was an initial P immobilization in all, except seven of the twenty-eight soils used, and that this immobilization occurred in all except three cases to the end of the incubation period. This immobilization tended to rise with increased levels of available P, indicating a luxury absorption of P by microorganisms. Black and Goring (1953) reported that mineralization of organic P will occur if the organic C: organic P

ratio of the materials is below 200 while if the ratio is above 300, immobilization will occur, which has been observed when large amounts of energy-yielding materials are introduced into soils (Birch, 1961; Enwezor, 1966; 1967; Friend and Birch, 1969).

Cunningham (1963) found that organic P mineralizes at approximately the same rate as total nitrogen in forest soils in Ghana. Organic P mineralization seems also to depend on the percentage of the total P present in the organic form rather than on the organic C: organic P ratio with which mineralized P was poorly correlated (Enwezor, 1966; 1967). Jackman (1955), based on results from 18 field trials in New Zealand, found that average conversions of 20 to 30 per cent of added inorganic P, were found in the top inch of the soils he worked with, higher values of 40-40 per cent in yellow-brown loams and podzolic soils.

The reports of the effects of added phosphorus are conflicting. Acquaye (1963) found that the increase in extractable inorganic P due to incubation of some soils of Ghana was greater in the presence of added inorganic P and N. These results are in agreement with the work of Enwezor (1966). The addition of inorganic phosphorus, it is believed, has a twofold purpose. First, it replaces the organic phosphorus from the exchange sites, and thus making it readily available for mineralization. Secondly, the microbial activity is enhanced, and this leads to eventual increase in organic P mineralization.

The results of the experiments by Wier and Black (1968) on the other hand showed that the rate of organic P mineralization in soil was not enhanced by addition of inorganic P. This is in agreement with the results of Yoneda and Shigeputa (1956), and Jackman (1955) who found a greater content of organic P in cropped fields, and that this increase in organic P was associated with fertilization and accumulation of total P in the surface layer. Dormaar (1972) found that the effects of fertilizer levels on organic P were small during the first season. In the second year, addition of fertilizer often resulted in an increase in soil organic P. He also found that there was overwinter buildup of soil organic P. More recent work by Adebayo (1973), who worked with Nigerian soils, clearly indicates that the rate of orgnaic P and organic C mineralization was not enhanced by addition of inorganic P. On the contrary, the organic P level was constant throughout the experiment.

One of the best indicators that mineralization of organic phosphorus does indeed occur is evidenced by comparing uncultivated soils to those that have been cultivated. Cunningham (1963), who followed the effects of clearing a forest in Ghana over a three year period observed that there was a decline in the total organic P content. This is in agreement with the work of Omotoso (1971) who found that there was, in general, a lower organic P content in the cultivated soils than in the uncultivated soils of Nigeria. This, he concluded, suggests that the organic P can be potentially available for plant nutrition.

Temperature is one of the most important factors that affect organic P mineralization in the soil. Field experiments on a clayey Ultisol in Puerto Rico have shown that there was no response to applied inorganic phosphorus in a warm season, but that there was a definite response in a cool season (R. H. Fox, Dept. Agron., Cornell Univ. Ithaca, N.Y. personal communication). Acquaye (1963) found that for some Ghanaian soils more organic P was mineralized during laboratory incubation at 50°C than at 40° or 27°C. Wetting and drying the soil may also have an effect on organic P mineralization (Birch, 1960a; 1961; Friend and Birch, 1961). Birch (1960a) points out that the drying effect involves changes in the organic fraction of the soil and that the organic material involved is a product of microbial decomposition of complex organic matter. In their experiment, Friend and Birch (1961) reported that organic P was completely mineralized after 204 cycles of wetting and drying, but not organic C and N. The effect of wetting and drying may be due to changes in the organic colloids.

Soil reaction also greatly influences organic P mineralization. Omotoso (1971) observed in a calcareous soil that the decrease of organic P as a result of cultivation was much greater than that in acid soils. This greater decline in the organic P was attributed to rapid mineralization at higher pH values. Apparently, increased soil pH stimulates microbial activity and consequently organic P mineralization (Awan, 1964; Halstead et al., 1963; Islam and Ahmed, 1973). Awan (1964), working

with Zamorano soils showed that there was a decrease in organic P after two years of cultivation in soils that were limed; and the effect was even greater when lime was applied with inorganic P. These results are in line with those of Halstead et al. (1963) and Islam and Ahmed (1973). Halstead et al. (1963) found that liming resulted in an average decline of 3.6 per cent in the total organic P content of incubated surface samples of seven acid soils from eastern Canada. Reduction in soil organic P due to liming is assocaited with an increase in the number of organisms, and CO_2 and nitrate production. One of the hypotheses is that the organic P esters may be in the form of Al- or Fe- inositol hexaphosphates, and raising the pH to about 6.0-6.5 may transform them into more soluble Ca-salts which can be easily mineralized.

Determination of Organic Phosphorus.

There has been a considerable amount of effort on the development of methods for estimation of total soil organic phosphorus. The methods currently used may be classified as either ignition or extraction procedures. In ignition-type procedures, total organic P is determined as the increase in the amount of extractable P that results from ignition of the soil as compared to an unignited sample. In extraction methods, the soil is treated with suitable reagents so as to remove both organic and inorganic P. After determination of inorganic P, total extractable P is determined by treatment of the extract so as to convert organic P to inorganic P.

Organic P is then taken as the difference between total extractable P and inorganic P.

The more commonly used ignition procedures are those of Saunders and Williams (1955) in which samples ignited at 550°C are extracted with 0.2 N or 2N H_2SO_4, and Legg and Black (1965) in which samples are ignited at 240°C and are extracted with concentrated HCl. Generally speaking, ignition procedures are advantageous in that they are relatively rapid and simple, and give more reproducible results than extraction methods. There are, however, several possible errors that may occur with ignition procedures. One of these is that the destruction of organic matter by ignition may change the inorganic P already present in the soil.

Bornemisza and Igue (1967) found that there was a reduced efficiency of the Saunders and Williams method in that during ignition, a portion of the mineralized organic P reacted with soil constituents so as to produce inorganic forms of P that were not extractable with 0.2N H_2SO_4. The latter occurrence can be partially prevented by use of a stronger acid such as 2N H_2SO_4. However, this will increase the possibility that some organic P may be hydrolyzed during extraction of inorganic P from the unignited sample. This was pointed out by Anderson (1960) who found that overnight extraction with 2N H_2SO_4 gave no hydrolysis of inositol hexaphosphate, but it did affect other esters, and mineralized glucose-1-phosphate quantitatively.

Not only do ignition procedures suffer from changes in extractability of inorganic P resulting from ignition, but from incomplete oxidation of organic P with low temperature ignition, and volatilization of P during ignition. Williams et al. (1970) pointed out that low temperature ashing (LTA) using excited oxygen can be of much use in estimating organic P. It has advantages in that it eliminates volatilization of P, and that it also minimizes the changes in the extractability of inorganic P as a result of heating.

Most of the extraction methods for organic P in one form or another consist of treatment of a soil sample with an acidic reagent followed by an alkali reagent. The purpose of the acidic reagent is to remove Ca, Mg, and other polyvalent cations which otherwise could cause precipitation of organic P compounds during the alkali extraction. The acid extraction also releases organic P that may be occluded within iron and aluminum oxides. The most widely accepted method is that of Mehta et al. (1954). Briefly, this method consists of treatment of a soil sample with hot, concentrated HCl followed with 0.5N NaOH at room temperature and then with 0.5N NaOH at 80°C. Although the Mehta et al. extraction procedure is generally accepted as a reference procedure (Bornemisza and Igue, 1967; Enwezor and Moore, 1966a; Legg and Black, 1965), it has two possible sources of error. These are incomplete extraction of organic P and/or hydrolysis of organic P during extraction.

Accordingly various modifications of the Mehta procedure have been proposed to circumvent these sources of error. Anderson (1960) modified the Mehta et al, method by first extracting with dilute alkali (70 ml of 0.3N NaOH) overnight prior to application of the Mehta et al. method. The overnight extraction with dilute alkali removes some of the organic P that otherwise would have been hydrolyzed by concentrated HCl or 0.5N NaOH. Saxena (1972) suggested the use of 1.5N NH_4OH at 75°C for removal of sodium hydroxide hydrolyzable fraction of soil organic P prior to the second 0.5N NaOH treatment at 90°C, and found this method superior to Mehta et al. method. The latest development in this area has been by Steward and Oades (1972) who suggested pre-extraction of the soil with 1M HCl (15 ml), then ultrasonic vibration of the soil suspended in 0.5N NaOH, using maximum current for 3 minutes. Use of 1M acid pretreatment with a single, vigorous NaOH extraction gave values as high as, or higher than those of Mehta. The method also eliminates a second NaOH extraction.

One of the biggest problems in the selection of a method for estimation of organic P is that there is a distinct qualitative difference in the phosphate esters present in various soil types or soils of different regions (Anderson, 1960). Soils from acid regions may behave quite differently from those of alkaline regions. It is also very useful to know the relationship between the clay-sesquioxide fractions and organic fractions, since different forms of complexes might have different reacitons to the procedures developed from a few areas.

Anderson and Arlidge (1962) report that soil clays and clay minerals and hydrated sesquioxides adsorb some inositol phosphates and glycerophosphate. Although this case has not been extensively pursued, it needs to be investigated even more in the highly weathered soils of the tropics which have greater amounts of sesquioxides. Thus the reliability of any given method could be better assessed if more information were available about the nature of the interaction between the organic matter and clay-sesquioxide fractions.

Phosphorus in Soils of Malawi.

Most of the virgin soils in Malawi have not been found to be deficient in phosphorus, but in some soils the deficiency is induced by continuous cultivation in a short time (Brown, 1966; Brown and Young, 1964; Young and Brown, 1962). These P deficiencies more generally appear on heavier red soils than those on the sandier yellow and grey soils (Brown, 1966). Responses are common in the plateau and hill areas of Central and Northern Regions, but not in the Southern Region, although this is the most densely populated and cultivated area in the country.

Brown (1966) reported on some of the results of manuring carried out in all three regions (Northern, Central and Southern) of Malawi. He observed that there were marked responses to manure application on less fertile soils than on the better soils, and that this response may be due to nutrient content of the manure rather than the presence of organic matter *per se*. Enwezor (1967) pointed out that where inorganic forms

of P account for the bulk of the total soil P. a study of the organic P would seem pointless unless the inorganic forms are low in availability.

Objectives

To date, no studies have been conducted on the relationship of organic phosphorus to crop yields in Malawi. In view of this, the purpose of the present study is to investigate: 1) The physical, chemical. and mineralogical properties; 2) Total-P, inorganic-P fractions, and organic-P content; 3) Phosphorus adsorption characteristics; and 4) Mineralization of organic P in incubated samples of some Malawi soils.

MATERIALS AND METHODS

Description of Soils

The soils used in this study were sent from Malawi, and the author is very grateful to Mr. R. W. Borden, University of Malawi, Bunda College of Agriculture, Lilongwe, Malawi who sent the soils and gave most of the profile descriptions. All the samples were from the surface layer (0-15 cm). Figure 1 shows the map of Malawi and the locations where the soil samples were taken.

Mulanje Site Mimosa or Mulanje Series - taken in a young Eucalyptus plantation which was about 1-2 years old at the time of sampling on the Thornewood Estate, is likely a Mimosa or Mulanje series. The soil appears to be a Ferrisol (Belgium system) (Ustox, by the new U.S. soil taxonomy) but no profile description was available yet. Young (1962) gave a profile description of the Mimosa series, and this lies on a deep, red, clay, having typical properties of a Ferrisol. The profile is a uniform dark red from the top downwards, and has a marked lack of textural differentiation, remaining clay or sandy clay from the subsoil to a depth of 240-300 cm or more. The subsoil has a moderate blocky structure, well-developed in depth. The consistency is friable and soft. These morphological characteristics result from complete predominance of kaolinitic clay minerals, and the profile is strongly acid, pH 4.5-5.0, and the subsoil base saturation is low.

Bvumbwe Site - Mullon series, which is classified as a Ferrallitic latosol, or Eutrorthox by the new U. S. soil taxononomy. It is

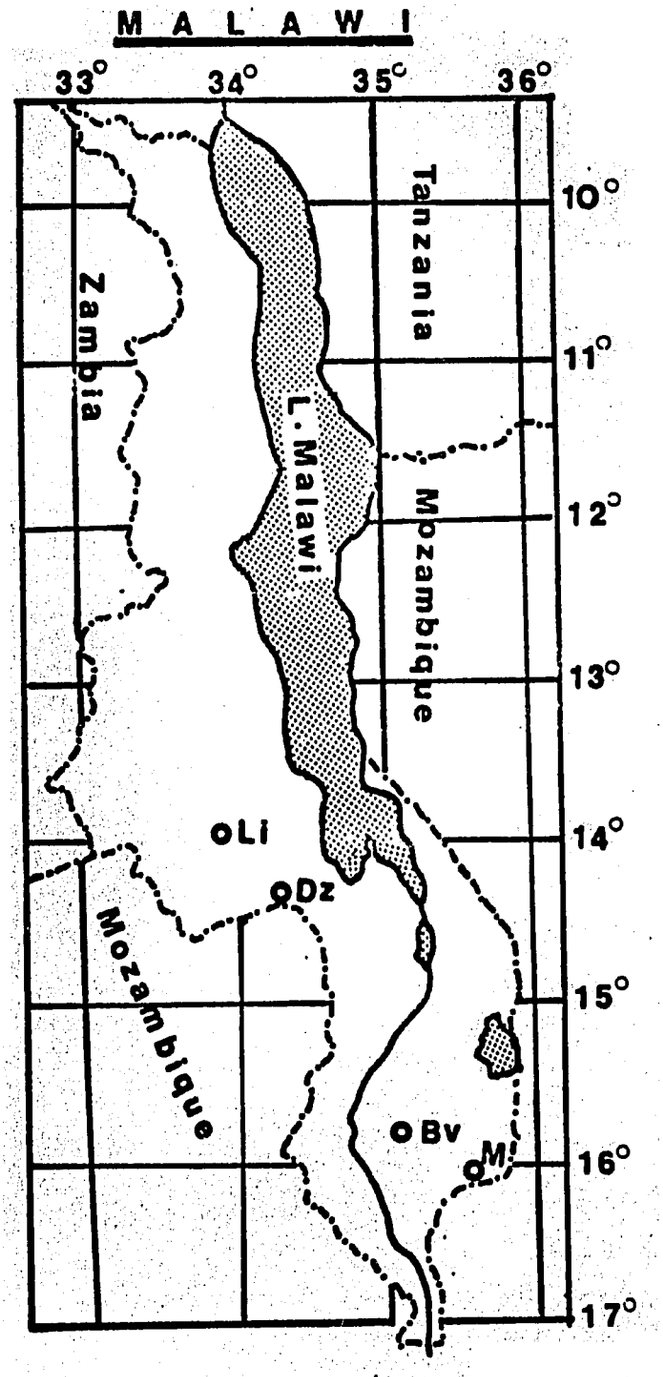


Figure 1. Map of Malawi showing places where the soil samples were taken.

The following abbreviations indicate:

Li = Lilongwe (Bunda soil)

Dz = Dedza

Bv = Bvumbwe

the top member of a catenary sequence. The top soil is dark red, sandy clay or sandy clay loam, with 30 per cent clay. The subsoil is bright red clay; no textural or structural B horizon; clay content usually increases to at least 180 cm; weak crumb structure is sometimes present; low C.E.C. suggests kaolinite is predominant; numerous quartz crystals; other weatherable materials are negligible (Re. Bvumbwe Agri. Res. Sta. Soil Map, unpublished).

Dedza Site - This soil belongs to Dedza series, a Ferruginous latosol of high altitude type (1440-1560 m). Brown and Young (1964) gave the following description:

Top soil is a dark reddish sandy clay loam, or is less commonly sandy clay. The dark color continues to a depth of 30 to 60 cm, and the profile is characterized by a contrast between the reddish brown (2.5 YR hue) or a dusky red subsoil, and a red lower subsoil. The subsoil is dusky red clay, strong medium block, clear ped cutans, weatherable minerals are common. Weathered rock commences at 100-120 cm.

Bunda Site - The soil belongs to Lilongwe series, A Ferruginous latosol. 0-15 cm: Dark reddish brown (5 YR 3/2) sandy clay loam; moderate fine crumb; slightly sticky, plastic, very friable, slightly hard; common coarse sand and fine quartz gravel; frequent roots; clear smooth boundary.

Characterization of Soil Samples

Physical and chemical properties.

Organic matter was determined by the modified wet combustion method of Walkley and Black, as described by Greweling and

Peech (1965). The pH was measured in water and 0.01M $CaCl_2$ at a soil: solution ratio of 1:1. The glass electrode of the pH meter was positioned in the supernatant.

Cation exchange capacity was measured by saturation with neutral N ammonium acetate. The soil was then washed with isopropyl alcohol; leached with 10 per cent weight/volume NaCl in 0.005N HCl, and NH_4 in the extract was determined by nesslerization. Ammonium acetate extraction was used for exchangeable bases. The organic matter in the extracts was destroyed by H_2O_2 and silica dehydrated with concentrated HCl. Lanthanum sufficient to give a 5% concentration was added to the residue, and the exchangeable bases were determined with a Jarrel Ash atomic absorption spectrophotometer.

Exchangeable acidity was measured by the $BaCl_2$-TEA method (Groweling and Peech, 1965).

Mineralogical Properties.

The soil samples were treated with sodium hypochlorite (NaOCl adjusted to pH 9.5) to remove organic matter. The method of Jackson (1969) was used to separate the sand, silt and clay size fractions. This method involves wet sieving, centrifugation and decantation.

The clay size fractions were K- and Mg-saturated, and mounted as parallel-oriented samples on glass slides, after which X-ray diffraction (XRD) analysis was used to determine the qualitative composition of the soil samples. XRD analysis was also used on random powder samples of the coarse materials to give a qualitative idea of the nature of the sand and silt

fractions. The XRD analyses were carried out on a Norelco diffractometer using CuK and X-radiation (35 KV, 15 ma).

The amounts of gibbsite and kaolinite in soil clay fractions were determined semiquantitatively using differential thermal analysis (DTA). 80 mg of the clay size fractions that had been Ca-saturated were mixed with 160 mg of aluminum oxide (Al_2O_3) and the samples were heated at the rate of 10°C per minute on an R. L. Stone DTA. The areas under the endothermic peaks of gibbsite and kaolinite were calculated and referred to a calibration curve prepared with known amounts of reference gibbsite and kaolinite specimens:

$$\text{Per cent in clay} = \frac{\%\ \text{by calibration curve} \times 100}{\%\ \text{soil clay in the mixture with } Al_2O_3}$$

Iron oxides were removed by citrate-bicarbonate-dithionite (CBD) extraction and the iron was determined by the ortho-phenanthroline method (Jackson, 1969). XRD analysis was run on these residues to observe the difference between soil with and without amorphous materials and iron. The 'active' amorphous materials were determined by the Tweneboah et al. (1967) procedure. The total amorphous materials (aluminosilicates) were determined by selective dissolution analysis (SDA) in hot 0.5N NaOH (Hashimoto and Jackson, 1960).

Phosphorus Chemistry

Total phosphorus.

The $HClO_4$ procedure of Jackson (1958) was used for the determination of total P. Samples were treated with HNO_3 for preliminary oxidation of organic matter after which $HClO_4$ was

used for digestion of the samples on a Kjeldahl digestion apparatus. Phosphorus was determined by the ascorbic acid method of Watanabe and Olsen (1965).

Fractionation of inorganic phosphorus.

The fractionation procedure of Chang and Jackson (1957) as described by Petersen and Corey (1966) along with several modifications was used. First, since the fractionation procedure of Chang and Jackson extracts both the adsorbed and crystalline P from soils, the adsorbed P was removed prior to fractionation by five successive extractions with 0.5N $NaHCO_3$ + 0.5N NaCl as suggested by Robarge (1971). Secondly, NH_4F extraction for Al-P was done for 24 hours instead of one hour (Fife, 1962; Williams et al. (1967). Thirdly, the extent of re-adsorption of P during the NH_4F extraction of Al-P was taken into account by the method of Williams et al. (1967). This is done by extracting an additional 0.5N $NaHCO_3$ pre-extracted sample with 0.5N NH_4F that contains 1 ppm P and Al-P values are then corrected on the basis of the recovery of the added phosphate:

$$Sa = 1 - \frac{\text{difference in P conc. (ug/ml)}}{1}$$

Sa = proportion of added P adsorbed by soil during extraction;

$$\text{Corrected Al-P} = \text{uncorrected Al-P} \times \frac{1}{1 - Sa}$$

Corrected Fe-P = uncorrected Fe-P = (corrected Al-P = uncorrected Al-P.

To determine the citrate-bicarbonate-dithionite extractable P (reductant-soluble), the procedure of Weaver (1974) was followed.

Phosphorus adsorption.

Phosphorus adsorption isotherms were determined essentially as described by Fox et al. (1971). Two gram air-dried samples were equilibrated at room temperature with various amounts of phosphorus (KH_2PO_4) in 0.01M $CaCl_2$ for 48 hours of continuous shaking, after which P in solution was determined by the ascorbic acid method of Watanabe and Olsen (1965). The P adsorption data were analyzed in terms of the Freundlich and the Langmuir equations. The Freundlich equation is given as:

$$x = KC^n$$

where x = ug of P adsorbed per gram of soil;

C = equilibrium solution concentration of P;

K, n = constants.

The Langmuir equation, in a linear form, is given as:

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

where x = ug of P adsorbed per gram of soil;

b = adsorption maxima;

c = equilibrium solution concentration of P;

k = constant and related to energy of adsorption.

Determination of Organic Phosphorus

A comparative study of procedures for estimating organic P was considered to be necessary so as to select the most suitable procedure for evaluation of organic P mineralization during

the incubation studies. Accordingly, organic P was determined by several ignition and extraction procedures.

Extraction methods.

1. Mehta et al. (1954).- The soil sample was extracted with hot concentrated HCl followed by cold 0.5N NaOH and then hot 0.5N NaOH. Inorganic P (P_i) was determined on an aliquot of the extract by the ascorbic acid method of Watanabe and Olsen (1965). Total extractable P (P_t) was also determined by the ascorbic method after as aliquot of the extract had been treated with acidified potassium persulfate and digested on a hot plate (Robarge, 1971). Organic P was taken as the difference ($P_t - P_i$).

2. Anderson method - The procedure of Mehta et al. (1954) as modified by Anderson (1960). This involves overnight extraction of the soil sample with 70 ml of 0.3N NaOH, to remove forms of organic P which would otherwise be hydrolized by the concentrated HCl. After centrifugation, the residue was treated as in the Mehta et al. method.

3. Anderson method modified - The soil samples were first extracted with 0.5N $NaHCO_3$ + 0.5N NaCl, and total and inorganic P were determined in the extracts. The residues were treated as in (2).

Ignition methods.

Saunders and Williams methods - These involve the ignition of the soil sample at 550°C or 240°C for one hour. The samples were then extracted with 0.2N H_2SO_4 or 2N H_2SO_4 for 17 hours.

Phosphorus was determined in the ignited and unignited samples, and organic P was estimated by difference.

Incubation Studies.

Continuous Incubation

Mulanje and Dedza soils were selected for this study. To each soil enough lime, $Ca(OH)_2$ was added to almost neutralize the exchangeable aluminum as determined from N KCl. (See Appendix 1) Four treatments were made as follows:

1. No corn Stover added; incubation at room temperature;
2. Addition of 2 per cent by weight of organic residue (ground corn Stover; 0.8% N and 0.24% phosphorus);
3. No corn Stover added; incubation at 35°C;
4. Addition of 2 per cent by weight of corn Stover; incubation at 35°C.

Before incubation, enough water was added to each soil so as to approximate field capacity. This was 40 ml water per 100 g of soil for mulanje soil, and 25 ml for Dedza soil.

Samples were taken at 3 week intervals over a total period of 12 weeks to study:

i. Total-, inorganic-, and organic-P by ignition at 550°C and 2N H_2SO_4 extraction;

ii. Adsorption of P. This was done by shaking 1 g (air-dry equivalent) of soil with a 0.01M $CaCl_2$ solution containing 50 ug P/ml for 48 hours.

At the end of 15 weeks additional analyses were carried out:

i. $NaHCO_3$-extractable total-, inorganic-, and organic-P were determined;

ii. NO_3^- and NH_4^+ were determined in 2N KCl extracts by Kjeldahl distillation;

iii. pH was determined in 0.01M $CaCl_2$.

Wet and Dry Incubation

The same Mulanje and Dedza soils were used in this study. Preparation of the samples was the same as in the treatments incubated continuously moist. The room temperature treatments were excluded. The samples were alternatively wetted and dried at one week intervals at a temperature of 35°C for a period of 8 weeks, after which the following studies were made:

i. Total-, inorganic-, and organic-P by ignition procedure as described before; and also by 0.5N $NaHCO_3$ extraction procedure;

ii. Adsorption of P, as described before, but using a solution of 25 ug P/ml.

iii. Fractionation of inorganic P as described before, but this time only the Al-P (one hour extraction), Fe-, and Ca-P were determined, together with the bicarbonate extractable P;

iv. NO_3^- and NH_4^+ were determined as before.

RESULTS AND DISCUSSION

Characterization of Soil Samples

Physical and chemical properties

Some selected analytical data for four Malawi soils are given in Table 1. The pH of the soils reflects the differences among the soils, as do the other physical and chemical properties. The pH as measured in water is higher than the pH measured in 0.01M $CaCl_2$, an indication that the soils have a net negative charge (van Raj, 1971). The low pH and the relatively low percentage base saturation in Table 1 for the Mulanje series are characteristic of a highly weathered latosol - a Ferrisol (believed to be an Ustox in the USDA new classification)

The relatively high amount of exchangeable bases for the Bunda soil are characteristic of the less weathered Ferruginous latosols (Ustalf). Bvumbwe series is believed to be a Ferrallitic latosol, or Eutrorthox by the USDA new classification (Ref.: Bvumbwe Agr. Res. Sta. Soil Map, unpublished). The fact that it is a Eutrorthox is not reflected in the slightly lower exchangeable base content than is usually expected. Although the Dedza series is classfied as a Ferruginous latosol (Young and Brown, 1964), this is not reflected in the analytical data in that the top soil (0-15 cm) has low exchangeable base content compared to the highly weathered Ferrallitic soil from Bvumbwe. This is based on the assumption that Ferruginous soils are the least weathered while the Ferrallitic soils are the most weathered, with the Ferrisols as intermediate (Brown,

Table 1. Some chemical characteristics of the four Malawi soils (0-15 cm).

Soil [1/]	C	pH		Exchangeable bases				$BaCl_2$-TEA		
		H_2O	$CaCl_2$	K	Ca	Mg	Sum	Extr. acid.	C.E.C.	Base sat.
	%			meq/100 g						%
Mulanje	1.52	4.8	4.2	0.10	0.24	0.30	0.64	14	17.2	3.7
Bvumbwe	1.99	5.6	5.2	0.39	4.11	1.55	6.05	5	18.8	32.2
Dedza	1.05	5.5	4.9	0.32	1.88	0.68	2.88	9	13.4	21.5
Bunda	1.37	6.1	5.6	0.53	4.99	1.88	7.40	9	15.5	47.7

1/ Mulanje soil - Ferrisol (Ustox);
Bvumbwe soil - Ferrallitic latosol (Eutrorthox);
Dedza soil - Ferruginous latosol (Ustult?);
Bunda soil - Ferruginous latosol (Ustalf)

1964; Young and Stephen, 1965).

The cation exchange capacity, on the other hand, does not reflect the relative age of the soils. The cation exchange capacity of the Mulanje soil and that of Bvumbwe soil is surprisingly high. This is probably a reflection of the higher organic carbon content of these two soils. There is a high correlation of the organic carbon and the C.E.C. (r = 0.9), and organic matter apparently contributes a considerable proprotion of the C.E.C. as measured by neutral N NH_4OAc. Pratt (1957) pointed out that the organic matter may contribute as much as 4.9 meq for every per cent increase in organic carbon (490 meq/ 100 g organic matter). Young and Stephen (1965), worked with high altitude Ferrallitic latosols (Ustox) of high organic matter (5-10 per cent) which had total exchangeable cations as high as 10 meq/100 g soil in the top soil, but less than 2 meq/100 g soil in the lower horizons. This clearly indicates the importance of organic matter to cation retention capacity.

The four soils showed a wide range of particle size distribution ranging from as high as 48 per cent clay for Mulanje soil to as low as 22 per cent clay for Bunda soil (Table 2) while Bvumbwe and Dedza soils are intermediate at 38 and 36 per cent clay, respectively. The per cent sand changes in the reverse order with Mulanje, Bvumbwe, Dedza and Bunda soils having 42, 48, 49, and 62 per cent sand, respectively.

Mineralogical properties

The random powder XRD patterns showed that the predominant mineral in the sand and silt fractions is quartz, although there are traces of apatite in the Dedza and Bvumbwe soils, and this was shown at 2.76 Å and 2.712 Å. An XRD peak at 1.90 Å may relfect some anatase in the

Table 2. Particle size distribution in four Malawi soils.

Sample	Sand 2.0-0.05 mm	Silt 0.05-0.002 mm	Clay <0.002 mm
	%		
Mulanje	42	10	48
Bvumbwe	48	14	38
Dedza	49	14	36
Bunda	67	11	22

Bunda soil, although there was no sign of the presence of the 3.51 Å peak for anatase. Young and Stephen (1965) noted the occurrence of olivine and apatite in the bedrocks of the plateau soil, although these were absent in soils.

The examination of the XRD patterns of the clay size fractions (Figures 2 to 5) indicates a wide range of variations with respect to mineralogical composition which may reflect differences in the degree of weathering that these soils have undergone. Kaolinite is the predominant mineral in all soils as shown by XRD peaks at 7.2, 3.58, and 2.38 Å units. Gibbsite is present in the

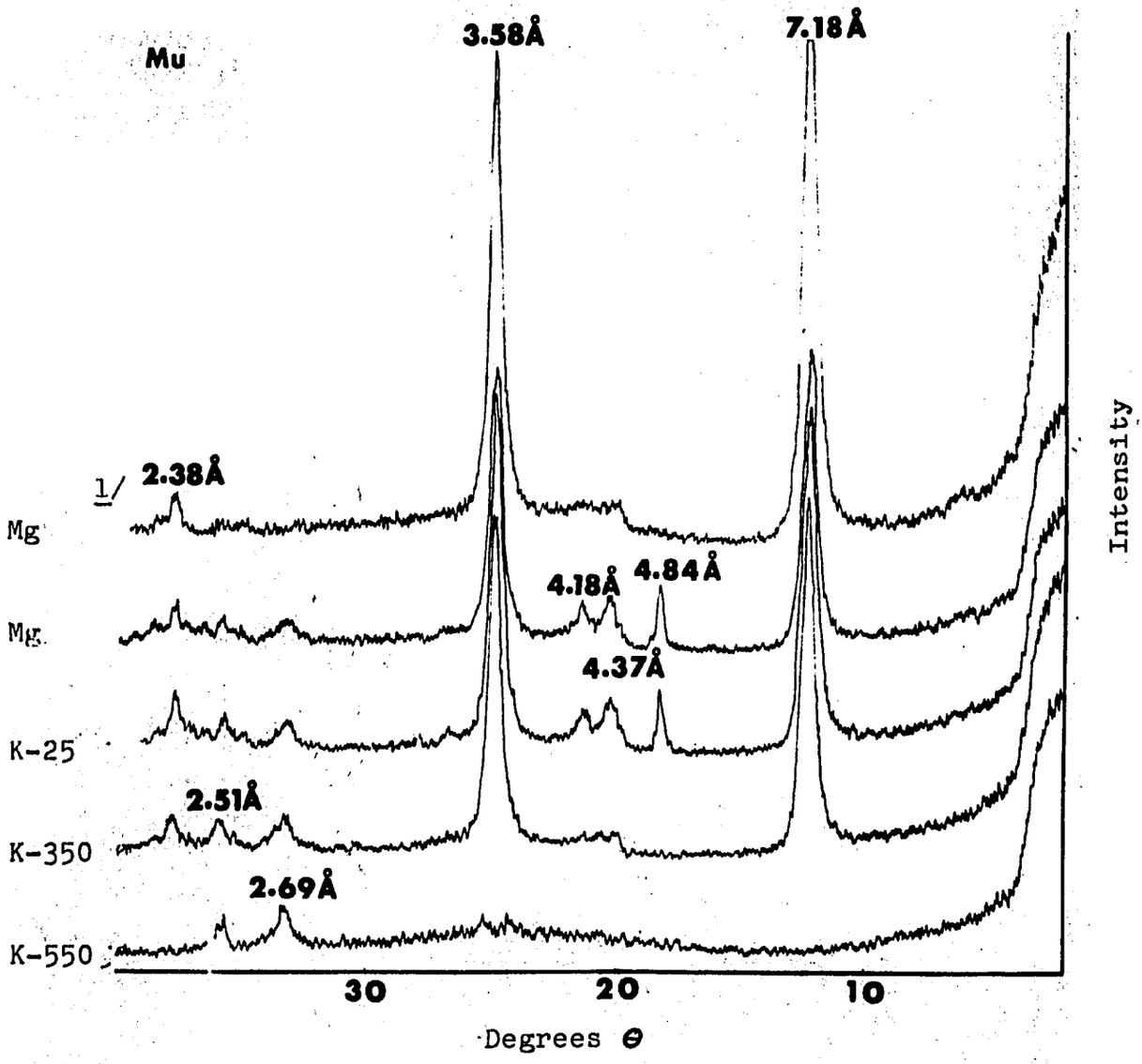


Figure 2. X-ray diffractions of the clay fraction of Ferrisol from Mulanje.

Mg 1/ - X-ray diffractions after removal of amorphous material and CBD-extractable Fe. (Figs. 2-5)

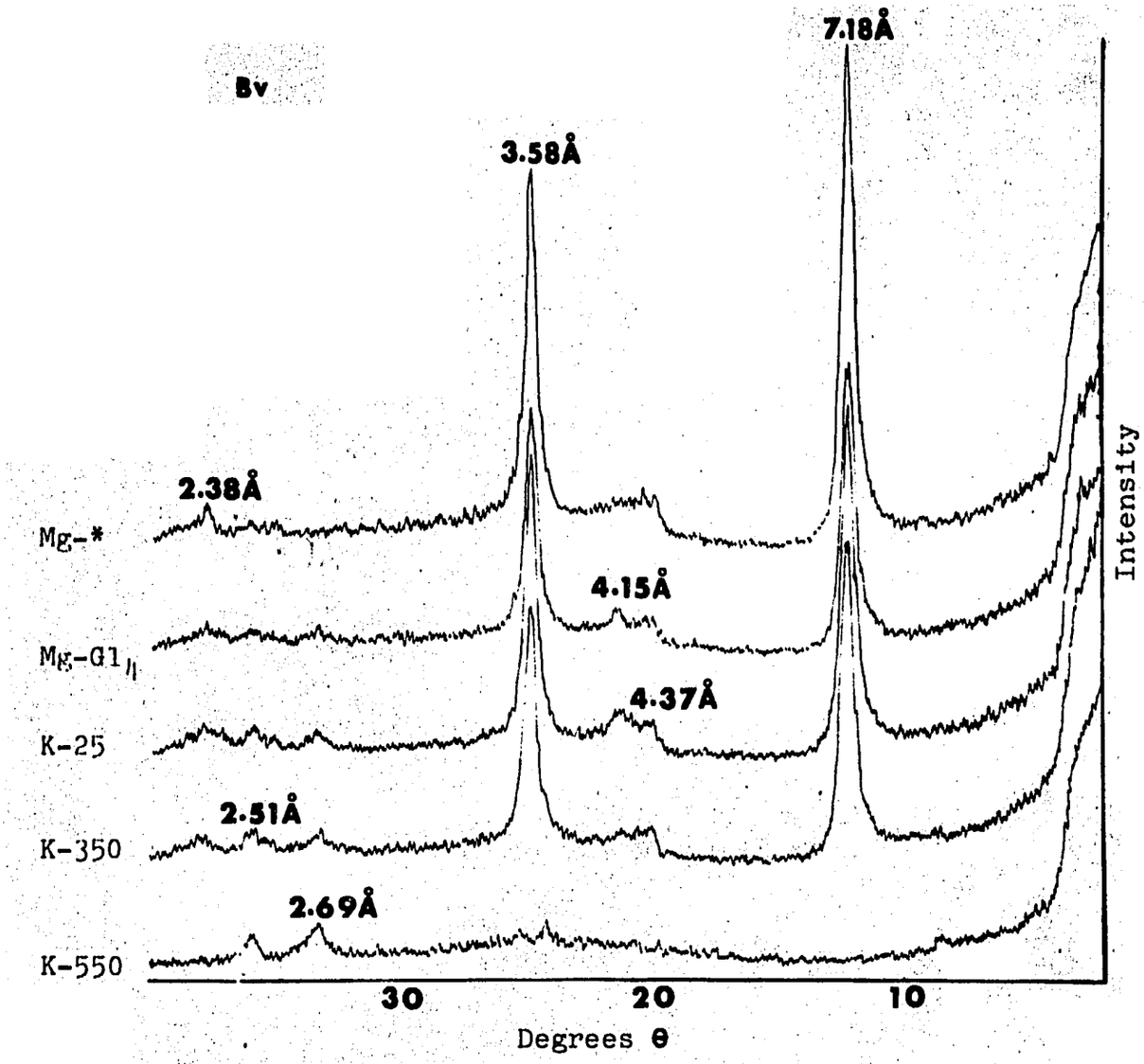


Figure 3. X-ray diffractions of the clay fraction of Ferralitic latosol from Bvumbwe.

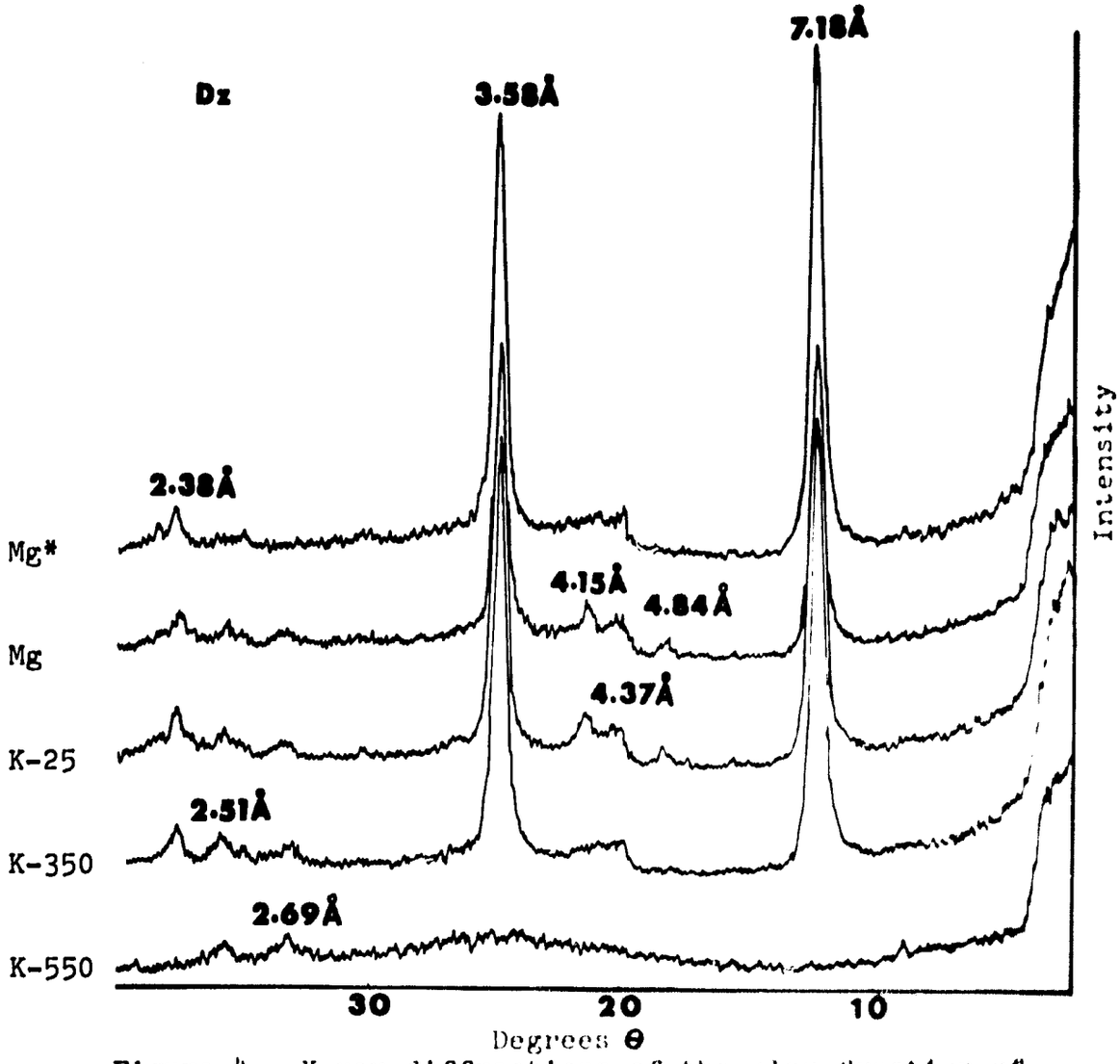


Figure 4. X-ray diffractions of the clay fraction of Ferruginous Latosol from Dedza.

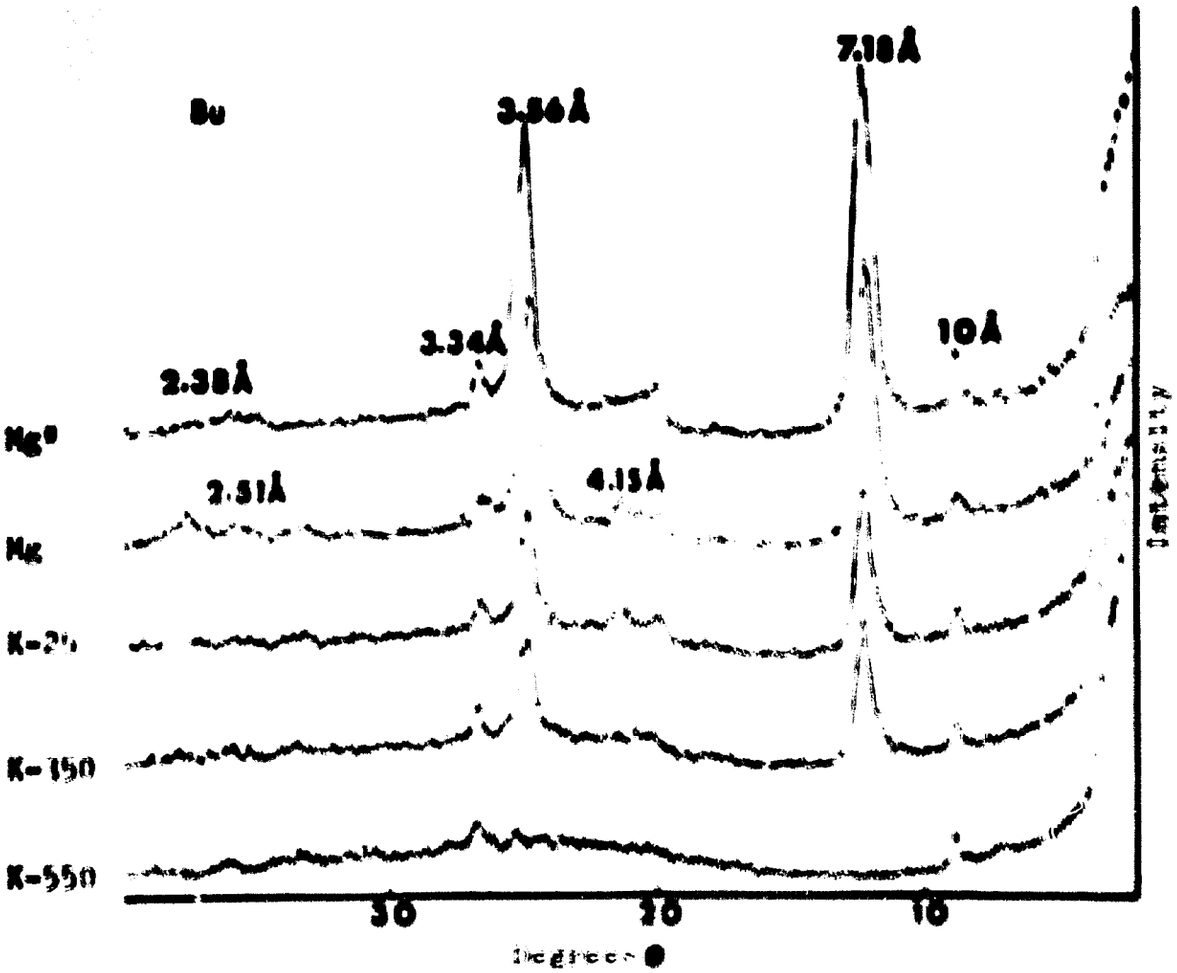


Figure 5. X-ray diffractions of the Clay fraction of Ferruginous Latosol from Bunda, Lilongwe.

Mulanje (Figure 2) and Dedza (Figure 4) soils as shown by XRD peaks at 4.87 and 4.37 Å, although the peaks for Dedza soil are not as intense as those of Mulanje soil. Crystalline iron oxides - goethite and hematite - were found in the clays in Mulanje and Dedza soils with peaks at 4.15 Å (goethite), and 2.69 and 2.51 Å (hematite). The present results are similar to those of Young and Stephen (1965) who found that the plateau soils of Malawi, including Mulanje and Dedza, had clay fractions consisting of gibbsite, kaolinite, goethite and hematite. As expected, the removal of iron oxides (CBD treatment), and amorphous material by the boiling 0.5N NaOH treatment caused the disappearance of the XRD reflections of goethite, hematite, and gibbsite for the Mulanje and Dedza soil clay fractions (Figures 2 and 4).

In addition to predominant XRD reflections for kaolinite, the Bunda clay fraction (Figure 5) showed XRD peaks corresponding to mica (10, 5.0, and 3.33 Å). There was also a small 10 Å peak for the Dedza soil clay detected on the K-saturated sample that had been heated at 550°C.

The differential thermal analysis (DTA) results verified the qualitative XRD results with respect to the presence of Kaolinite and gibbsite (Figure 6). The endothermic peak at 300-350°C signifies the presence of gibbsite in the Mulanje and Dedza soils, with values estimated at 13 and 6 per cent respectively, whereas the endothermic peaks are lacking for the Bvumbwe and Bunda soils. All soils exhibited a 560°C

endothermic peak, indicating the presence of kaolinite, with values estimated in the order of 43, 48, 54, and 45 per cent for Mulanje, Bvumbwe, Dedza, and Bunda soils respectively (Table 3).

Table 3. Mineralogical composition of the clay size fraction. (<0.002 mm) of soils from Malawi.

Sample	Free Fe_2O_3	Free Al_2O_3	Gibb	Kaol	Amorp	Total
	%					
Mulanje	11.0	0.11	13	43	20	88
Bvumbwe	11.0	0.10	--	48	26	85
Dedza	9.2	0.11	6	54	19	88
Bunda	10.0	0.10	--	45	21	76

The CBD-extractable iron oxide content (Table 3) which includes both crystalline and amorphous forms, did not vary much among the soil clay fractions. This is in contrast to the notable differences in the other chemical and physical properties of the soils (Tables 1-3). The nearly uniform iron oxide content of the clay fractions is, however, in agreement with the "saturation" concept of D'Hoore (1954) in which clay mineral surfaces accumulate iron oxides. Although it depends on a number of factors, occurrence of this process should cause the iron oxide contents of soil clay fractions, of from not too dissimilar parent materials, to tend towards a constant or "saturation" value at which all clay mineral surfaces are coated with iron oxides. D'Hoore arrived at a value of 10-12 per cent iron oxide content as the saturation point. The content of iron oxide in the present situation, 9-11 per cent, is near

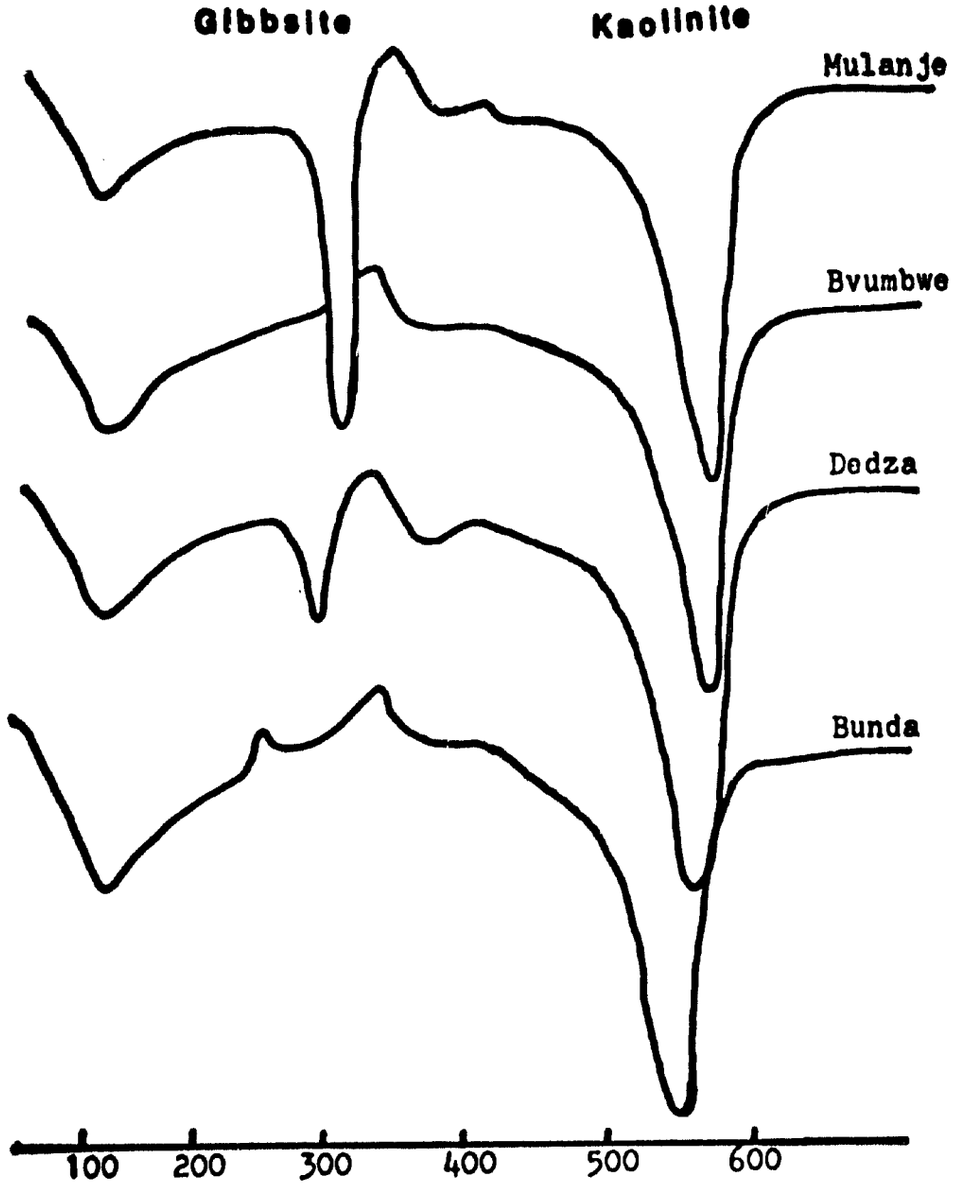


Figure 6. DTA peaks of the clay fraction of the four Malawi soils.

D'Hoore's value. The presence, however, of crystalline iron oxides, goethite and hematite, in the soil clay fractions would mean that not all of the iron oxides (Table 3) are associated with clay mineral surfaces and that further study would be necessary to explain the exact mode of occurrence of iron oxides in these soils.

Table 4. Composition of materials as extracted by 0.5N NaOH (Hashimoto and Jackson, 1960).

Soil	SiO_2	Al_2O_3 Total	Al_2O_3 Gibb	Al_2O_3 Amorp	Fe_2O_3	SiO_2/Al_2O_3
	%					
Mulanje	6.9	18.4	9.3	9.1	1.9	1.2
Bvumbwe	8.4	14.0	---	14.0	0.8	1.0
Dedza	6.9	12.7	4.1	8.6	1.2	1.4
Bunda	7.4	10.3	---	10.3	1.3	1.2

Selective dissolution analysis (SDA) results in Tables 3 and 4 show that amorphous materials constitute an appreciable amount of the soil clay fractions. This is in agreement with results reported on other highly weathered soils (Moniz and Jackson, 1967; Weaver, 1972; 1974). This amorphous material is probably a weathering product of kaolinite and may be an intermediate stage in a weathering sequence as suggested by Moniz and Jackson (1967):

Kaolinite ⟶ Amorphous ⟶ Gibbsite

The fact that the soil clay fractions which contained gibbsite (Mulanje and Dedza) also contained lesser amounts of amorphous materials is in support for the above sequence. In addition, SiO_2/Al_2O_3 ratios of the amorphous materials were considerably less than 2.0 which is the SiO_2/Al_2O_3 ratio for kaolinite. This means that the amorphous materials have been enriched in Al_2O_3 and/or depleted in SiO_2 relative to kaolinite.

Table 5. Active SiO_2, Al_2O_3, and Fe_2O_3 extracted from clay fractions by 0.5M $CaCl_2$ at pH 1.5.

Sample	SiO_2	Al_2O_3	Fe_2O_3	SiO_2/Al_2O_3
	ug/g clay			
Mulanje	3190	5440	1130	1.0
Bvumbwe	5220	6050	1090	1.5
Dedza	5320	5220	1420	1.7
Bunda	5640	4740	1740	2.0

The amounts of "active" amorphous materials (Table 5) as extracted by 0.5M $CaCl_2$ of pH 1.5 (Tweneboah et al., 1965) were much lower than that extracted by the more vigorous, boiling 0.5N NaOH procedure of Hashimoto and Jackson (1960). Presumably the extraction procedure of Tweneboah may be considered to remove surface-active amorphous components of the clay fraction that largely determine the surface charge properties of the soils.

Interestingly enough the SiO_2/Al_2O_3 ratios of the materials extracted by the Tweneboah procedure were higher than those of the Hashimoto and Jackson extraction (Table 4). This is the exact opposite of what was found for some Ustox of the Central Plateau, Brazil (Weaver, 1974). There were, however, some

similarities. For example, the sand content of the four soils was positively correlated with the active SiO_2 content of the clay fractions (r = 0.71), and also with the SiO_2/Al_2O_3 ratios of the clay fractions (r = 0.89). Presumably for these Malawi soils, as was described for those of Brazil, the quartz which dominates the sand fractions undergoes a slow, irreversible dissolution to release monosilicic acid $Si(OH)_4$, which is then adsorbed by the aluminous surfaces present in the clay fractions.

It should be pointed out that the sum of the mineralogical components in Table 3 are considerably less than 100 per cent. The differences probably result from uncertainities in the hydration status of the iron oxides and 0.5N NaOH extractable amorphous materials, and the presence of undetermined minerals. An example of the latter would be mica that was shown by XRD analysis to be present in the Bunda clay fraction, and indeed the amount could be as much as 10 per cent.

On the basis of chemical, physical, and mineralogical properties, it can be concluded that the Mulanje soil is more weathered than the other soils, and Bunda soil is the least weathered, with Bvumbwe and Dedza soils as intermediate. The use of gibbsite as an indicator of an extreme degree of desilication and advanced weathering stage, as suggested by Moniz and Jackson (1967) does not, in the present study, appear to be consistent with the classification of the Bvumbwe and Dedza soils. The former has been designated as an Oxisol but

contains no gibbsite, while the Dedza soil, classified ad a Ferruginous latosol (Alfisol?), has gibbsite in the clay fraction. Generally speaking, Oxisols are considered to be more highly weathered than Alfisols. However, it should be kept in mind that only surface horizons were studied and examination of the diagnostic subsurface horizons of these soils might allow a resolution of the apparent discrepancy.

Phosphorus Chemistry

Inorganic phosphorus fractions.

Results of the inorganic phosphate fractions are summarized in Table 6. It was observed that on the average, the 0.5N NH_4F- extractable Al-P was the predominant form of inorganic P, with values in the order of Al-P (148 ppm), Red-P (110 ppm), Fe-P (104), second NH_4F-extractable Al-P (89 ppm), adsorbed P (76 ppm) and Ca-P (31 ppm).

The proportion of sodium bicarbonate-extractable P (adsorbed P) in the soils under study was much greater than the values reported by Weaver et al. (1975) for some highly weathered soils of Puerto Rico. The soils from Malawi seem to have relatively higher contents of adsorbed P, with results ranging from a low of 60 ppm P for Mulanje soil to a high of 88 ppm for Bunda soil, with Bvumbwe (79 ppm) and Dedza (87 ppm) being intermediate. Presumably the bicarbonate extractable P may be taken to represent a reasonable approximation to the amount of labile P in these soils.

The results reported in the present study (Table 6) are not in agreement with what has been reported for some soils of the humid tropics. Generally, it has been shown that in highly weathered, acid soils, Ca-P (apatite) readily weathers to form Al-P, Fe-P, and reductant-soluble-P (Chang and Jackson, 1957; Hsu and Jackson, 1960; Dahnke et al., 1964; Weaver et al., 1975). Thus with increasing weathering the order of abundance should be Red-P>Fe-P>Al-P>Ca-P. The Malawi soils agree with the latter sequence only in that Ca-P is the fraction present in lowest amounts.

The greater amounts of Al-P in the Mulanje (118 ppm P) and Bvumbwe (220 ppm P) soils in relation to that of Fe-P may reflect recently fertilized soils, thus supporting the theory that there is a strong and rapid formation of Al-P which, upon aging, will be transformed into Fe-P and reductant-soluble P. Shelton and Coleman (1968) observed that in the highly weathered red soils, the initial increase in Al-P was greater than Fe-P at all rates of fertilizer P application, and this may be attributed to greater reactivity of aluminum oxides relative to those of iron in regard to formation of P reaction products. With increasing elapsed time after application, there was a relative decrease of Al-P and increase in Fe-P. As for the other two soils, Dedza and Bunda, there was no significant difference between the Al-P and Fe-P fractions.

Table 6. Inorganic phosphate fractions of four Malawi soils.

Soil	Adsorb-P	Al-P	Fe-P	Ca-P	Red-P	Al-P*	Sum (P_I)
	ppm						
Mulanje	60	118	42	16	78	63	377
Bvumbwe	79	220	118	41	148	113	719
Dedza	87	153	154	30	124	112	660
Bunda	88	103	104	36	91	70	492
Mean	79	149	105	31	110	90	562

Al-P - corrected;

Fe-P - uncorrected;

Al-P*- NH_4F-extractable Al-P after citrate-bicarbonate-dithionite extraction of reductant-soluble-P.

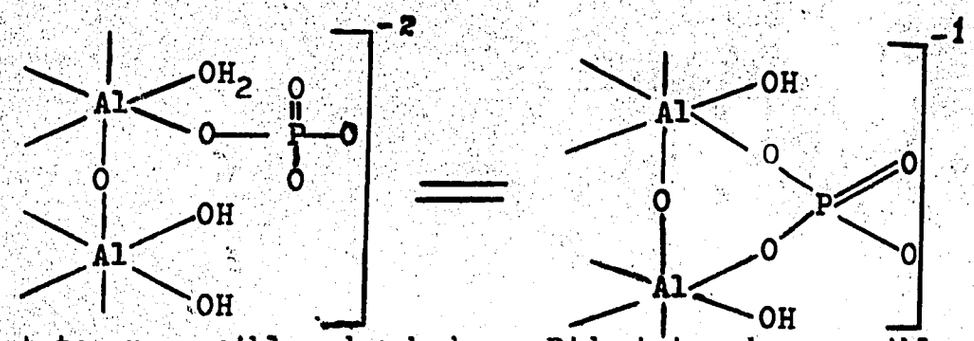
In addition to the effect of recent P fertilizer additions, the relative high proportion of Al-P to Fe-P may in part be a result of some of the modifications incorporated into the fractionation procedure. For example, the 0.5N NH_4F extraction for Al-P had been changed from one hour as suggested by Chang and Jackson (1957) to 24 hours as suggested by Fife (1962) and this may have resulted in the removal of inorganic P that would otherwise have been estimated as Fe-P. Furthermore, application of the correction for adsorption of P by active iron oxides during the NH_4F extraction for Al-P fraction causes this fraction to increase at the expense of the Fe-P fraction. For Mulanje and Bvumbwe soils, there was quite a high proportion of Al-P which was re-adsorbed as Fe-P (35 ppm and 42 ppm respectivelv) whereas very little was re-adsorbed in Dedza soil (17 ppm P) and Bunda soil (14 ppm P).

Because the bicarbonate-extractable P fraction is probably the most important fraction in regard to plant uptake, simple regression analyses were carried out to relate the amount of this fraction with some of the soil properties. It was found that $NaHCO_3$-extractable P was negatively correlated with per cent clay ($r = -0.828$). This is somewhat unexpected as ordinarily it is the clay fraction or minerals associated with the clay fraction, that are chiefly responsible for adsorption of P by soils. Thus it would generally be expected that the amount of adsorbed P would increase with increasing clay content, rather than the opposite as found in this case.

It was also found that the amount of bicarbonate extractable P was correlated with the amount of SiO_2 extracted by 0.5M $CaCl_2$ of pH 1.5 (r = 0.978) and to the SiO_2/Al_2O_3 ratio of the acidified $CaCl_2$ extracts (r = 0.948). Apparently, the degree of the silication of the amorphous surfaces of the clay fractions has an important influence on the amount of adsorbed P, and the greater the proportion of active SiO_2 the greater the amount of adsorbed or bicarbonate-extractable P. This would also explain why the adsorbed P content is inversely proportional to the clay content as noted above. That is, it has been shown previously that the amount of active SiO_2 and the active SiO_2/Al_2O_3 ratios are directly proportional to the amount of sand or inversely correlated with the clay content. Thus, if an increased degree of silication of the amorphous surfaces in the clay fraction causes an increase in the adsorbed P content, it would indeed be expected that adsorbed P should increase as the clay content decreases, in view of the forementioned relationship between soil texture and degree of silication.

Some recent work by Hingston et al. (1974) on the desorption of P from goethite (FeOOH) and gibbsite ($Al_2O_3 \cdot 3H_2O$) may afford an explanation of the mechanism by which the degree of silication influences the bicarbonate-extractable P content. According to these workers, P may be adsorbed on to Fe or Al oxide surfaces as a monodentate or bidentate Fe or Al-phosphate

complex as given below:



Monodentate, reversibly adsorbed, bicarbonate-extractable **Bidentate, irreversibly adsorbed, non-bicarbonate-extractable.**

Because of the increase in entropy that probably results from ring formation, the bidentate complex is probably more stable than the monodentate complex, and while it has not been verified experimentally, it is within reason to expect that the monodentate complex should be much more likely to be extracted by $NaHCO_3$ than the more stable, bidentate complex. Silica or monosilicic acid can be adsorbed by Fe and Al oxides in a manner similar to that of P. This being the case, then it would seem plausible that an increased amount of adsorbed silica would have the effect of limiting the potential adsorption sites in which P could form the bidentate complex. Up to a point then, with increasing degree of silication, the form of adsorbed P might be increasingly the more labile, monodentate complex.

Total phosphorus

The results of the $HClO_4$-extractable total phosphorus (P_T) using Jackson's procedure (1958) are shown in Table 7. It is noted that the Dedza soil which has the largest pool of total P (1625 ppm P) has only 5 per cent of the total extracted by $NaHCO_3$, whereas the Bunda soil which has only 835 ppm total P

had 10 per cent of the total extractable by $NaHCO_3$. The values for the ratio of the sum of the inorganic fractions and total P (P_I/P_T) suggest that nearly half of the total P in the soils is present as organic P. Interestingly enough the Dedza and Bvumbwe soils which gave apatite XRD peaks in the sand and silt fractions at 2.76 and 2.712 Å, are the soils with the highest total content of P, but most of this is not extractable during fractionation.

Table 7. Sum of inorganic-P (P_I) and adsorbed-P as per cent of total.

Soil	Total-P (P_T)	P_I	Adsorb-P	P_I/P_T	Adsorb/P_T
	ppm			%	%
Mulanje	744	376	60	50	8
Bvumbwe	1250	719	79	57	6
Dedza	1630	661	87	41	5
Bunda	835	491	88	59	10

Adsorption of phosphorus

Phosphorus adsorption isotherms were used in this study for the characterization of the soils with regard to phosphorus requirements. Figure 7, Table 8 and Appendix 2 summarize the results. The data were interpreted in terms of the Freundlich equation ($X = kc^n$) and the Langmuir equation ($\frac{c}{x} = \frac{1}{kb} + \frac{c}{b}$). The correlation coefficients that resulted when the adsorption data were fitted to the Freundlich equation were r = 0.976, r = 0.996, r = 0.991, and r = 0.986 for Mulanje, Bvumbwe, Dedza and Bunda

soils, respectively. For the Langmuir equation or plots of $\frac{c}{x}$ against c, values of r = 0.998, r = 0.990, r = 0.996 and r = 0.993 were obtained for the soils in the same order. The higher correlations with the Langmuir equation shows that within the range of concentrations used in the present study, the Langmuir equation best describes the P adsorption. Thus plots of c/x versus c to calculate the slope (1/b) from which adsorption maximum (b) can be calculated, and a constant (k) relating to the bonding energy can be calculated from the intercept (Bache and Williams, 1971; Olsen and Watanabe, 1957).

From the results in Figure 7 it is quite clear that the four soils differ not only in the amount of P adsorbed but also in the slopes of the adsorption isotherms. The adsorption maxima (Table 8) as calculated according to the Langmuir equation, had values that ranged from as high as 898 ppm P for the most highly weathered Mulanje soil to as low as 187 ppm for the more coarse textured, moderately weathered Bunia soil, with 778 ppm P for Bvumbwe and 460 ppm P for Dedza soil. Interpretation of the adsorption maxima values can be of great use agronomically. Woodruff and Kamprath (1965) related the degree of saturation of the phosphorus adsorption maxima to the availability of P to millet. They worked with P rates ranging from 0 to 1-1/2 times the adsorption maxima. From their greenhouse results they observed that soils with a large P adsorption maxima did not require as much saturation of the adsorption maximum as those with low adsorption maximum, for optimum growth. Liming also de-

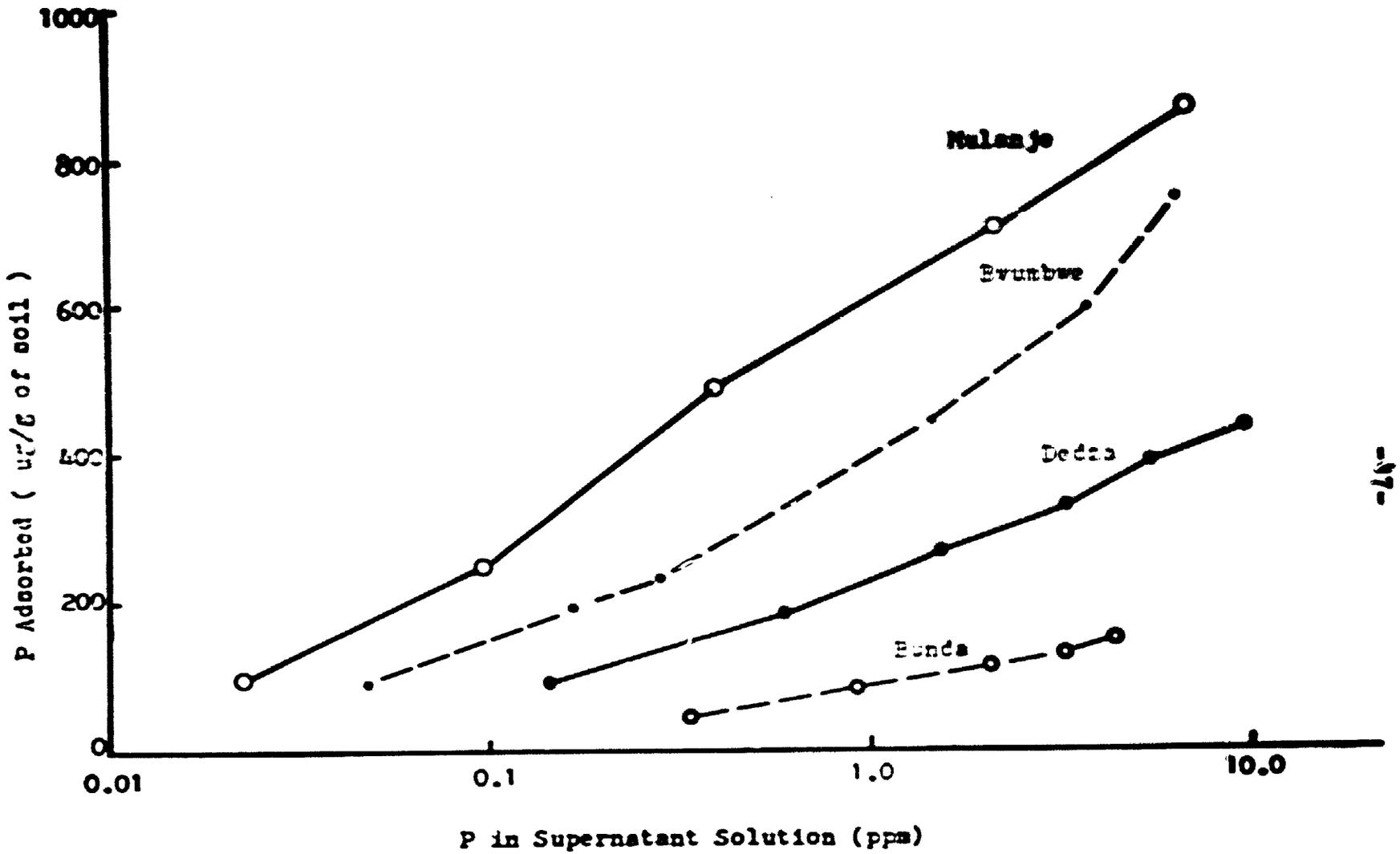


Figure 7. P adsorption isotherms of the four soils from Malawi.

Table 8. Some adsorption data for the four Malawi soils.

Soil	Adsorption maxima	sorbed P at 0.2 ppm solution P	K
	ppm		ml/ug
Mulanje	898	375	2.68
Bvumbwe	778	205	1.50
Dedza	460	115	1.05
Bunda	187	27	0.74

creased the requirement for P saturation.

Fox et al. (1968) suggested that the values of adsorbed P at 0.2 ppm P in the supernatant solution can be used to evaluate the P requirements of Hawaiian soils for maximum plant growth. If the requirements for the four Malawi soils are calculated on the same basis, the values are in the order of 375, 205, 115, and 27 ppm P for Mulanje, Bvumbwe, Dedza and Bunda soils, respectively. As predicted from adsorption isotherms in Figure 7, the sandier and least weathered Bunda soil does not require much P whereas Mulanje soil, which is highly weathered requres a much higher P

Table 9. Relationship between P adsorption maxima and soil properties.

Soil property	Corr. coeff.	Regression equation
Clay (%)	0.96	Y = -438 + 28.2X
CBD Fe_2O_3 (%)	0.98	Y = -324 + 241X
NaOH-Al_2O_3 (%)	0.91	Y = -34.4 + 114X
Active Fe_2O_3 (ug/g)	0.58	Y = -579 + 2.5X
Active Al_2O_3 (ug/g)	0.98	Y = -330 + 0.46X
Active SiO_2/Al_2O_3	-0.95	Y = 1,681 - 710X
Base saturation (%)	-0.78	Y = 935 - 13.5X
pH (H_2O)	-0.85	Y = 3,386 - 510X
pH ($CaCl_2$)	-0.83	Y = 2,885 - 467X

application. On the average, the values in the present study are much lower than those reported for the highly weathered soils of Hawaii (Fox et al., 1971), Puerto Rico (Weaver et al., 1975), or Brazil (Weaver, 1974). The requirements for some Hawaiian

soil were as high as 1200 ppm P.

The results of simple regression analyses that relate the phosphorus adsorption maxima to soil properties are listed in Table 9. The values of CBD Fe_2O_3; active Fe_2O_3 and Al_2O_3; and NaOH-Al_2O_3, which had been determined on the clay fractions were re-calculated on a whole soils basis prior to determination of the regression relationships. Overall, the results show that clay content and oxides of aluminum and iron are highly correlated with the adsorption maxima which is generally found for acid soils (Hsu, 1964). The contribution of the clay probably results from the fact that the iron and aluminum oxides, active in P retention, predominantly occur in the clay sized fraction.

It is of interest to note that the active Fe_2O_3 content or that extracted by 0.5M $CaCl_2$ of pH 1.5, was not too well correlated with the adsorption maxima. This has also been observed for some Oxisols from the Central Plateau of Brazil (Weaver, 1974). In latter study, it was found, however, that the active Fe_2O_3 contents were highly correlated with the organic C contents of the soils. It was suggested that the iron extracted by 0.5M $CaCl_2$ of pH 1.5 was that in combination with organic matter and therefore would not be active in P retention. Apparently a similar situation exists for these Malawian soils.

It should also be pointed out that the active SiO_2/Al_2O_3 ratios were inversely related ($r = -0.95$) to the adsorption maxima. This relationship in combination with the one shown

previously - that the active SiO_2/Al_2O_3 ratios were correlated with the sand content, is identical to earlier observations reported for some Brazilian Oxisols (Weaver, 1974). The basis of this relationship as described by Weaver, is that the slow dissolution of quartz in the sand fractions, over long periods of time, produces monosilicic acid which is adsorbed by aluminous surfaces in the clay fraction. The nature of quartz dissolution causes the active SiO_2/Al_2O_3 ratios of clay fractions to be proportional to the sand (quartz) content.

Determination of organic phosphorus

Table 10 shows the average values for all the soils from Table 11 to 14 for the extractable total-, inorganic-, and organic-P 1/. In general, the ignition methods - 240°C or 550°C, both mild (0.2N H_2SO_4) and vigorous (2N H_2SO_4) extractions gave higher values for the organic P content of the four acid soils than the extraction methods. The best extraction method (Anderson-modified) gave only about 50 per cent and 33 per cent of the mild and vigorous extractions respectively. This is somewhat different from the results of Bornemisza and Igue (1967) who found that the Mehta extraction method gave larger estimates of organic P than ignition methods or Omotoso

1/ Total P (P_t) in this section refers to the sum of inorganic (P_i) and organic (P_o) P extracted by a given procedure for organic - P. It will not necessarily be identical to the total P (P_Y) value as given by $HClO_4$ digestion nor will values for inorganic extractable P be identical to the sum of the inorganic fractions as determined in the previous section (P_I).

(1971) who could not find any difference between extraction and ignition methods when applied to Nigerian soils.

On individual soil basis (Tables 11-14), there was a great variation in the amount of organic P determined depending upon the method used for estimation. Except for Dedza soil (Table 13), the extraction method gave higher values for total P (P_t) than either of the ignition methods, and the ignition method with mild extraction gave the least values. The higher values of total P for extraction gave the least values. The higher values of total P for extraction methods as compared to ignition methods have been noted by Bornemisza and Igue (1967). It is believed that pretreatment with concentrated HCl plays an important role in facilitating the extraction of organic P by removing Ca, Mg and other polyvalent cations that may cause precipitation of dissolved organic phosphates, and also disintegrates clay complexes, thus releasing adsorbed organic P (Saxena, 1964).

The extraction methods also gave about twice as much inorganic P as did the ignition methods. This strongly suggests that the lower estimates of organic P as obtained by extraction methods is a result of hydrolysis of organic P during extraction rather than incomplete extraction. This is in agreement with Enwezor and Moore (1966a) who worked with 11 Nigerian soils and found that the extraction values for organic P were only half those of ignition.

Explanation of the type of methods used in Tables 8-12.

Anderson - 0.3N NaOH; conc. HCl then cold and hot 0.5N NaOH;

Mehta* - conc. HCl and cold and hot 0.5N NaOH; 0.3N NaOH;

Anderson*- 0.5N $NaHCO_3$; then as Anderson above;

Ignition I - Ignited soil at 550°C minus unignited soil (2N H_2SO_4)

Ignition II - As above, but using 0.2N H_2SO_4.

Ignition III - As ignition I, but at 240°C;

P_T-P_I - P_T is total-P in $HClO_4$ digestion; P_I is sum of inorganic P fractions.

Total P - Sum of inorganic and organic P

Table 10. Average of extractable total-P, inorganic-P, and organic-P for four Malawi soils

Method	Total-P	Inorganic-P	Organic-P	% Organic-P
	ppm			
Anderson	903	764	139	15.4
Mehta*	931	783	148	15.9
Anderson*	816	660	156	19.1
Ignition I	859	396	463	53.9
Ignition II	591	232	359	60.7
Ignition III	610	396	214	35.1
P_T - P_I	1113	562	551	49.5

Table 11. A comparison of different methods for estimating total-P, inorganic-P, and organic-P in Mulanje soil.

Method	Total-P	Inorganic-P	Organic-P	% Organic-P
	ppm			
Anderson	680	531	149	21.9
Mehta*	705	574	131	18.6
Anderson*	598	461	137	22.9
Ignition I	526	262	264	50.2
Ignition II	298	137	161	54.0
Ignition III	375	262	113	30.1
$P_T - P_I$	744	376	368	49.5

Table 12. A comparison of different methods for estimating total-P, inorganic-P, and organic-P in Bvumbwe soil.

Method	Total-P	Inorganic-P	Organic-P	% Organic-P
	ppm			
Anderson	1112	926	186	16.7
Mehta*	1172	960	212	18.1
Anderson*	1038	813	225	21.7
Ignition I	992	528	464	46.8
Ignition II	684	311	373	54.5
Ignition III	878	528	350	39.9
$P_T - P_I$	1250	719	531	42.5

Table 13. A comparison of different methods for estimating total-P inorganic-P, and organic-P in Dedza soil.

Method	Total-P	Inorganic-P	Organic-P	% Organic-P
	ppm			
Anderson	1120	1012	108	9.6
Mehta	1122	1000	122	10.9
Anderson*	1001	867	134	13.3
Ignition I	1281	424	857	66.9
Ignition II	929	242	687	74.0
Ignition III	622	424	198	31.8
$P_T - P_I$	1625	660	965	59.4

Table 14. A comparison of different methods for estimating total-P, inorganic-P, and organic-P in Bunda soil.

Method	Total-P	Inorganic-P	Organic-P	% Organic-P
	ppm			
Anderson	700	586	113	16.1
Mehta*	725	597	128	17.6
Anderson*	627	500	127	20.2
Ignition I	638	372	266	41.7
Ignition II	452	238	214	47.3
Ignition III	564	372	192	34.0
$P_T - P_I$	835	491	344	41.2

Except for the Mulanje soil (Table 11), the Anderson method gave the least estimates of organic P, followed by the Mehta-modified method. Pre-extraction of the samples with 0.3N NaOH is believed to remove some of the organic P that may be hydrolyzed by concentrated HCl (Anderson, 1960). In the present study, the Mehta-modified (concentrated HCl, cold and hot NaOH and 17-hour extraction with 0.3N NaOH) and the Anderson method (17 hour extraction with 0.3N NaOH, concentrated HCl, then cold and hot NaOH) were compared. It was observed that there were no significant differences between the two procedures. As a matter of fact, the pre-extraction with 0.3N NaOH as suggested in the Anderson method suppresses the extraction of both the inorganic and organic P. A modification of the two methods was made by first pre-extracting the soil with 0.5N $NaHCO_3$ + 0.5N NaCl. This procedure slightly suppresses the extraction of both the total and inorganic P by about 100 ppm, but it gives a much higher estimate of organic P than either the Mehta or the Anderson methods. It may indicate that there is a decreased degree of hydrolysis of organic P. MacLean (1965) working with some highly acid (pH 4.6) podzols in Quebec, Canada found that not only does the effectiveness of sodium bicarbonate increase with increasing temperature at which organic P is extracted, but also as the pH of the extractant is increased. Furthermore, pre-extraction of the samples with HCl increased organic P extracted by $NaHCO_3$,

and the results were in the order of 98 per cent of the total organic P estimated by Mehta et al method. Thus, the present modification of the Mehta-Anderson procedure is superior to the original methods, although small number of samples makes it difficult to make concrete recommendations.

Although all of the ignition procedures gave higher estimates of organic P than did the extraction methods, there was considerable difference among the ignition procedures. With ignition at 550°C, the 2N H_2SO_4 extractant gave much larger estimates of organic P than that of 0.2N H_2SO_4. This is probably due to the fact that a proportion of organic P mineralized by ignition has formed reaction products with iron and aluminum oxides which are not attacked by the weaker 0.2N H_2SO_4 extractant. Similar results have been reported for other highly weathered soils (Bornemisza and Igue, 1967; Weaver et al., 1975).

Ignition temperature (550°C versus 240°C) also influenced the organic P estimates with the higher temperature giving the largest estimates presumably as a result of more complete oxidation of organic P. The tendency for the 550°C ignition temperature to give higher values of organic P is greater in the Dedza soil (Table 13) for which the 550°C treatment gave 857 ppm organic P while the 240°C gave only 238 ppm.

In addition to incomplete extraction and/or incomplete oxidation which lead to low estimates of organic P, ignition procedures can give erroneously high estimates if there is an increased extractability of the inorganic P induced by ignition. Black and Goring (1953) reported that ignition may increase the dilute-acid solubility of certain naturally occurring iron and

aluminum phosphates. Williams et al. (1970) found that for nodules from strongly weathered soils - dominantly composed of gibbsite and kaolinite - extractable inorganic P increased sharply between 550°C and 650°C. Norrish (1968) found that the Plumbogummite group of phosphate minerals when heated above 400°C, lose their structural water and become amorphous in which form they can be extracted by 0.2N or 2N H_2SO_4. This would cause the ignition values of organic P to be greater than the Anderson-Mehta extraction values. Dahnke et al. (1964) disputed the idea that ignition increases the extractability of inorganic P in that they found that the amounts of organic P in the subsurface horizons, as determined by ignition, were very low and apparently the ignition treatment had little effect on the inorganic P. Hance and Anderson (1962) arrived at a similar conclusion in a comparative study of ignition versus extraction methods.

A somewhat independent approximate estimation of organic P is given by the following:

$$P_T - P_I,$$

where P_T = total P as determined by the $HClO_4$ method of Jackson (1958);

P_I = sum of inorganic P fractions from the fractionation results as determined by the method of Chang and Jackson (1957) as modified.

Looking at each soil individually (Tables 11-14), the $P_T - P_I$ gave the highest estimates of organic P, and the values are closer to those of ignition values than those of extraction. This procedure gives a very approximate estimate of organic P since not all the inorganic P fractions may have been completely removed. An example of such an inorganic fraction would be the quartz-included apatite of Syers et al. (1967).

A summary statement is not easy to make but it seems that the method of ignition at 550°C followed by 2N H_2SO_4 extraction is the most suitable one for estimation of organic P in these Malawi soils. This method apparently gives the maximum extraction of organic P with a minimum hydrolysis. Furthermore, the simplicity of the ignition method, compared to the extraction techniques should enable more reproducible results to be obtained.

Incubation Studies

Continuous incubation

Inorganic and organic phosphorus.

The inorganic and organic P contents of the continuously moist incubated samples, as given by ignition at 550°C and 2N H_2SO_4 extraction, are shown in Figures 8 and 9 and in Table 15. As suggested by Wier and Black (1968), mineralization of organic P was taken as the average of the increase in inorganic P and decrease in organic P as compared to unincubated samples. Thus an increase in inorganic P was assigned a positive sign while a decrease was given a negative sign. For organic P, an increase was given a negative sign and a decrease, a positive sign. In this manner if the algebraic average of the

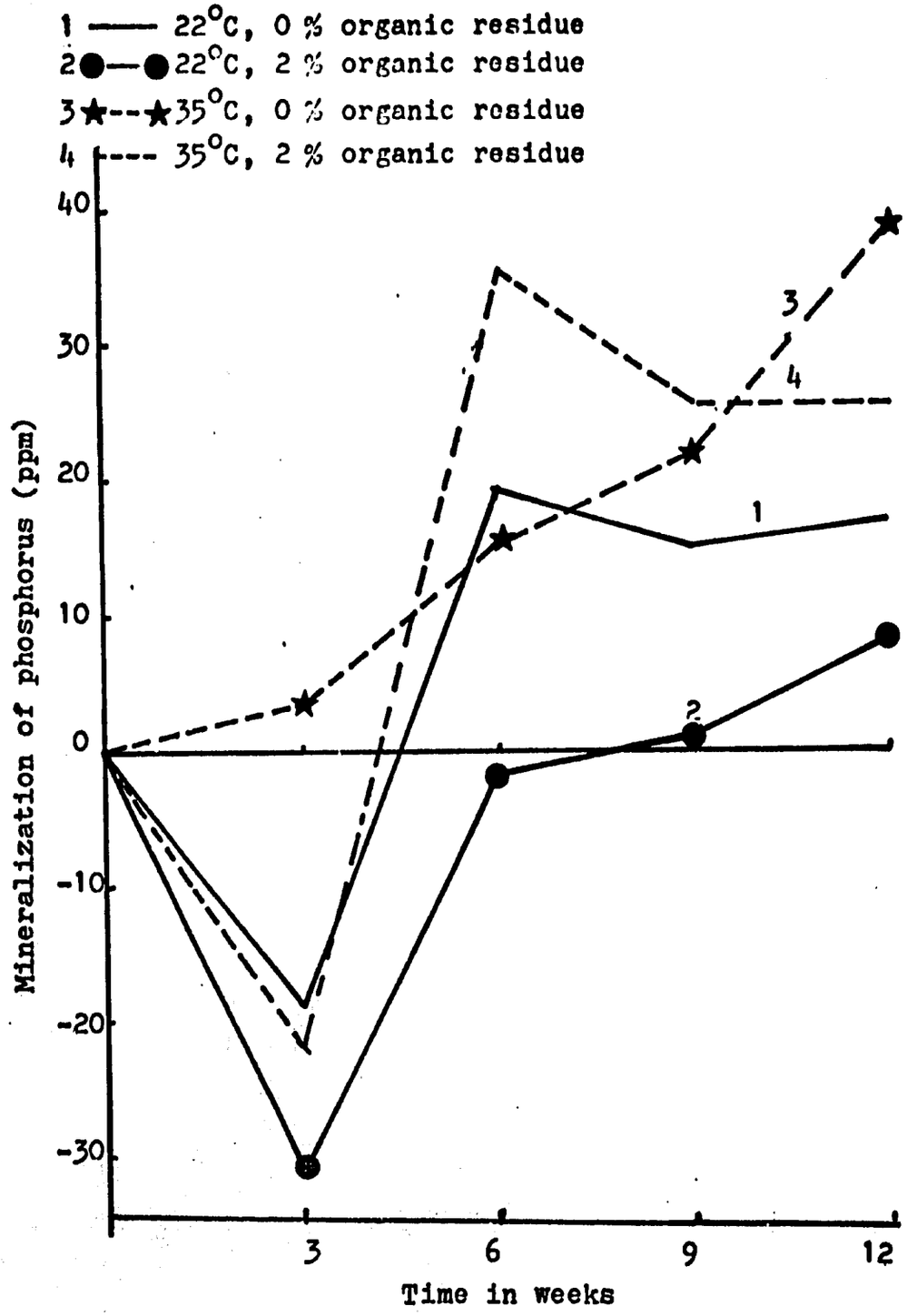


Figure 8. Mean of the inorganic and organic phosphorus as estimated by subtracting the values at a particular time of incubation from the zero time of incubation. (Mulanje soil).

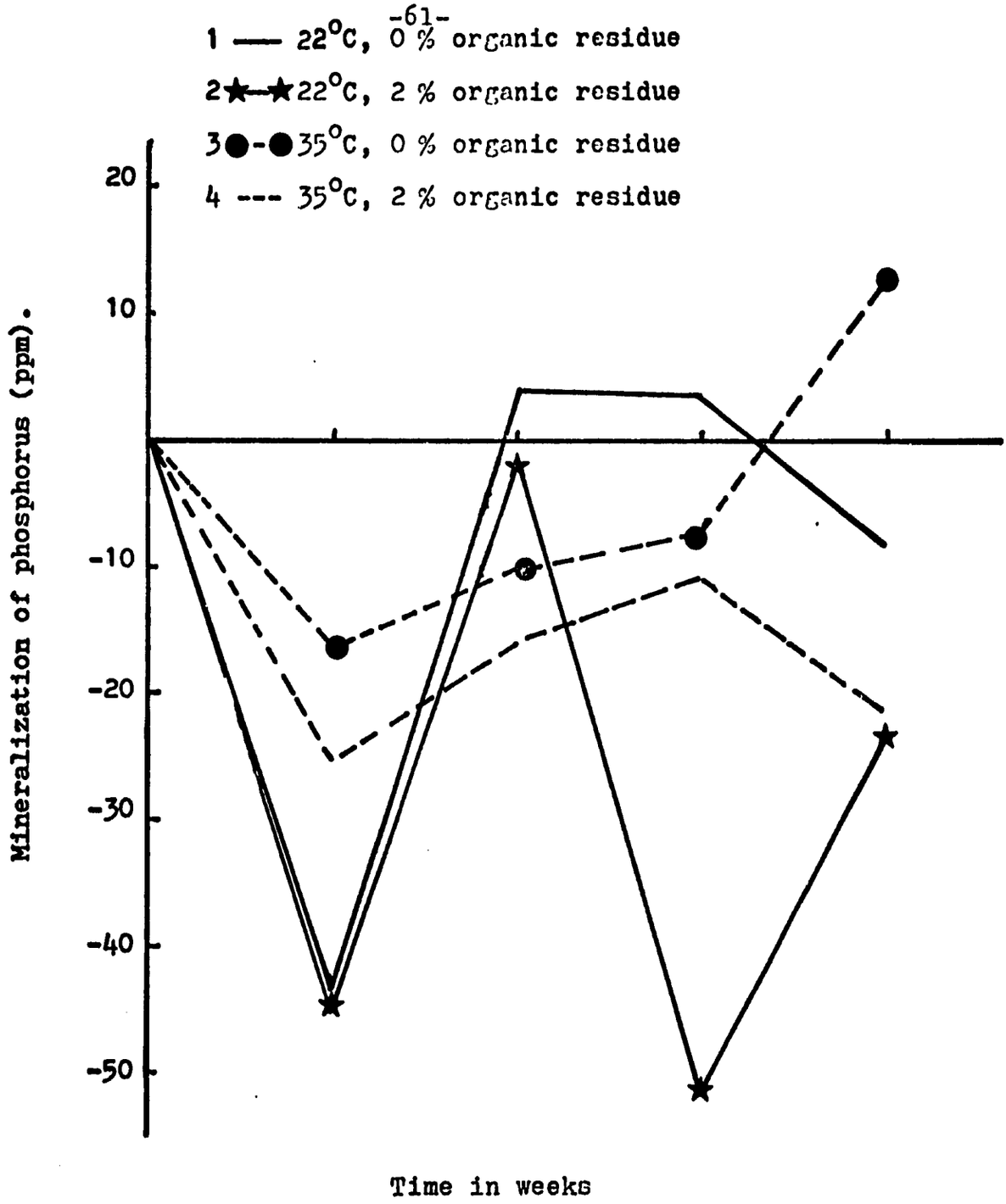


Figure 9. Mean of the inorganic and organic phosphorus as estimated by subtracting the values at a particular time of incubation from the zero time of incubation (Dedza soil).

Table 15. Mineralization of organic phosphorus during incubation. 1/

Soil:		Mulanje			Dedza		
Treatment	Week	ΔI.P.	ΔO.P.	Ave.	ΔI.P.	ΔO.P.	Ave
		ppm					
	3	-10.4	-26.8	-18.6	-2.0	-85.5	-43.8
	6	21.2	17.2	19.2	47.4	-39.5	4.0
0% org. res. 22°C	9	16.2	14.2	15.2	54.4	-47.3	3.6
	12	33.9	0.5	17.2	53.8	-70.0	-8.1
	3	-27.9	-32.7	-30.3	-41.4	-49.0	-45.2
	6	-11.1	- 7.5	- 1.8	- 2.7	- 0.9	- 1.8
2% org. res. 22°C	9	- 6.8	9.5	1.4	-37.9	-65.1	-51.5
	12	10.9	5.6	8.5	6.9	-54.4	-23.8
	3	9.5	-2.1	3.7	0.9	-33.6	-16.4
0% org. res. 35°C	6	14.9	15.7	15.3	34.9	-55.1	-10.1
	9	20.4	24.4	22.4	35.3	-49.3	- 7.0
	12	47.5	30.2	38.8	61.0	-37.1	12.0
	3	-27.9	-15.5	-21.7	-25.4	-25.2	-25.3
	6	8.5	62.2	35.4	-18.7	-13.1	-15.9
	9	15.1	36.0	25.6	- 5.9	-16.6	-11.2
	12	15.7	35.5	25.6	3.2	-46.0	-21.4

1/
ΔI.P. - change in inorganic-P as compared with zero time of incubation;
ΔO.P. - change in organic-P as compared with zero time of incubation.

changes in inorganic and organic P has a positive sign, it indicates a net mineralization of organic P to inorganic, whereas a negative sign means that there was a net immobilization of inorganic P to organic P.

From Figures 8 and 9 and Table 15, it is shown that there was an initial immobilization of inorganic P during first three weeks for both soils, after which there was a net mineralization of organic P to inorganic P. The latter appeared to be the most pronounced for the Mulanje soil. Similar results have been reported by other workers (Acquaye, 1963; Birch, 1961; Enwezor, 1966; 1967), and the initial period of apparent immobilization was attributed to microbial assimilation of inorganic P. It has also been observed that the tendency for immobilization increases along with the level of available P (Enwezor, 1967).

The effect of added ground corn stover for both soils was to increase the extent of immobilization in the early stages of incubation which was carried over into the later stages of incubation period. According to Birch (1961), who studied phosphorus transformations during plant decomposition, the inorganic plant P may be utilized by microbial populations and the recovery of this microbial organic P which was synthesized from both plant and soil inorganic P during the early stages of decomposition will depend primarily on the rate of decomposition and thus the exhaustion of substrate, after which the microorganisms will undergo autolysis, and release inorganic P. For mature plant tissues, such as that used in this study, the de-

compositon can be relatively slow and the exhaustion of the substrate does not occur as readily as for younger tissues. Hence, the observed, longer-lasting immobilization influence of added organic matter in the present study should be expected.

The magnitude of the phosphorus transformations during incubation varied depending on the incubation temperature. In general, there was decreased immobilization of inorganic P into the organic form at the higher temperature during the initial stage of the incubation period and an increased mineralization of organic P in the later stage. This is in agreement with Acquaye (1963) who found that for some soils of Ghana, more organic P was mineralized at 50°C than at 27°C or 40°C. Similar temperature effects were also reported by Cunningham (1963).

Although the two soils exhibited the same general trend during the incubation procedure, it is obvious from Figures 8 and 9 and Table 15 that there were marked differences in the extent to which the trends were expressed in the two soils. The Mulanje soil, after an initial immobilization of inorganic P, gave a net mineralization of organic P during subsequent periods. For the Dedza soil, there was also an initial immobilization of inorganic P. Subsequent mineralization of organic P did occur, but only for the sample incubated at 35°C and without organic matter, was there a net mineralization of organic phosphorus.

There was generally a decreased pH with increased time of incubation, and thus increased mineralization (Table 16). Halstead et al. (1963) pointed out that liming resulted in a decline of the organic P content of incubated samples. In the present study, the effect of liming these acid soils had a greater influence on the Mulanje soil where the magnitude of increase was much higher than in the Dedza soil. The decline in pH after incubation was also much greater in the Mulanje soil than the Dedza soil, which may indicate a much faster chemical and microbiological reaction.

Sodium bicarbonate extractable phosphorus.

The sodium bicarbonate extractable inorganic and organic P (Table 17) showed very little overall change as a result of incubation. The only pronounced effect was the non-recovery of the appreciable amount of inorganic P that was associated with the organic matter. Apparently this fraction reacted with soil inorganic constituents in such a manner as to become non-extractable to bicarbonate. It is also a possibility that the inorganic P was immobilized into a form of organic P that is non-extractable by sodium bicarbonate. The former seems more plausible than the latter.

The results of the sodium bicarbonate extractions contrast sharply those obtained with ignition and 2N H_2SO_4 extraction in which marked changes in inorganic and organic P were observed as a result of incubation. It would appear that the dilute alkali-extractable P - organic or inorganic - does not actively participate in immobilization or mineralization re-

Table 16. pH determined in 0.01M $CaCl_2$ for the incubated and unincubated soils.

Treatment: 1/	I	II	III	IV	V	VI	VII	VIII
				Mulanje				
	4.25	4.45	5.99	6.20	5.14	5.46	5.02	5.23
				Dedza				
	4.64	5.02	5.02	5.33	4.83	5.44	4.70	5.23

1/

I. Zero time, 0% organic residue, no lime;

II. Zero time, 2% organic residue, no lime;

III. Zero time, 0% organic residue. lime added;

IV. Zero time, 2% organic residue, lime added;

V. 15th week, 0% organic residue, room temperature;

VI. 15th week, 2% organic residue, room temperature;

VII. 15th week, 0% organic residue. 35°C.

VIII. 15th week, 2% organic residue. 35°C.

Table 17. $NaHCO_3$-extractable total-, inorganic-, and organic-P for incubated and unincubated samples.

Soils:	Mulanje			Dedza		
Treatment 1/	Inorg.	Org.	Total	Inorg.	Org.	Total
	ppm					
I	24.6	15.1	39.7	43.9	9.2	53.1
II	46.6	14.9	61.5	69.7	9.2	78.9
III	23.1	13.6	36.7	46.2	10.9	57.1
IV	24.2	16.7	40.9	45.8	14.5	60.3
V	21.0	12.7	33.7	45.4	9.4	54.8
VI	23.6	13.2	36.8	42.4	10.6	53.0

1/

I. Zero time, 0% organic residue;

II. Zero time, 2% organic residue;

III. 15th week, 0% organic residue, room temperature

IV. 15th week, 2% organic residue, room temperature;

V. 15th week, 0% organic residue; 35°C;

VI. 15th week, 2% organic residue, 35°C.

actions.

Mineralizable Nitrogen.

The amounts of inorganic nitrogen (Table 18) present in the soils prior to incubation were low compared to those found in some highly weathered soils of Puerto Rico (Lathwell et al., 1972). Nitrogen immobilization occurs in the Dedza soil where organic residue was added at both temperatures. On the other hand, there was a marked nitrogen mineralization in both soils at both temperatures where no organic material was added, with greatest values in the samples that were incubated at 35°C. This is similar to organic P mineralization as estimated by changes in inorganic and organic P (Table 15). The results clearly indicate that mineralization of organic P accompanies the mineralization of nitrogen. This is identical to the results of Thompson et al. (1954) who found that organic P mineralized at 40°C was correlated positively with nitrogen and carbon mineralized concurrently. This supports the earlier theory by Thompson and Black (1949) that mineralization of organic P accompanies the mineralization of carbon. Cunningham (1963) working with forest soils in Ghana also found that the rate of organic P mineralization was at the same rate as that of nitrogen.

Adsorption of phosphorus.

One of the complications in the evaluation of the current contribution of soil organic P mineralization is that the inorganic P released by mineralization may be precipitated by

Table 18. Inorganic nitrogen in incubated and unincubated samples.

Soil:	Mulanje			Dedza		
Treatment 1/	NH_4^+-N	NO_3^--N	Total-N	NH_4^+-N	NO_3^--N	Total-N
	ppm					
I	0.51	0.33	0.84	0.63	0.32	0.95
II	0.35	0.54	0.89	0.42	0.39	0.81
III	0.10	3.31	3.41	0.17	2.98	3.15
IV	0.23	0.79	1.02	0.11	0.08	0.19
V	0.08	2.34	2.42	0.08	5.90	5.98
VI	0.23	5.11	5.34	0.14	0.41	0.55

1/

I. Zero time, 0% organic residue;

II. Zero time, 2% organic residue;

III. 15th week, 0% organic residue, room temperature;

IV. 15th week, 2% organic residue, room temperature;

V. 15th week, 0% organic residue, 35°C;

VI. 15 week, 2% organic residue, 35°C.

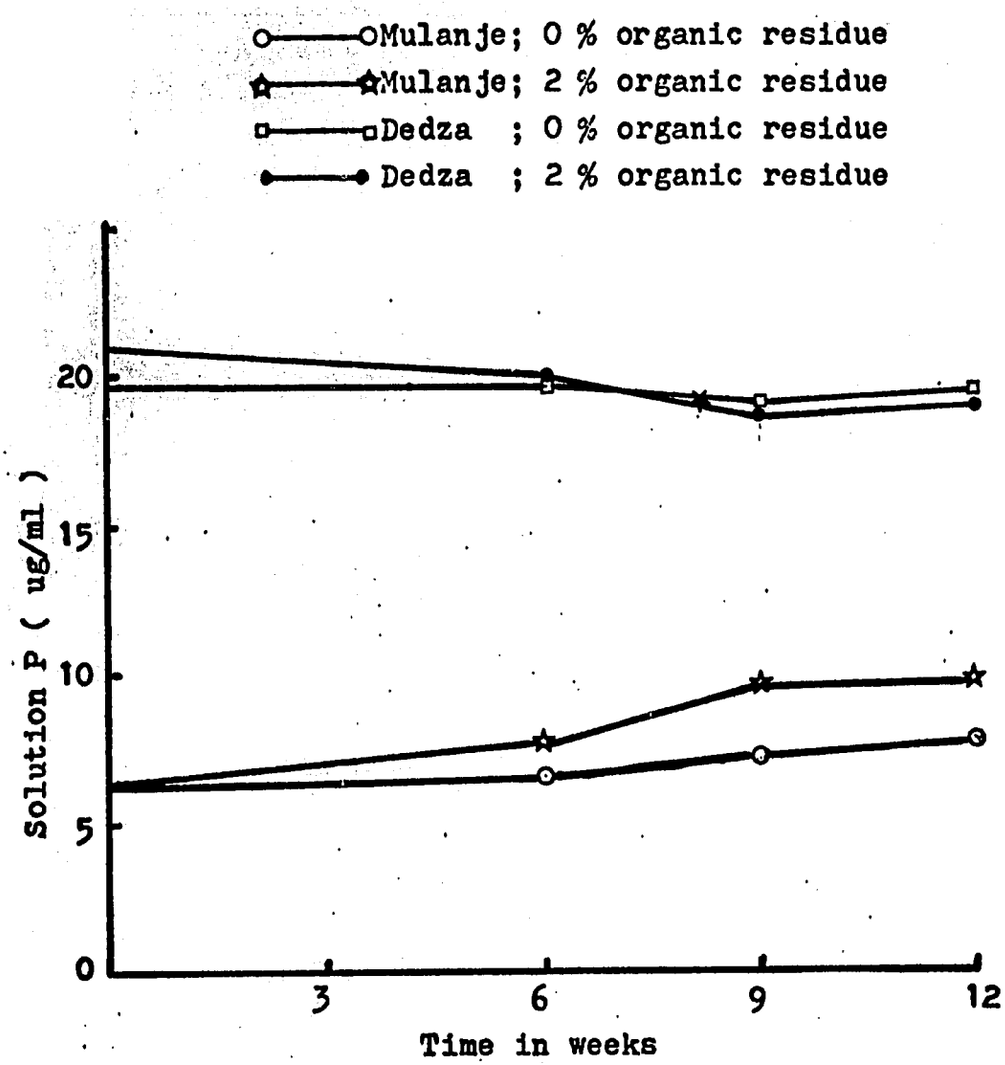


Figure 10. Phosphorus recovered (ug/ml) after 1000 ppm phosphorus were equilibrated for 48 hours with one gram samples from soils incubated at room temperature.

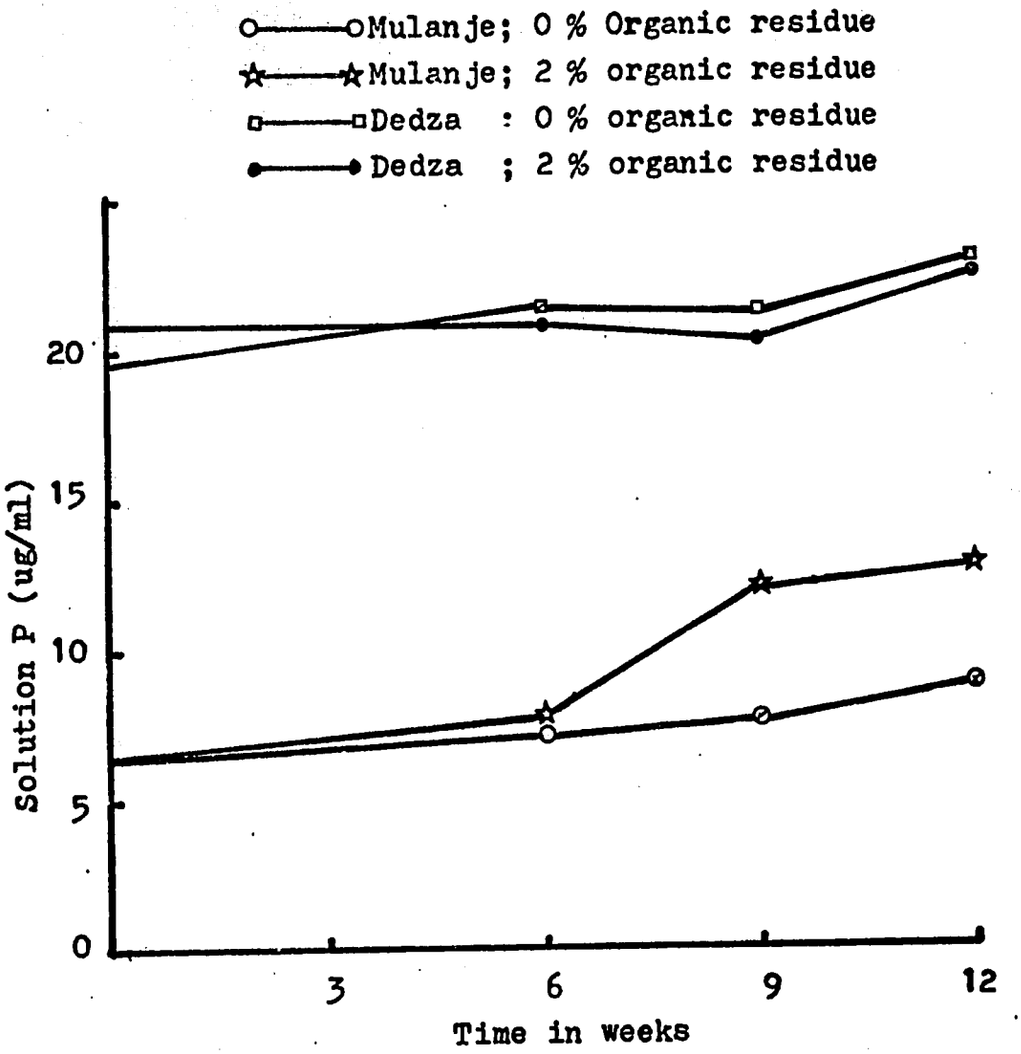


Figure 11, Phosphorus recovered (ug/ml) after 1000 ppm phosphorus were equilibrated for 48 hours with one gram samples from soils incubated at 35°C.

amorphous aluminum hydroxides and iron oxides (Birch, 1961; Friend and Birch, 1960), thus reducing the availability to plants. In view of this fact, the adsorption of P from a constant amount of added phosphate (a single-point method) was determined at various times during the incubation period. It was assumed that the equilibrium solution concentration may reflect the adsorption of inorganic P that has been produced by mineralization of organic P. The results (Figures 10 and 11) showed that P adsorption of the Mulanje soil was decreased by the addition of organic matter while increased incubation temperature decreased P adsorption for both soils.

The decrease in phosphorus adsorption in the presence of organic matter could be a result of several factors. First, the adsorption of inorganic P present in the organic matter and that from mineralization of organic P would decrease the number of P adsorption sites. Secondly, carboxylic and phenolic functional groups of the organic matter degradation products could have reacted with P adsorption sites. Othieno (1973) attributed the latter as the reason why organic mulches improved utilization of applied P for some acid soils of East Africa. Thirdly, the addition of organic matter generally caused an increase in pH (Table 16) which should mean a reduction in the number of protonated surface-hydroxyl groups which are active phosphorus adsorption sites (Muljadi et al., 1966). The neutralizing effect of organic matter was also noted by Santiago (1972) who found that organic matter was active in the inhibition of aluminum toxicity of an Ultisol from Puerto Rico. He attributed this to the release of Ca

by organic residue to neutralize the exchangeable Al in the soil.

Failure of the Dedza soil to show the changes resulting from incubation with and without organic matter (Figures 10 and 11) may be due to the lesser adsorption capacity of this soil, or to the fact that there is not much mineraliztion of organic P in comparison to Mulanje soil.

Whatever the explanation is with regard to the effects of added organic materials, the effect was greatly accentuated when the incubation temperature was increased from room temperature (22°C) to 35°C (Figures 10 and 11). The P adsorption measurements in Figures 10 and 11 were all carried out at room temperature. This means that the decreased adsoprtion associated with increased temperature resulted from changes induced during incubation. These changes could very well be some of those mentioned above for the effect of organic matter, and the increased incubation temperature could have caused them to proceed to a greater extent.

Wet and dry incubation

Inorganic and organic phosphorus.

To further study phosphorus transformation, a second incubation experiment was conducted by alternate wet and dry incubation at one week cycles at 35°C. Figures 12 and 13 illustrates the nature of the activities, and it is evident from the results that there is a great variability in the behavior of P, both in the inorganic and organic forms. Overall, for both soils, with and without added organic matter, there was an initial mineral-

ization of organic P followed by a period of immobilization and then another period of mineralization. Furthermore, in the first half of the incubation period, mineralization of organic P was associated with moist incubation and immobiliza- with dry incubation. In the second half of the incubation period, the pattern was reversed and mineralization was associated with dry incubation and immobilization with moist incubation.

Birch (1959; 1960a) has shown that when a dried soil is wetted, a portion of the soil organic matter is made more accessible to microbial attack and this causes a "flush" of carbon dioxide and nitrate production. This could indeed be the reason for mineralization of organic P during the moist cycles in the first half of the incubation period. The apparent dominance of immobilization during the dry cycles may be a reflection of a depression of phosphatase enzyme activity, known to be induced by drying (Ramirez-Martinez, 1968) and which would cause an accumulation of organic P.

The reasons for the reversal of the mineralization-immobilization pattern in the last 4 weeks of the incubation period cannot be definitely stated. Birch's studies (1959; 1960a) on the effect of wetting and drying showed that the flush of mineralization of carbon and nitrogen was a continuous process and the magnitude decreased only slowly with the number of times of wetting and drying. Apparently the influence of wetting and drying on the mineralization of organic P may be more complicated than that on carbon or nitrogen mineralization.

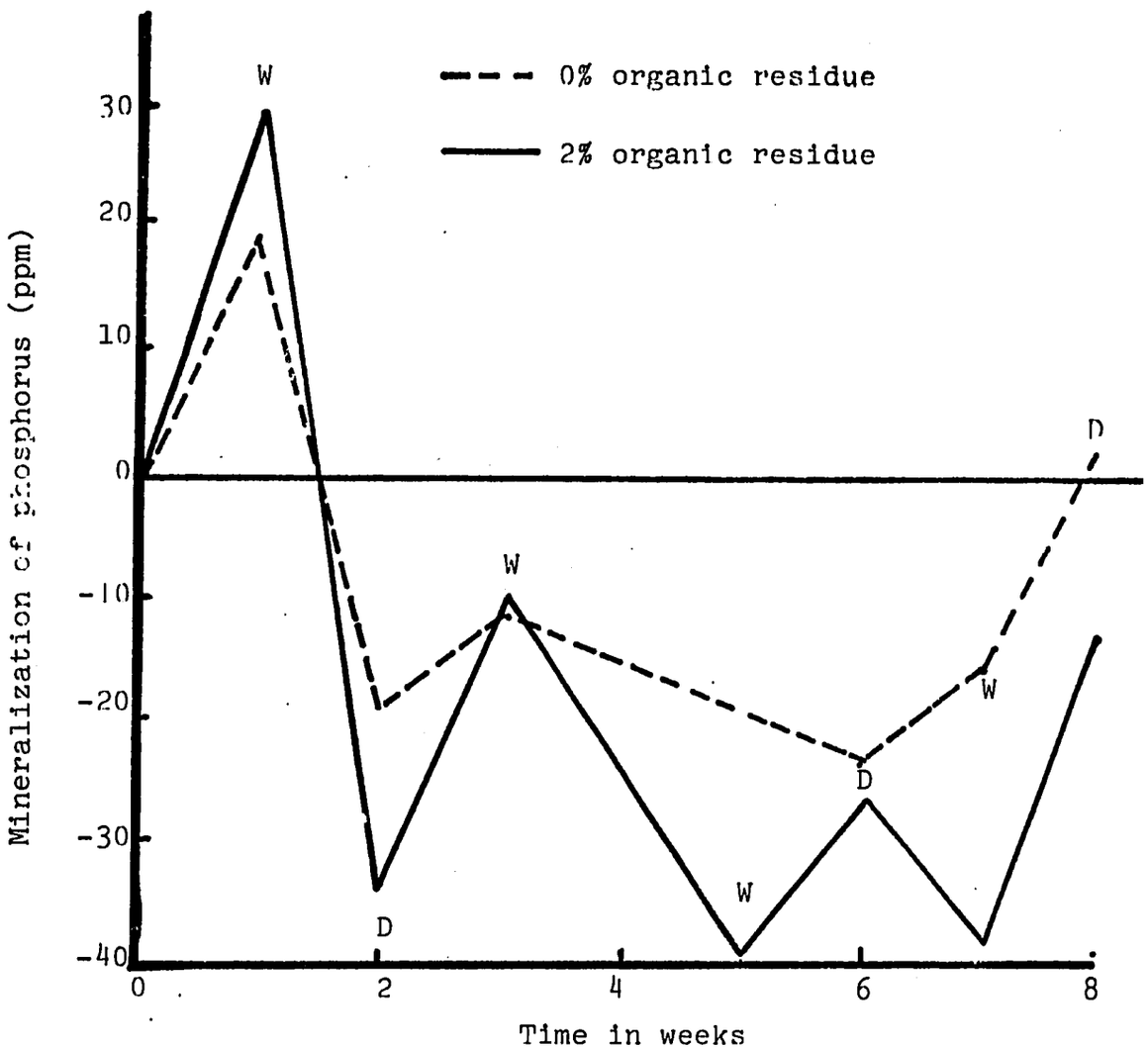


Figure 12. Mean of the inorganic and organic phosphorus as estimated by subtracting the values at a particular time of incubation from the zero time of incubation. (Mulanje soil).

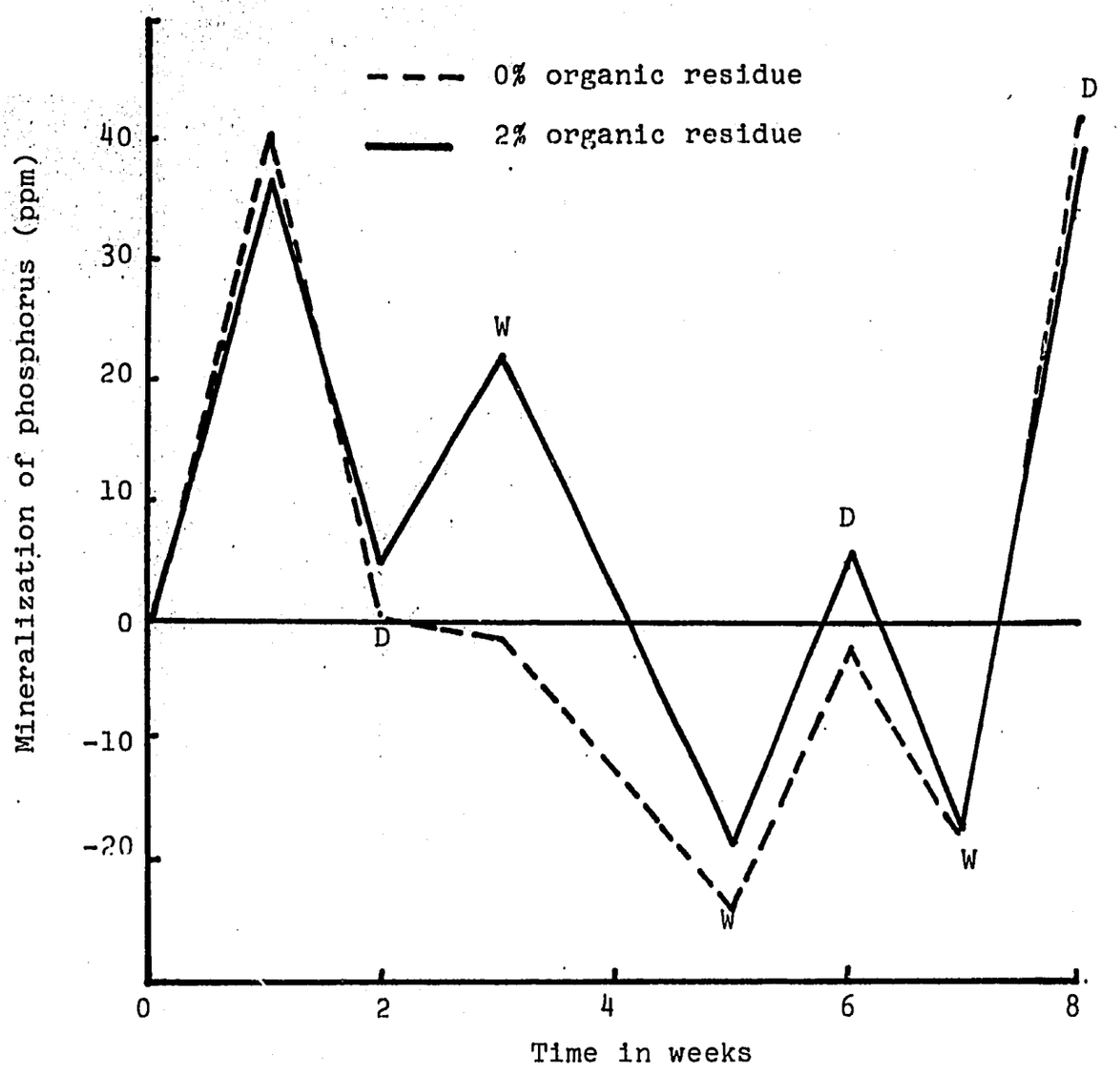


Figure 13. Mean of the inorganic and organic phosphorus as estimated by subtracting the values at a particular time of incubation from the zero time of incubation. (Dedza soil)

It was originally thought that the wet and dry incubation might accelerate and/or intensify the immobilization or mineralization processes that occurred during continuous, moist incubation. However, comparison of the wet and dry incubation results (Fig. 12 and 13) with those of the moist incubation (Fig. 8 and 9) indicate that this was not necessarily the case. In fact, the results of the wet and dry incubation show that the Dedza soil had a greater mineralization of organic P than the Mulanje soil, while with moist incubation the opposite was found with the Mulanje soil having a greater mineralization of organic P than the Dedza soil. It should be kept in mind that the moist incubation experiments were carried out for 12 weeks while the wet and dry incubations were carried out for only 8 weeks. It is possible that if the latter had been carried out longer, more definite trends might have emerged.

The presence of added organic matter during wet and dry incubations had only a slight influence. The most pronounced effect was observed for the Mulanje soil (Figure 12) in which the additon of organic matter appeared to increase the immobilization of inorganic P.

Sodium bicarbonate extractable phosphorus

The use of sodium bicarbonate extraction to trace the organic P mineralization is shown in Figures 14 and 15. In both soils where no organic matter was added (Fig. 14), there was an initial immobilization after which there was a slight net

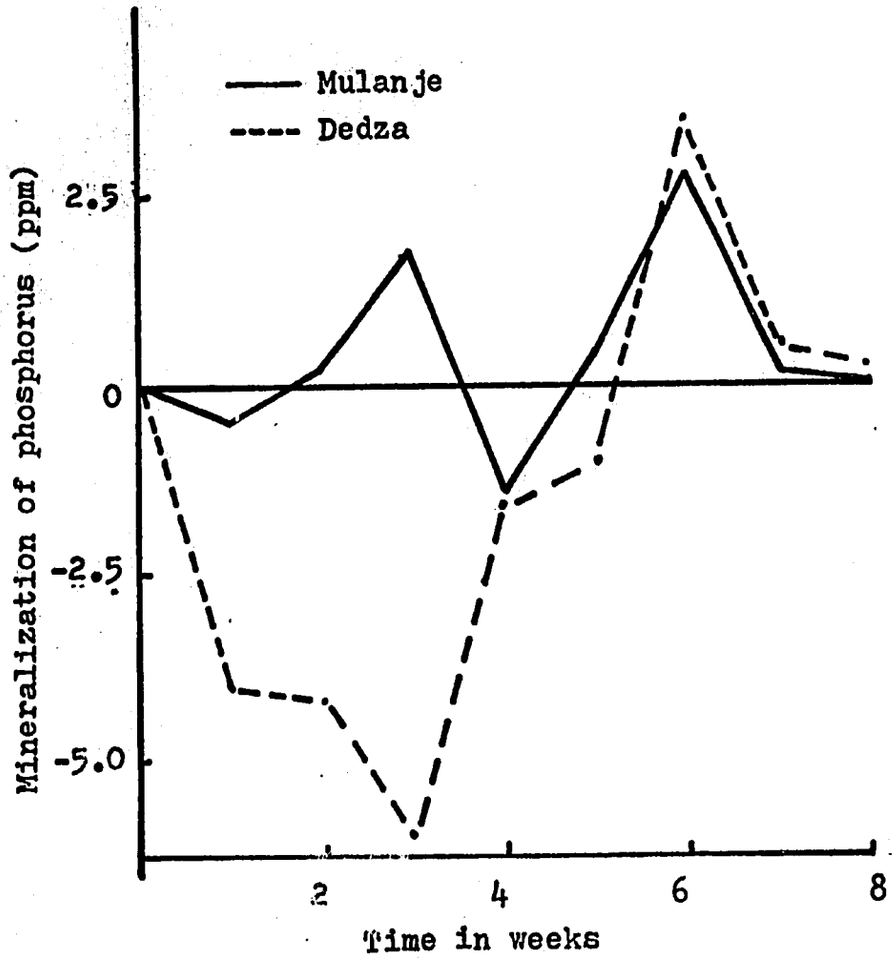


Figure 14. $NaHCO_3$ extractable P.

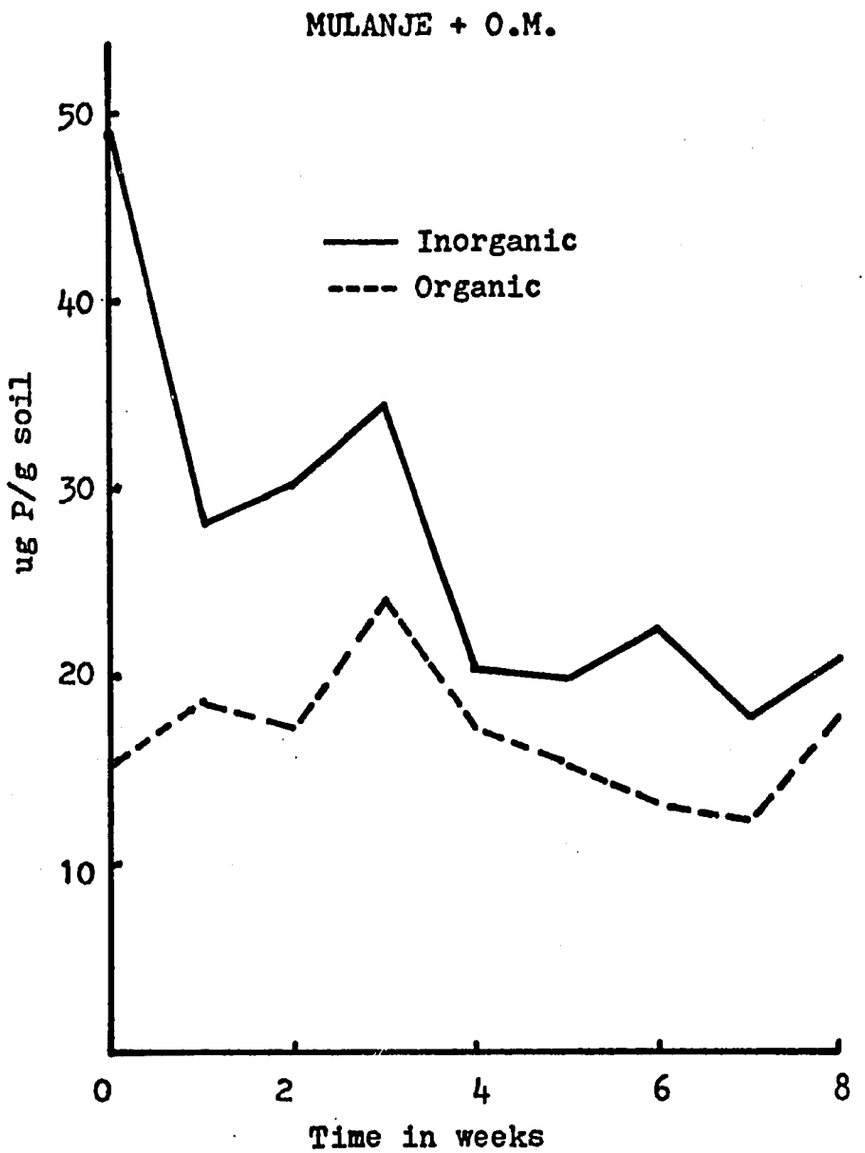


Figure 15a. Bicarbonate-extractable inorganic and organic phosphorus of Mulanje soil with 2 % organic residue added.

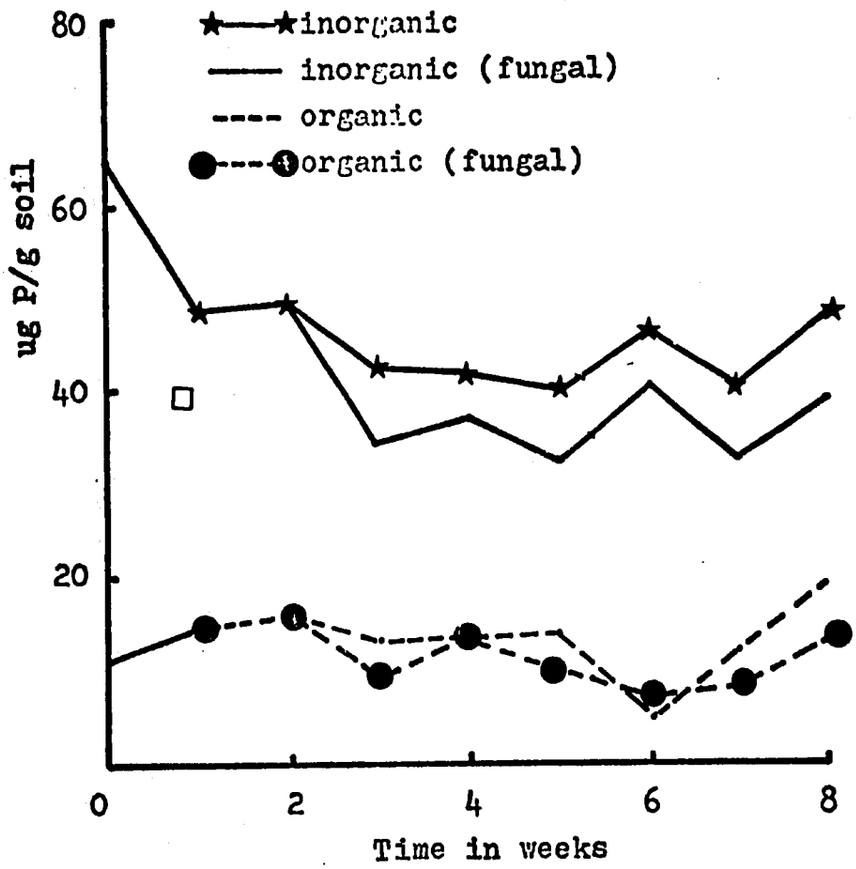


Figure 15b. Bicarbonate-extractable inorganic and organic phosphorus of the Dedza soil with 2 % organic residue added.

mineralization of organic P. This pattern was most pronounced for the Dedza soil. At the end of the experiment, however, the soils had largely returned to their initial values.

For the samples which were incubated with added organic material, (Fig. 15a, b) the most notable feature was the rapid conversion of the relatively large amount of inorganic, bicarbonate-extractable P to a non-extractable form. Inasmuch as there was not a corresponding increase in the bicarbonate extractable organic P, the decrease is probably a result of an inorganic fixation reaction. There was, however, some evidence of microbial activity. In one of the duplicates of the Dedza soil, there was a white-colored mycelial growth observed at the second week of incubation. Coincidental to this, there was an increase in organic P and a decrease in inorganic P in the same sample relative to the sample where there was no mycelial growth. The effect of fungi in immobilizing P can only be speculated since the effect of the unseen microbial population is not known. It is important, though, to note that whereas the ignition procedure did not show this difference due to fungal growth would indicate that the 2N H_2SO_4 extracts some of the microbial organic P that would be included as inorganic P, and thus giving erroneous results.

Overall, the results suggest that the distribution of bicarbonate-extractable organic and inorganic P could vary considerably throughout a growing season. This could complicate the assessment of the contribution of organic P mineralization. That is, it is quite possible that at various stages during the growing season, in response to changing microbial activities,

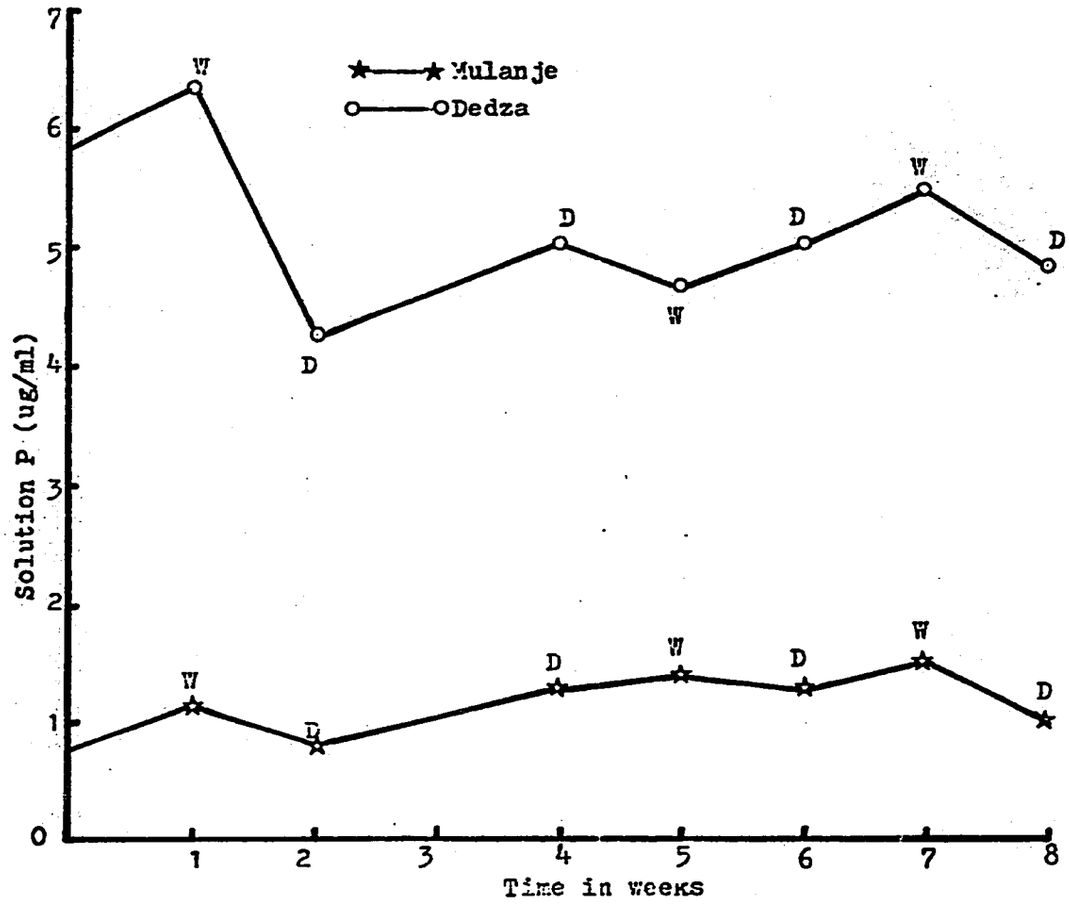


Figure 16. Phosphorus recovered (ug/ml) after 500 ppm P were equilibrated for 48 hours with one gram sample from soil that underwent "wetting and drying" incubation; 0 % organic residue added.

mineralization of a labile form of organic P (bicarbonate-extractable) could contribute inorganic P for plant uptake. Subsequently, replenishment of this relatively small pool of labile organic P could occur by disintegration of complex organic P compounds in the remaining soil organic P fraction. Analyses made before and after the growing season would, therefore, show no change in the pool of labile organic P. Additionally, for the remaining organic P fraction, extractable only in strongly basic or acidic solutions, the decrease necessary to maintain the labile pool constant may be so small relative to the total amount that it cannot be detected as a significant difference. Field and greenhouse work would be necessary to verify this.

Adsorption of phosphorus.

The adsorption of inorganic P from solution was found to fluctuate widely during the incubation period (Figure 16 and 17) There was a general pattern to the variation in that the adsorption of P was generally greater following dry cycles than that after moist cycles. Unpublished work in this laboratory has shown that Oxisols and Ultisols of Puerto Rico show similar pattern of P adsorption in response to wetting and drying. There could be a number of possible mechanisms explaining this phenomenom. The most obvious would be that during incubation, anaerobic conditons may develop, causing a reduction and mobilization of a portion of iron oxides, and consequently a decrease in P adsorption. Upon drying, the reduced iron would

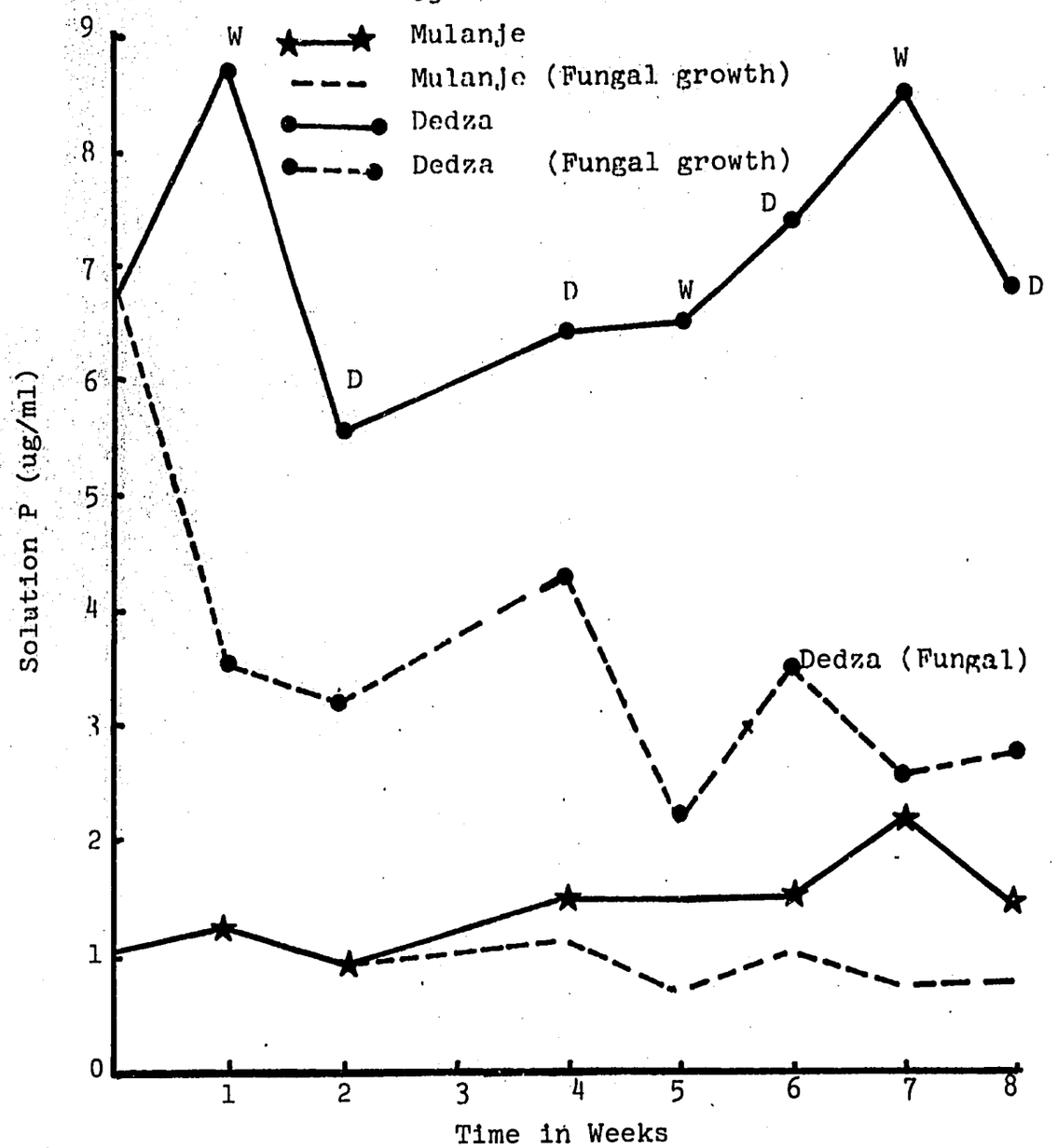


Figure 17. Phosphorus recovered (ug/ml) after 500 ppm P were equilibrated for 48 hours with one gram sample from soil that underwent "Wet and dry incubation"; 2% organic residue was added.

be reoxidized to hydrous ferric oxides that are active in P adsorption. Another possibility and perhaps more probable is the influence of the wetting and drying on the surface charge properties of the soils. That is, as the soil solution becomes more concentrated, the hydrogen ion activity should increase and correspondingly cause an increase in surface Al-Fe-OH_2^+ groups that are active in P adsorption.

Organic material had a notable effect on the Dedza soil, in that the amount of added phosphorus remaining in solution was greatly depressed (Fig. 17). A similar occurrence was noted for one of the replicates of the Mulanje soil, although of lesser magnitude. If fungi were responsible for the latter, they must have been in a finely divided state as no mycelia were visible. The association of the fungal growth with an increased adsorption of phosphorus is an interesting observation, but one for which an explanation is not readily available. In conclusion, it can be pointed out that at any one time, the organic material added to any soil would not only cause microvariabilities in the physical and chemical processes, but also in the microbial processes. The variability would also depend upon the nature and quantity of the added substrate. Another important point is the difference between the continuously moist incubation and the drying and re-wetting incubation experiments. The continuously moist incubation seemed to have a fairly buffered system whereas the drying-rewetting incubation showed a diversity in the reactivity both in inorganic and organic P and also adsorptions.

Inorganic phosphorus fractions.

The mineralized organic P may contribute to the supply of the labile P, but that, as already pointed out, this may suffer from immobilization either by microorganisms or by the hydrated oxides of aluminum and the iron, and the clay fraction, and also that one of these processes may predominate or that they may occur simultaneously. The purpose of the present experiment was to observe the effect of incubation on the P fractions.

From the results in Table 18, it can be pointed out that in general, there was no marked increase in the inorganic fractions resulting from incubation, although there was a large decrease in the adsorbed fraction as determined by sodium bicarbonate extraction. There was a slight increase in aluminum and calcium phosphate, and a higher increase of iron phosphate resulting from incubation in the Mulanje soil. In the Dedza soil, there was no significant difference between treatments in the aluminum and iron phosphates, but that there was a slight increase in the calcium phosphate for the sample incubated at 2 per cent organic residue. This may indicate that the initial reaction in these soils is the formation of the calcium phosphate resulting from the interaction between the added $Ca(OH)_2$ and the P in the soil, and that with time, this fraction which is unstable at low pH, may be transformed into Al-P and eventually into Fe-P (Chang and Jackson, 1958).

Table 19. Inorganic phosphorus fractions for the wet and dry incubation.

Treatment	Adsorb-P	Al-P[1/]	Fe-P	Ca-P	Total
	ppm				
			MULANJE		
Zero time, 0% org. res.	46	37	137	22	243
Zero time, 2% org. res.	88	40	135	21	284
8th week, 0% org. res.	51	37	137	20	245
8th week, 2% org. res.	51	41	153	25	270
			DEDZA		
Zero time, 0% org. res.	82	59	278	36	455
Zero time, 2% org. res.	107	61	280	40	488
8th week, 0% org. res.	83	56	282	41	462
8th week, 2% org. res.	85	57	277	46	465

1/ Al-P determined after one hour extraction.

It is interesting to note that P content of the organic material which initially increased the inorganic P fractions was not entirely recovered after incubation. This may indicate that some of the transformation of organic P is microbial rather than chemical.

SUMMARY AND CONCLUSIONS

The work in the present study showed that the four soils of Malawi selected for investigation differ greatly in their chemical, physical and mineralogical characteristics. In general, chemical, physical and mineralogical properties indicate that the Mulanje soil is the most highly weathered. This is reflected by such characteristics as the presence of high quantities of gibbsite, high P adsorption maximum, low pH and per cent base saturation, and also a low, active SiO_2/Al_2O_3 ratio. The extremely low P adsorption maximum, higher active SiO_2/Al_2O_3 ratio and also the presence of considerable amounts of mica in the Bunda soil is clearly indicative of a moderatelv weathered soil.

The active SiO_2/AlO_3 ratios were found to be a function of soil texture and apparently, as previously noted for some Oxisols in Brazil, dissolution of quartz in the sand fractions, over long periods of time, has greatly influenced the nature of the active surfaces in the clay fractions.

The comparative study of organic P procedures showed that the method of ignition at 550°C followed by 2N H_2SO_4 extraction was the most suitable one for estimating organic P in these soils. This is because of its simiplicity and also for its apparent maximum extraction of organic P with minimum hydrolysis.

Of greatest interest were the results from incubation experiments. In the continuously moist incubation experiment, there was an initial immobilization of phosphorus in both soils (except one Mulanje sample where no organic matter was added, and incubated at 35°C) and that for the Dedza soil, immobilization continued up to the end of the incubation period in the samples that had organic residue added to them. On the other hand, after initial immobilization in the Mulanje soil, there was a rapid mineralization in all cases up to the end of the incubation period. The high temperature coupled with organic matter additions accentuated the rate of mineralization at later stages in the incubation period. This is reflected in the greater amounts of solution P in the adsorption experiments.

The wet and dry incubation results, on the other hand, were quite different with the Dedza soil showing a greater increase in net mineralization initially and towards the end of the incubation period. The Mulanje soil showed an initial mineralization of P just as in the Dedza soil, but that subsequent incubation resulted in immobilization of P, except for one sample where no organic residue was added which showed a slight increase in mineralization on the eighth week.

The adsorption and fractionation studies clearly indicate that there was limited chemical transformation of the inorganic forms present in these soils.

From the experiments, it can be concluded that the effect of added organic material on supplying P for plant use will depend on several factors. One of these factors is the nature and quantity of the added organic matter. This will influence the microbial and hence the chemical activities. The initial processes will be such that the plant will compete with the microbial populations in the uptake of phosphorus. and that subsequent increase in inorganic P for plant use will depend upon the rate of substrate exhaustion, which may lead to autolysis of microbial cells. The climatic influence is that high temperatures favor a rapid decomposition of organic matter, and thus may lead to a rapid release of organic P into inorganic forms. In addition to this, the nature and distribution of rainfall in a growing season will influence organic matter decomposition, with high moisture saturations favoring a reduced rate of decomposition of the organic matter, although the availability of P may not follow the same pattern. On the other hand, drying of the soil will affect the ezymatic activity. Lastly, the chemical and physical nature of the soils will greatly affect net organic P mineralization.

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APPENDICES

Appendix 1. Lime added to the soil based on the exchangeable Al determined in 1 N KCl extracts (Kamprath, 1970)

Soil	Exchangeable Al
	me/100g
Mulanje	1.78
Bvumbwe	0.07
Dedza	0.17
Bunda	0.06

Lime was applied to Mulanje and Dedza samples in the form of $Ca(OH)_2$.

Mulanje	1.78 x 74	= 131.7 mg
Dedza	0.19 x 74	= 12.5 mg

The soils were shaken thoroughly for 30 minutes on a mechanical shaker.

Appendix 2. Phosphate sorption by four Malawi soils after 48 hours equilibration with added phosphorus.

Sample	Initial amount added, ug-P/2g	Amount recovered ug/ml.	Amount sorbed ug/g-soil
Mulanje	200	0.02	99
	500	0.10	248
	1000	0.58	488
	1500	2.37	703
	2000	6.83	863
Bvumbwe	200	0.05	98
	400	0.17	193
	500	0.28	239
	1000	1.45	442
	1500	3.70	608
	2000	6.44	742
Dedza	200	0.14	97
	400	0.60	188
	600	1.58	268
	800	3.59	328
	1000	5.53	389
	1250	9.84	428
Bunda	0	0.03	---
	100	0.37	42
	200	0.92	81
	300	2.18	107
	400	3.48	130
	500	4.92	151

CONTINUOUSLY MOIST INCUBATION

Appendix 3. Total-, inorganic-, and organic-P determined in incubated (22°C) and unincubated samples extracted with 2N H_2SO_4; no organic residue added.

Soil	Week:	0	3	6	9	12
		ppm				
	Total-P	492	508	496	494	525
MULANJE	Inorg-P	271	260	292	288	305
	Organ-P	221	248	204	206	220
	Total-P	1162	1247	1248	1264	1286
DEDZA	Inorg-P	418	418	465	472	471
	Organ-P	755	804	756	821	810

Appendix 4. Total-, inorganic-, and organic-P determined in incubated (22°C) and unincubated samples extracted with 2N H_2SO_4; 2% organic residue added.

Soil	Week:	0	3	6	9	12
		ppm				
	Total-P	543	548	525	527	549
MULANJE	Inorg-P	305	277	294	298	316
	Organ-P	238	271	231	228	233
	Total-P	1242	1250	1240	1270	1304
DEDZA	Inorg-P	487	446	484	449	494
	Organ-P	755	804	756	821	810

Appendix 5. Total-, inorganic-, and organic-P determined in incubated (35°C) and unincubated samples extracted with 2N H_2SO_4; no organic residue added.

Soil	Week:	0	3	6	9	12
		ppm				
	Total-P	492	504	491	488	509
MULANJE	Inorg-P	271	280	286	291	318
	Organ-P	221	224	205	197	191
		ppm				
	Total-P	1162	1197	1252	1247	1260
DEDZA	Inorg-P	418	419	453	454	479
	Organ-P	744	778	799	793	781

Appendix 6. Total-, inorganic-, and organic-P determined in incubated (35°C) and unincubated samples extracted with 2N H_2SO_4; 2% organic residue added.

Soil	Week:	0	3	6	9	12
		ppm				
	Total-P	543	531	490	522	524
MULANJE	Inorg-P	305	277	314	320	321
	Organ-P	238	254	176	202	203
	Total-P	1242	1242	1236	1253	1291
DEDZA	Inorg-P	487	462	468	481	490
	Organ-P	755	780	768	772	801

WET AND DRY INCUBATION

Appendix 7. Total-, inorganic-, and organic-P determined in incubated and unincubated samples extracted with 2N H_2SO_4; no organic residue added.

Soil	Week:	0	1	2	3	4	5	6	7	8
		ppm								
	Total-P	491	548	519	-	469	546	530	525	508
MULANJE	Inorg-P	271	279	266	-	266	283	266	271	281
	Organ-P	220	268	253	-	203	262	264	254	227
	Total-P	1195	1230	1237	-	1173	1332	1279	1231	1215
DEDZA	Inorg-P	436	478	441	-	407	464	459	420	471
	Organ-P	760	753	796	-	766	868	820	811	744

Appendix 8. Total-, inorganic-, and organic-P determined in incubated and unincubated samples extracted with 2N H_2SO_4; 2% organic residue added.

Soil	Week:	0	1	2	3	4	5	6	7	8
		ppm								
	Total-P	567	556	561	-	515	580	583	558	560
MULANJE	Inorg-P	331	356	295	-	296	299	313	288	315
	Organ-P	235	200	266	-	219	281	270	270	245
	Total-P	1285	1281	1315	-	1216	1356	1340	1301	1265
DEDZA	Inorg-P	467	502	487	-	454	484	500	458	496
	Organ-P	818	779	828	-	762	872	840	843	769

Appendix 9. Total-, inorganic-, and organic-P determined in incubated and unincubated samples extracted with $NaHCO_3$; no organic residue added.

Soil	Week:	0	1	2	3	4	5	6	7	8
		ppm								
	Total-P	36.9	38.1	41.9	49.2	29.8	29.7	30.1	29.2	34.4
MULANJE	Inorg-P	23.3	22.8	26.1	31.0	18.4	20.1	22.5	19.6	22.1
	Organ-P	13.6	15.4	15.8	18.2	11.4	9.6	7.5	9.6	12.3
	Total-P	46.9	55.4	56.3	45.2	46.9	47.3	48.4	45.4	52.4
DEDZA	Inorg-P	39.4	43.4	43.7	36.6	36.7	37.7	42.1	38.1	41.3
	Organ-P	9.7	21.6	22.3	19.0	10.2	10.2	6.3	7.3	11.1

Appendix 10. Total-, inorganic-, and organic-P determined in incubated and unincubated samples extracted with $NaHCO_3$; % organic residue added.

Soil	Week	0	1	2	3	4	5	6	7	8
		ppm								
	Total-P	64.8	47.0	47.9	58.7	38.1	35.5	36.0	30.2	38.7
MULANJE	Inorg-P	49.3	28.4	30.3	34.5	20.8	20.1	22.7	17.8	20.8
	Organ-P	15.5	18.7	17.6	24.2	17.3	15.4	13.3	12.4	17.9
	Total-P	78.2	64.7	66.2	51.9	55.2	50.6	53.8	48.8	61.1
					48.1	50.8	46.9	46.6	43.8	57.5
DEDZA	Inorg-P	62.2	49.4	50.2	42.4	42.0	40.5	46.5	40.9	48.0
					34.9	37.5	32.8	40.6	32.7	38.6
	Organ-P	11.0	15.2	16.0	9.5	13.2	10.2	7.3	7.8	13.2
					13.2	13.2	14.1	4.9	11.1	19.0