

THE UNIVERSITY OF MANITOBA

THE EFFECT OF ORGANIC MULCHES
ON THE FIXATION AND FORMS
OF PHOSPHATE IN ACID SOILS

by

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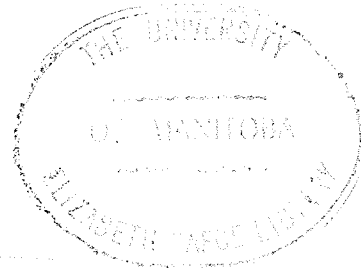
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ABSTRACT

Acid soils have a high capacity for fixing added phosphate. Due to fixation, the availability and/or movement of the added phosphate is limited. However, when organic residues are left to accumulate on the surface of the soil, the availability of phosphate has been shown to increase. In order to study the effect of organic mulches on the fixation and forms of phosphate in acid soils, several acid soils treated with mulch and/or phosphate for a period of 15 years were selected. It was found that long-term mulching increased the organic matter and phosphorus contents of the soils. The application of mulch with phosphate increased the amount of soil phosphorus to a greater extent than did mulching alone. The application of mulch was also found to increase the mobility of phosphorus. Long-term mulching also increased the calcium and potassium contents of the soils. These increases were very marked in the surface soil but less pronounced in the subsurface soils.

An acid Manitoba soil (Keld) and the East African soils were found to have similar phosphorus adsorption or fixation characteristics. The soils with a high organic matter content adsorbed more phosphate than did the soils with a low organic matter content. Over 80% of the adsorbed phosphate was extracted as aluminum and iron phosphates. Aluminum, however, was the most active adsorber. The phosphate adsorbed by aluminum showed a linear relationship with the total amount

of phosphate adsorbed by the soils. The adsorbed phosphate was only partially exchangeable with ^{32}P . The fraction of the adsorbed phosphate that exchanged with ^{32}P decreased with increases in the amount of total adsorbed phosphate. The aluminum, iron and calcium phosphate fractions were equally exchangeable with ^{32}P .

Humic acid, added to the soils, decreased the amount of added phosphate fixed and increased the amount of phosphorus remaining in solution.

The solubility of native phosphorus in the soil with a high organic matter content was greater than in the soils with a low organic matter content. The solubility of native phosphorus in the Manitoba soil (Keld B) was close to that of variscite. In the other soils, native soil phosphorus was more soluble than variscite or strengite and the soils appeared to be supersaturated with respect to these compounds. Equilibrating the soils for 120 hours with amounts of KH_2PO_4 and K_2HPO_4 approximating that found in a fertilizer pellet zone, resulted in very high phosphorus concentrations in the soil extracts. The solubility of phosphorus approximated that of hydroxyapatite or dicalcium phosphate dihydrate when low amounts of KH_2PO_4 or K_2HPO_4 were added. The solubility of phosphorus in the soils was usually greater than the solubility of the aluminum or iron phosphates thought to occur in soils. Incubating the soils for one or two months with various amounts of $\text{NH}_4\text{H}_2\text{PO}_4$ showed that the solubility of phosphorus approximated that of hydroxyapatite or dicalcium phosphate dihydrate, when low amounts of phosphate were added.

The effect of an organic mulch on the growth of plants and availability of surface applied phosphate was found to be due to two factors: First, mulching resulted in a better root distribution near the soil surface, hence the plants were able to utilize the surface applied phosphate. About 70% of the effect of mulch on phosphate utilization by plants could be attributed to the above factor. Secondly, mulching increased the mobility of phosphorus and decreased the amount of phosphorus fixed by the soils.

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I INTRODUCTION

Most East African soils planted to tea have developed from volcanic ash under abundant rainfall and high temperatures. Hydrolysis of the silicate constituents of the parent material have taken place and thus silicic acid, bases, aluminum, iron and manganese have been set free. The silicic acid and bases have been leached from the upper soil leaving the bulk of the soil body rich in aluminum, iron and manganese.

These soils are inherently very low in phosphorus and due to their very high aluminum, iron and manganese contents have a very high capacity for fixing added phosphate. The availability of added phosphate is generally limited by the very low solubility and/or mobility of the fixed phosphate. Attempts to increase phosphate availability by adding very large amounts of phosphate fertilizers have not been very successful. Increases in yield of tea have not been large enough to offset the cost of applying large amounts of phosphate fertilizers. It has also been observed that the application of large phosphate fertilizers may, in some instances, cause other nutrient deficiencies thus leading to more problems (67). The practice of incorporating the fertilizer into the soil as is done with annual crops, makes the phosphate accessible to plant roots even though the mobility of the added phosphate is very low. Incorporation of phosphate

fertilizer for tea production, however, can only be done at the seedling stage. Further applications of phosphate are generally surface applied. It has been shown that the availability of surface applied phosphate in tea plantations is increased when organic residues in the form of leaf-fall, pruning liter, or applied from other sources is left to accumulate on the soil surface (58). Uptake of phosphorus and yield of tea was greater on the plots with mulch than on the plots without mulch. Recent work (68) has shown that the quality of tea increased when phosphorus uptake was enhanced. It has also been shown that tea utilized and gave a better return to nitrogen fertilization when the phosphate supply was increased (58).

The effect of organic residues or mulches on phosphorus availability to tea is not clearly understood. It is not known if the effect of the mulch on plant growth is due to phosphate-organic matter interactions which increase the availability of the added phosphate or to physical changes at the soil surface. It is possible that during mulch decomposition some organic acids are released which may block or satisfy adsorption sites and hence reduce the adsorption of added phosphate. It is also possible that some of the released products may be able to react with aluminum and iron phosphates and increase their solubility. The effect of the organic mulch could be physical, whereby it provides an environment suitable for the growth of feeder roots. The roots could therefore be able to reach the phosphate held at or near the

surface of the soil.

Previous workers (5, 11, 17, 24, 25, 26, 28, 39, 46, 64) have attributed the benefits derived from organic mulches to either its physical or chemical effect. In some instances the two were thought to have operated simultaneously. No attempts have been made to separate these effects.

The objective of this study was to determine the effect of organic mulches on the fixation and forms of phosphate in acid soils. Experiments were conducted to determine:

- (a) the forms and solubility of native and applied phosphates in acid soils,
- (b) the effect of an organic mulch on the availability of added phosphate,
- and (c) the chemical and physical effects of mulches on plant growth and phosphate uptake.

II LITERATURE REVIEW

Numerous investigators (1, 7, 8, 13, 14, 22, 23, 36) have established that compounds of aluminum and iron, and calcium and magnesium are responsible for the fixation of phosphate in acid and calcareous soils, respectively. In acid soils aluminum and iron hold phosphate in several ways (36): 1. anion exchange adsorption of orthophosphate on positive sites; 2. cation-exchange adsorption of positively charged complexes of phosphate ions with hydroxyl-aluminum and hydroxyliron ions; 3. precipitation of sparingly soluble aluminum and iron phosphates on internal and external surfaces of clay minerals; and 4. cation-exchange adsorption of phosphate complexes with metal-humate ions.

Hsu (22), recognized two reactions operating at different rates in the process of phosphate fixation by aluminum and/or iron. One reaction proceeded rapidly and was attributed to surface fixation of phosphate on the amorphous aluminum hydroxides and iron oxides. The second, a slower reaction was also due to surface fixation on similar amorphous hydroxides and oxides but resulted in the formation of aluminum and iron phosphate compounds during the reaction. Hsu (23), further showed that adsorption and precipitation result from the same chemical force. Whether precipitation or adsorption occurs is dependent on the form of aluminum and/or iron present at the moment of reaction. In most acid soils, because of the effect of pH, surface-reactive amorphous aluminum hydroxides

and iron oxides dominate the process of phosphate fixation rather than Al^{3+} and Fe^{3+} in solution.

Davis (16) and Kurtz et al. (31), found that phosphate adsorption by soils followed the Freundlich adsorption isotherm. Cole et al. (15), showed that phosphate adsorption in calcareous soils closely followed the Langmuir adsorption isotherm. They pointed out that the major advantage of the Langmuir equation over the Freundlich equation is that an adsorption maximum can be calculated. Olsen and Watanabe (40), showed that the adsorption maximum calculated by the Langmuir isotherm was very closely correlated with the surface area of soils as measured by ethylene glycol retention. Beckwith (4) and Fox et al. (19), have used this relationship to calculate the percent saturation of adsorption capacity by phosphate. They found that percentage phosphate saturation was an excellent index for predicting the yield of phosphorus in plants. Younge and Plucknett (71) showed that the high adsorptive capacity of Hawaiian aluminous ferruginous latosols could be satisfied by the addition of a very large amount of phosphate fertilizer.

The Chang and Jackson (9) method for phosphorus fractionation have been employed by many workers (1, 8, 12, 56, 65, 72) to investigate the relative distribution of native or added soil phosphorus. Yuan et al. (72) found that greater than 80 percent of phosphate added to three acid sandy soils was retained by aluminum and iron. They found that the ratio of aluminum phosphates to iron phosphates increased with

increased rates of added phosphorus, implying that aluminum was the most active adsorber. Phosphate, added to six soils of pH 5.3 to 7.5 and kept at field moisture content for three days was fixed mainly as aluminum followed by iron and calcium phosphates. When the soils were incubated for 100 days, the amount of iron phosphate increased and that of aluminum and calcium decreased(8). A similar behaviour of added phosphate was found to occur in volcanic ash-derived soils of Southern Chile (1) and acid soils of the Eastern United States (51). Weir and Soper (65) showed that calcium was the most active initial adsorber of phosphate added to calcareous soils. Most workers have found that the amount of the various phosphates in acid soils decrease in the order: Fe-P, Al-P, Ca-P. Added phosphate, however, is initially distributed as follows $Al-P > Fe-P > Ca-P$. When the soil is aged the distribution shifts to that of native soils.

A number of reasons have been advanced in an attempt to explain the differences in fixation of added phosphate by aluminum and iron in acid soils. Chang and Chu (8) suggested that the clay fraction is the main site of phosphate fixation. The aluminum content of clays is much higher than that of iron or calcium. Therefore, the added phosphate is most likely fixed as aluminum phosphate followed by the formation of iron phosphates in the initial reaction stage. With time the aluminum phosphates change to the less soluble iron phosphates. The shift from aluminum phosphates to iron phosphates is thought to be due to the lower solubility of the iron phosphates as

compared to that of the aluminum phosphates (72). According to Hsu (23), all phases of phosphate fixation are due to the attraction between phosphate and aluminum or iron. Therefore, the difference in the initial fixation reaction can also be attributed to the differences in the amount of aluminum or iron initially available for reaction.

It has been postulated that aluminum and iron phosphates can exist in several precipitated forms in the soil. The most important forms being variscite ($\text{AlPO}_4 \cdot 2\text{H}_2\text{O}$), strengite ($\text{FePO}_4 \cdot 2\text{H}_2\text{O}$) and barrandite (a mixture of variscite and strengite in any proportion)(47).

Several workers have studied the solubilities of variscite and strengite in pure and soil systems. Lindsay and Moreno (34) suggested that in acid soils, the hydroxides, gibbsite and goethite control aluminum and iron concentrations and that these concentrations in turn control the phosphate concentration in accordance with the solubility products of variscite and strengite. Cole and Jackson (13) found the solubility equilibrium constant (pK_{sp}) of variscite crystal species to be 29.5. However, the solubility of purified laboratory prepared variscite was found to be 30.5 at 25°C (34). The initial reaction products of applied phosphate in acid soils are much more soluble than variscite, but upon ageing, these intermediate reaction products are slowly transformed into variscite which may coexist with gibbsite as stable solid phases. Chang and Jackson (10) found the solubility product for strengite to vary from 33.0 to 35.1. The

pK_{sp} increased several fold with increased solid to solution ratio. Chakravarti and Talibudeen (7) showed that variscite and strengite minerals occur in tropical soils, but were unable to confirm their presence in temperate soils. Taylor and Gurney (57) determined the aluminum phosphate ion products in solutions equilibrated with an acid phosphate deficient soil and showed that the phosphate status of the undisturbed soil was compatible with the existence of variscite. They produced no evidence that variscite has any effect in controlling the composition of dilute phosphate solutions equilibrated with the soil for periods less than 32 days. LeMare (33) observed that Triple superphosphate applied at a rate of 896 kg per hectare to a Uganda acid soil was converted within two years to a very insoluble form, having a solubility product similar to that of variscite. The phosphate concentration in soil solution was much greater when 1792 kg per hectare was added and the soils appeared supersaturated with respect to variscite.

Bache (3) has suggested that solubility equilibria in soils are not relevant for this purpose. His work suggests that thermodynamic solubility constants are not maintained at pH values above 3.1 and 1.4 for variscite and strengite, respectively, and that surface reactions appear to be more important than precipitation reactions. He concluded that although solubility constants of the order of those for variscite and strengite may be obtained, these constants do not provide sufficient evidence for the existence of these minerals in soils. LeMare (33) observed that solubility product

values are difficult to obtain, because of the slow rate of dissolution and the difficulty of ensuring equilibrium. Furthermore, experimental values for solubility constants are dependent upon particle size and degree of crystallinity of the compound (38).

Behaviour of phosphates in soils has been studied extensively by the use of radioactive phosphorus (^{32}P). A number of investigators have determined reactivity of soil phosphorus and also added phosphate by its capacity to exchange with ^{32}P (12, 56, 65). In recent years the exchangeability of different phosphate fractions has been investigated by combining the isotopic dilution technique for exchangeable phosphorus with the procedure of Change and Jackson (9) for phosphorus fractionation (12, 56, 65). The results of these workers showed that, in general, the exchangeability of phosphorus fractions in widely different soils followed the sequence: $\text{Al-P} > \text{Fe-P} > \text{Ca-P}$. Tandon and Kurtz (56) found that the source of most of the isotopically exchangeable phosphorus in widely different soils was in the aluminum and iron fractions. Chu and Chang (12) observed that calcium phosphate showed greater exchangeability in acid soils than in alkaline soils.

Attention has been focused in the effects of organic matter and organic acids on phosphate fixation and phosphate availability to plants. Rennie and McKercher (44) and Weir and Soper (65) have observed the high phosphate adsorptive capacity of the soil organic fraction. Swenson et al. (54) showed

that organic acids prevented fixation of phosphate by aluminum and iron. Manojlovic (35) reported that humic acid derived from dung and manure decreased phosphate fixation by a soil treated with a dilute phosphate solution. It also decreased phosphate fixation when granular superphosphate was in contact with the soil for four months. Weir and Soper (66) found that humic acid extracts of soil organic matter had the capacity to complex ferric ions. The acid-iron complex was able to hold phosphate ions against exchange with an anion resin.

Jelenc et al. (29) found that 6 to 24 mg of sodium humate in 3 kg of soil increased percent utilization of superphosphate labelled with ^{32}P in pseudology and brown forest soils. Hajdukovic and Ulrich (21) showed that 10 mg of sodium humate, prepared from lignite, applied to 2.5 kg loess soil of pH 7.0 significantly increased the number of roots, especially root hairs, and promoted phosphorus utilization from labelled superphosphate by maize.

Mulching has been widely used for many years for fruit trees and bushes. The use of mulches are more prevalent in the tropics particularly for crops such as coffee and tea.

Jacks et al. (26) reviewed the practice of mulching with grass, straw and other organic residues. In general, they stated that increased yields due to mulching result from suppressed weed growth, conservation of moisture by reducing evaporation and runoff, protection from erosion, increased

infiltration of water, alteration of soil temperature fluctuations, enhanced availability of mineral nutrients, enhanced nitrification, addition of nutrients and organic matter and preservation or improvement of soil structure. Russell (47) stated that the general effects of mulches on the soil is due to organic matter decomposition. He suggested that the moist conditions under mulch favoured soil microorganism and small animal activity and that decomposition, brought about by these microorganism, improved and stabilized the soil structure. Thus the permeability of the superficial soil layer would be maintained. The small animals by their activity in the surface soil would also increase the number of the surface channels through which the water can leach. Furthermore, the decomposition of the organic mulch would result in an increase in plant nutrients at the surface of the soil.

The effects of organic mulches on crop yields, soil properties and root growth have been studied in detail by several workers. Ashrif and Thornton (2) attributed the yield increases of groundnuts as a result of a grass mulch to physical factors. However, they also reported that mulching resulted in a significant increase in exchangeable soil potassium. Studies on the effect of mulch on groundnuts, maize and cassava by Nye (39) in Ghana showed modest yield increases, and he suggested that phosphorus from decomposing mulch was partially responsible for the observed effects. As there was no clear interaction between added nitrogen and phosphorus, Nye concluded that the effect of mulches was mainly physical

and noted that mulches suppressed weed growth and loosened the top soil where the surface tended to harden. Sharma (50), in India, found that removing the tea prunings resulted in a 5 to 10 percent decrease in crop yields. When the prunings were removed but mulch added at the rate of 3.5 tonnes per hectare, the yield was 5 to 6 percent less than when the prunings were not removed.

In a series of experiments, the Tea Research Institute of East Africa has observed the beneficial effects of using mulches (58). Often the benefits have been associated with increased uptake of phosphate and a better utilization of added nitrogen. Recently, the Institute has shown that mulch in the form of napier grass increased yields of tea only in the presence of added superphosphate. Mulch or phosphate alone failed to give a yield response. In Antigua, West Indies, Turner et al. (60) found that sulphate of ammonia gave rise to a paying increment in yield of sugar cane on a highly calcareous soil only in the presence of a mulch of decomposing trash. The authors considered that the trash mulch increased the yield of canes by supplying available phosphate, and perhaps potash which tended to be deficient in these highly calcareous soils formed over weathered limestone. They stated that on similar calcareous soils in Trinidad sugar cane responded to dressings of sulphate of ammonia only when small doses of readily available phosphate and in some cases potash were applied. In an experiment using ^{32}P and ^{86}Rb , Kim et al. (30) recently showed that the leaves and

shoots of trees contained more dry-matter and phosphorus when the crops were mulched than when treated only with mineral phosphate fertilizer especially in the year following treatment. In a pot experiment, Wasowicz (63) explained the increases in phosphorus content observed in cacao seedlings under grass mulch by the phosphate contained in the grass, but increases under sawdust containing only a trace of phosphorus was explained by the formation and subsequent decomposition of organic-phosphate compounds. Ingham (24) leached various mulches with 30 inches of water, and found appreciable amounts of ammonium, nitrate, phosphorus, and potassium in the leachate without appreciable decomposition of the mulch.

Robinson and Hosegood (46) reported that mulch (napier grass) applied to latosolic coffee soils in Kenya decreased soil acidity and exchangeable calcium and manganese. It increased organic carbon, Kjeldahl nitrogen, exchangeable potassium and phosphorus. It also increased total pore space, free draining pore space and rate of rainfall infiltration in the surface soil. They found that mulch increased phosphorus, potassium, and in some cases nitrogen in the coffee leaves, but reduced calcium and magnesium levels. Robinson and Chenery (45) also observed that mulches increased the potassium and decreased the magnesium content of coffee leaves. Increases in exchangeable potassium and available phosphorus under mulched plots have also been reported by Jaiyebo (28). Weeks et al. (64) observed strong residual effects of mulching on the nutrients content of a soil in an apple orchard. They showed that available phosphorus content of the mulched soil

was eight times greater at the surface and five times greater at a depth of 45 cm than the available phosphorus content of soils not mulched and cultivated. The enhanced mobility or availability of phosphorus in mulched soils was ascribed by Swenson et al. (54) to the action of organic acids produced from the mulch that prevented the combination of phosphate with iron and aluminum.

Effects of organic mulches on root development and distribution, with the subsequent benefits derived from a better root system, has attracted the attention of several workers. In an experiment comparing the effects of Jungle weed, maize stalk, napier grass and eragrostis grass mulches, The Tea Research Institute of East Africa (58) observed that tea grown on the eragrostis grass mulch which had the lowest decomposition rate and nutrient content, had a dense network of active fibrous roots growing profusely into the mulch layer all year round. The tea grown on the eragrostis mulch consistently gave higher yields than the tea grown on the other types of mulches. In part of an apple orchard which had been mulched for 35 years, Bekenbach and Gourlay (5) observed a dense mass of fine roots in the matted mulch layer beneath which was a network of larger roots. Eggert et al. (17) compared root development of apple trees under mulch and sod. They found that in mulched soils fibrous roots occurred in the humified lower part of the mulch and above the mineral soil, whereas under sod, fibrous roots were not found in the top two inches of soil. Strortzer (53) attributed the beneficial effects of

mulching on potassium absorption to an increased root mass, but mainly due to the higher quantity of fibrous roots near the surface.

Tamasi (55), compared the effects of different cultural practices on the root development of apple trees and showed that the trees had 20.5, 27.2 and 42.2 percent of their roots in the top 30 cm of soil, under a green manure crop, clean cultivation and straw mulch, respectively. Top and root growth were most vigorous in the moist, mulched soil, and the fresh weight of the mulched trees was 2.4 times that of the green manured trees and 1.8 times that obtained on the clean cultivation treatment.

Chiba (11) found that mulches of rice straw, wheat straw and sawdust tended to increase foliar phosphorus, potassium, linear plant growth and root density.

Bull (6) showed that the downward growth of coffee tap roots was reduced by irrigation and increased by mulching with banana trash. He found that mulching also increased the development of primary and secondary lateral roots. A combination of irrigation and mulching produced the greatest development of the root system. Yocum (70) observed a lateral, largely superficial type of root development of young apple trees after two years of mulching with straw. Root development under clean cultivation was of a general type with less lateral roots. He explained the response of the root systems on the basis of soil moisture content. Isenberg and Odland (25) who obtained substantial vegetable yields under various mulches, observed that as a result of extra moisture especially in the

lower part of the mulch, plant roots grew profusely in the surface layers of soil and in the mulch itself. Thus giving mulched plants an additional volume of soil from which to obtain nutrients and water.

It can be seen, from the literature review, that the effects of organic mulches on crop yields have been attributed to many factors. The effect on the availability and uptake of soil phosphorus has been attributed to physical or chemical factors without much evidence. Therefore, it appears that the physical and chemical effects of mulches on phosphorus uptake by plants need be further investigated.

III METHODS AND MATERIALS

The methods and materials described in this section do not include the experimental methods used for the several individual studies conducted. Details of the methods and materials used for each of these studies are presented with the results and discussion under appropriate subsections.

Chemical Determinations

Soil pH

The pH of samples or solutions was measured electrometrically on an Ionalyzer Model 801 digital pH meter. A soil : water ratio of 1:10 (W/W) was used, unless otherwise stated.

Soil Organic Matter

Soil organic matter was determined by oxidation of the organic carbon with excess potassium dichromate solution, followed by titration of the excess dichromate with ferrous sulfate solution (62).

Aluminum, Iron and Manganese

The aluminum, iron and manganese in solution were determined by the use of a Perkin-Elmer Atomic Absorption Spectrophotometer Model 303 (41).

Calcium plus Magnesium

Calcium plus magnesium in solution was determined by titration with ethylenediaminetetraacetic acid (EDTA), using Eriochrome Black T as indicator (59).

Phosphorus Determinations

- (a) Total Phosphorus content of soils. A two g sample of soil was digested with HClO_4 for one hour. The phosphorus in the digest was determined colorimetrically using the vanomolybdophosphoric yellow method as described by Jackson (27).
- (b) Fractionation of inorganic soil phosphorus. The inorganic soil phosphorus was fractionated according to the procedure of Chang and Jackson (9) as modified by Petersen and Corey (42). A one g sample of soil was used, unless otherwise stated.
- (i) Water soluble and loosely-bound phosphate

The water soluble and loosely-bound phosphate was extracted by shaking the soils with 50 ml of 1 N NH_4Cl for 30 min. The suspensions were centrifuged and the phosphorus in the extracts determined colorimetrically using the molybdophosphoric blue method. The Bray reductant reagent (amino - naphthol - sulfonic acid reductant) as described by Petersen and Corey (42) was used for color development. This reagent was used to avoid dilution of the extracts. Also the color developed by the Bray reductant reagent has a greater

stability than that developed using chlorostannous reagent as the reductant.

(ii) Aluminum phosphates

The aluminum phosphates were extracted by shaking the soils, previously extracted with NH_4Cl , with 50 ml of 0.5 N NH_4F (pH 8.2) for one hour. The suspensions were centrifuged. The solutions were highly colored, and therefore filtered through a Whatman No. 42 filter paper containing about 0.5 g phosphorus-free activated charcoal to remove organic matter. Phosphorus in the extracts was determined colorimetrically using the Bray reductant reagent as outlined for water soluble and loosely-bound phosphates.

(iii) Iron phosphates

Following extraction of the soils with NH_4F for the aluminum phosphates, the soils were shaken with 50 ml of 0.1 N NaOH for 17 hours to extract the iron phosphates. The dispersed organic matter in the extracts was flocculated and removed by the addition of five drops of concentrated H_2SO_4 and filtering through charcoal as outlined for aluminum phosphates. Phosphorus in the extracts was determined as outlined for water soluble and loosely-bound phosphates.

(iv) Calcium phosphates

Calcium phosphates were extracted from the soils

after water soluble, aluminum and iron phosphates had been removed by shaking the soils with 50 ml of 0.5 N H_2SO_4 for one hour. Phosphorus in the extracts was determined as outlined for the water soluble and loosely-bound phosphates.

(v) Reductant soluble (occluded) phosphates

Reductant soluble or occluded phosphate was extracted, following the extraction for the calcium phosphates, by shaking the soils with 50 ml of 0.3 M sodium citrate containing 1 g of sodium dithionite for 5 min. The suspensions were then heated in a water bath for one hour at 75 - 80°C. The suspensions were cooled, equilibrated by shaking for 5 min and centrifuged. Excess citrate and dithionite in the supernatant were oxidised with 0.25 M $KMnO_4$. Phosphorus in the solutions was then extracted with isobutyl alcohol and the molybdophosphoric blue color complex developed in the alcohol phase using chlorostannous reductant.

Radioactive Materials and Techniques

The radioactive isotope used in these studies was carrier-free ^{32}P , obtained from the Atomic Energy Agency of Canada, Ottawa. The ^{32}P was obtained as H_3PO_4 in HCl. ^{32}P has a half-life of 14.3 days, and decays by B^- emission.

(a) Radioactivity of soil solutions. A one ml aliquot of solution was placed in an aluminum planchet. After

evaporation, using an infra-red lamp as a heat source, the activity was measured by placing the planchet under the end window of a D - 34 G.M. tube, connected to a Nuclear Chicago Model 161A Basic Binary Scalar. The counts were corrected for background radiation.

(b) Radioactivity of plant digests. The plant material was air-dried and then placed in an oven at 70°C for 24 hours. The dry material was then finely ground. A representative sample of the plant material was weighed and digested with concentrated HNO_3 - HClO_4 - H_2SO_4 acid mixture (27). The activity of the wet-ashed material was measured using a G. M. tube according to the procedure outlined by Veall (61). The fraction of applied phosphorus absorbed by the plants was calculated from the radioactivity of the phosphorus in the plant and in the phosphate fertilizer applied.

Soils

(a) East African soils. The soil samples were collected from experimental plots of tea located in the Kericho district of Kenya. This district has the largest tea plantations in East Africa. The soils in the area are derived from a massive sheet-flow of hard phonolite lava, described by the Kenya Geological Department as being exceptionally free from fissures. The phonolites have weathered into very deep orous stone-free soils. The lack of underlying ground water provides additional evidence of the water-tight nature of the lava.

A recent survey of the virgin forest soil near the experimental plots by Scott (49) showed that there are two main soils in the area, which are deep friable clays. The two soils differ from each other only in that the parent material of one has a thin ash-derived soil overlying it. Table I shows the chemical characteristics of the main soil type within the experimental area as obtained by Scott (49).

The soils under forests, in general, have a layer of humus up to 12.5 cm in thickness. The soils are described as having a dark brown to dark reddish brown color and are non-sticky but slightly plastic when wet. Chemically the soils are very similar. As shown in Table I, these soils have very low total exchangeable bases and a low percent base saturation.

The rainfall pattern in the area is bimodal with the long rains occurring from March to May and the short rains occurring from August to October. There is no marked dry season.

The tea experiment was originally laid out as a 2^5 factorial to test the effects of two levels of nitrogen, phosphate, potassium, sulfur and mulch on the yield of tea. The experiment was continued for a period of five years then modified to a 4×2^2 factorial to test the effects of four levels of nitrogen and two levels of phosphate and potassium on the yield of tea. The treatments were split to include mulched and unmulched treatments. The modified experiment has been conducted for a period of 15 years. The soil samples used in this study were obtained at this time. Mulch had been

Table I

Chemical Characteristic of the East African main soil type.

Depth (cm)	O.M. (%)	pH 1:1	C (%)	N (%)	C/N	Exchangeable bases					Exch. H	Total E.C.	% Base Sat.
						Ca	Mg	Mn	K	Total			
0-5	20.8	5.5	10.40	0.934	14.8	6.70	2.80	0.25	1.41	11.2	16.2	27.4	40.8
5-20	14.3	5.0	7.14	0.616	15.4	1.15	1.02	0.05	0.64	2.9	17.8	20.7	13.8
20-45	6.1	5.3	3.06	0.294	13.9	0.04		0.006	0.29	0.3	14.3	14.6	2.3
45-75	7.6	5.9	3.77	0.222	22.6	0.03			0.16	0.2	15.8	16.0	1.2
75-100	2.4	5.7	1.22	0.116	14.0	0.04		0.005	0.24	0.3	11.2	11.5	2.4
100-175	2.6	5.6	1.28	0.118	14.5	0.11		0.004	0.29	0.4	10.9	11.3	3.6

applied in the form of leaf-fall and pruning liters. Phosphorus, as double supersphosphate, was applied at a rate of 22.4 kg P_2O_5 per hectare.

The soil samples were collected from the 0 to 5 cm and 5 to 10 cm depths, from the check and phosphate treated plots with and without mulch. The samples consisted of five auger holes per subplot per replicate. The samples, obtained from the various replicates, were bulked and air-dried. The dried soils were mixed thoroughly and then passed through a 0.5 cm mesh sieve.

Nine tenth kg of each sample was placed in a plastic bag and sealed. The sealed soils were sent to Canada for studies. The soils went via the Canadian Department of Agriculture, Plant Protection Division where they were inspected and treated for soil borne diseases. The treatment consisted of fumigating the soils with CH_3Br at the rate of 3.2 kg CH_3Br per $2.8 m^3$ of soil for 16 hours at $21^\circ C$.

The quantity of soil, imported from East Africa, was insufficient for both chemical and Greenhouse studies. Therefore, an acid Manitoba soil (Keld) was used in some of the chemical and all of the greenhouse studies. This soil was selected as it had a high phosphate fixing capacity and showed characteristics similar to the East African soils.

Organic mulch was required for the greenhouse studies. The Manitoba soil and organic mulch used in the greenhouse investigations are described below:

(a) Keld soils. Ehrlich *et al.* (18) have described the Keld soil as consisting of fine-textured soil material developed

on till consisting of strongly acid shale and granitic rock. The till is underlain by a soft, very strongly acid shale bedrock at depths ranging from 5 to 180 cm.

(i) Keld A. A sample consisting of surface soil was collected from a site which had been brought under cultivation only recently. The site is located about 4.35 km west and 1.24 km south of Dauphin, Manitoba. The soil was air-dried and passed through a 0.6 cm mesh sieve. A representative sample used for chemical characterization and other investigations was passed through a 2 mm mesh sieve.

(ii) Keld B. Detail of the sampling procedure and site were not available.

(c) Organic Mulch. Organic mulch consisting mostly of partially decomposed leaf litter was collected from under trees near a marsh depression. The trees were mostly acacia and spruce. The fresh fallen leaves were scraped off and the partially decomposed litter was scraped and collected. The collection depth ranged from 0.5 to 5.0 cm. The site is located in S. E. Manitoba about 1.24 km S. E. of Wampum junction on Highway No. 12.

Table II shows some chemical characteristics of the soils and mulch used in the studies. After characterization, it was found that the only differences in the East African soils were between mulch and unmulched treatments, and between soil depths. Therefore, the East African soils were bulked into mulched and unmulched samples. The bulked soils, derived from the 0 to 5 cm depth were used for most of the studies reported.

Table II Some Chemical Characteristics of the Soils and Mulch

Soil	pH 1:5	O.M. (%)	H ₂ O-Sol. P ² (ppm)	C E C (meq/100g)	Exchangeable Bases			Exch. Al (meq/100g) *	% Base Sat.
					Ca	Mg meq/100g	K		
East African Mulched	4.63	12.96	0	37.56	7.29	4.11	1.45	2.08	34.21
Unmulched	4.59	8.39	0	29.63	3.46	2.35	1.02	2.03	18.19
Manitoban Keld A	4.30	9.00	0	36.20	7.62	2.02	1.78	3.71	31.55
Keld B	3.95	2.96	0	21.0	ND	ND	ND	ND	ND
Mulch	5.00		80.00						

ND = not determined

* Extracted by 1 N KCl.

IV PRESENTATION OF EXPERIMENTAL

RESULTS AND DISCUSSION

Influence of Long-term Mulching and Phosphate Applications on the pH, organic matter, phosphorus, calcium, magnesium and potassium contents of soils.

Eight soil samples from East Africa were studied. The samples were selected from the following treatments: no phosphate or mulch added (check), mulched, phosphate added, and mulched with phosphate added. Samples from 0 to 5 cm and 5 to 10 cm depths were used. The pH, organic matter content, total phosphorus content and the amounts of the various inorganic phosphates present in the soils were determined. Acid soluble (0.1 N HCl + 0.025 N H₂SO₄) calcium, magnesium, potassium and phosphorus (available) were determined as outlined by Mehlich et al. (37). Acid soluble phosphorus which is used as an index of plant available phosphorus was determined on samples taken at 1 cm intervals to a depth of 10 cm in order to show the effect of treatments on the distribution of this form of phosphorus in the soil.

pH, organic matter content and total phosphorus content of the surface soil was found to be greater than that of soil obtained from a depth of 5 to 10 cm (Table III). With few exceptions, the inorganic phosphorus fractions followed the same pattern for all soils. The results also show that these soils hold phosphate very tightly since it was not

Table III

Influence of mulch and added phosphate on the pH,
organic matter and phosphate content of soils

Treatment	Depth (cm)	pH (1:5)	Organic Matter (%)	Total P(ppm)	NH ₄ Cl Ext. P (ppm)	NH ₄ F Ext. P (ppm)	NaOH Ext. P (ppm)	H ₂ SO ₄ Ext. P (ppm)	Red-Sol. P (ppm)
Check	0 to 5	4.65	8.15	530	0	42.0	183.5	21.0	194
	5 " 10	4.30	7.17	400	0	38.0	187.5	21.0	169
Mulch	0 " 5	4.75	12.85	720	0	58.0	222.0	34.0	169
	5 " 10	4.35	7.62	492	0	40.5	173.0	21.0	230
Phosphate	0 " 5	4.60	8.62	578	0	64.0	232.0	34.0	213
	5 " 10	4.20	7.37	416	0	24.0	125.0	18.0	180
Mulch + Phosphate	0 " 5	4.50	13.07	1,073	0	183.5	411.0	64.0	143
	5 " 10	4.15	8.15	593	0	49.0	204.0	41.0	200

extracted by a dilute neutral salt such as 1 N NH_4Cl . The organic matter content of the surface soil was increased by mulching. The organic matter content of the 5 to 10 cm depth of soil was slightly increased by mulching. Mulching also usually increased the total, NH_4F , NaOH and H_2SO_4 extractable phosphorus contents of the soils. The increases in the total and the different inorganic phosphate fractions are highly marked when mulching was combined with phosphate application. The increases in the organic matter and total phosphorus contents and inorganic phosphorus fractions in the mulched soils can be attributed to the organic matter and phosphate released from the mulch that was added. The increase in the phosphorus content of the subsurface soils was considerably lower than for the surface soil. Mulching increased pH only slightly in the 5 to 10 cm depth. Mulching in combination with phosphate slightly reduced pH. reductant soluble phosphate in the surface soils was reduced by mulching. This form of phosphate was variable in the subsurface soils and appeared to be unaffected by mulching.

Addition of phosphate slightly increased total phosphorus, and the NH_4F , NaOH and H_2SO_4 extractable phosphorus contents of the surface soils. The addition of phosphate and mulch increased total phosphorus and the amounts of the various phosphate forms to a greater extent than did the addition of phosphate alone. It appeared that NH_4F , NaOH and H_2SO_4 extractable phosphorus in the 5 to 10 cm depth

was reduced when phosphate was applied alone. The reason for these reductions are not clear and may be due to sampling error or soil variations within the experimental area. Phosphate added alone decreased pH slightly. The reduction in soil pH was greater when phosphate was combined with mulching. Reductant soluble phosphate was variable and appeared to be unaffected by phosphate addition to the soils.

Table IV Distribution of available
phosphorus (acid soluble) in soils (ppm)

Depth (cm)	<u>Treatments</u>			
	<u>Check</u>	<u>Mulch</u>	<u>Phosphate</u>	<u>Mulch + Phosphate</u>
0 to 1	16	36	50	105
1 to 2	17	26	22	51
2 to 3	19	17	19	24
3 to 5	20	18	19	22
5 to 7	20	19	22	19
7 to 10	18	20	20	22

The distribution of available phosphorus in the soil was influenced by the addition of mulch and/or phosphate (Table IV). Mulch and phosphate applied separately resulted in increases in the available phosphorus content of the surface soil. The available phosphorus content of the 1 to 2 cm depth of soil was only slightly increased when mulch or phosphate was added. The available phosphorus content of the surface layer of soil was greatly increased when mulch was combined with phosphate application. It is interesting to note that mulching in combination with phosphate addition resulted in a downward movement of available phosphate. Thus, indicating that mulching not only serves as a phosphate source but increases the solubility or mobility of added phosphate. This is of great importance when phosphate is applied to the soil surface. Mulching increases the mobility of the added phosphate and thus the phosphate moves to lower soil depths where plant roots can utilize the added phosphate.

Table V Acid soluble calcium, magnesium and
potassium contents of soils (meq/100g)

<u>Treatment</u>	<u>Depth (cm)</u>	<u>Ca</u>	<u>Mg</u>	<u>K</u>	(meq/100g)
Check	0 to 5	0.47	0.73	0.63	
	5 to 10	0.20	0.25	0.32	
Mulch	0 to 5	2.30	0.80	1.70	
	5 to 10	0.40	0.10	0.80	
Phosphate	0 to 5	0.45	0.35	0.49	
	5 to 10	0.40	0.30	0.46	
Mulch + Phosphate	0 to 5	5.25	1.40	1.01	
	5 to 10	0.40	0.40	0.82	

Table V shows the amounts of bases extracted from the soils with the dilute acid mixture (0.1 N HCl + 0.025 N H₂SO₄). The effect of treatments appeared to be restricted to the 0 to 5 cm depth of soil.

Long-term mulching increased the calcium and potassium contents of the surface soils. Mulch with phosphate, however, increased the calcium, magnesium and potassium contents of the soils. The increase in potassium content was greater when mulch was applied without phosphate. The addition of phosphate alone decreased the magnesium and potassium contents of the surface soils but did not affect the calcium content of the soils. There appeared to be no differences in the calcium, magnesium and potassium contents of the subsurface soils.

Nature of phosphate fixation in acid soils

Phosphate ions added to soils can become adsorbed on the soil colloids. In addition, soluble phosphates added to the soils may be precipitated as slightly soluble salts. It was shown, in the last subsection of this report, that long-term mulching and phosphate additions increased the aluminum and iron bound phosphates in the East African soils. The calcium bound phosphate was increased only slightly. Therefore, aluminum and iron ions played a major role in the phosphate behaviour of these soils.

Phosphate adsorption on soil colloids can be described by the Langmuir equation (32). This equation is usually used to study behaviour of phosphorus in soils when small amounts of phosphorus are added or are present in the soil solution.

An adsorption isotherm may be defined as the relationship between the amount of substance (phosphorus) adsorbed by an adsorbent and the final or equilibrium concentration of the substances in solution.

The Langmuir adsorption isotherm was originally developed to describe gas adsorption on solids. The same equation has been used successfully to describe the adsorption of liquids and ions from solutions by solids. The following equation was used in this study (40).

$$\frac{\bar{x}}{\bar{m}} = \frac{Kbc}{1 + Kc} \quad [1]$$

Where $\frac{\bar{x}}{\bar{m}}$ = μgP adsorbed per g soil,
 b = adsorption maximum,
 K = constant related to the bonding energy of the adsorbent for phosphate,
 and c = equilibrium phosphate concentration in μgP per ml.

The linear form of the equation is:

$$\frac{c/\bar{x}}{\bar{m}} = \frac{1}{Kb} + \frac{c}{b} \quad [2]$$

Where $\frac{1}{b}$ = slope. Therefore the adsorption maximum,

b = reciprocal of the slope,

$\frac{1}{Kb}$ = the intercept and therefore the

bonding energy, $K = \frac{\text{slope}}{\text{intercept}}$.

A straight line plot of $\frac{c/\bar{x}}{\bar{m}}$ versus c indicates an adsorption reaction. When such a reaction occurs, it is assumed that a unimolecular layer of adsorbed phosphate is present on the soil surface.

The experiments reported in this subsection were

conducted to provide some information on the following:

- (a) The rate of phosphate adsorption or fixation by soil,
 - (b) the nature and form of phosphate adsorbed on soil surfaces,
 - (c) isotopic exchangeability of the adsorbed phosphate,
- and (d) the effect of adding a humic acid to soils on the phosphate adsorption by soils.

(a) Rate of phosphate adsorption or fixation by soils. The rate of phosphate fixation of several soils was determined to provide information on the time required for completion of the initial adsorption reaction.

Soil samples from the 0 to 5 cm depth of the East African soils and the Keld B soil were used in this study. A one gram sample of soil was shaken with 50 ml of solution containing 50 $\mu\text{gP/ml}$ (KH_2PO_4) for $\frac{1}{4}$, $\frac{1}{2}$, 4, 8, 24, 48 or 96 hour at $25 \pm 1^\circ\text{C}$. The suspensions were filtered immediately after shaking. The samples shaken for long periods were strongly dispersed and therefore had to be passed through Whatman No. 42 filter paper several times to get clear solutions. The phosphorus content of the solutions were determined as described earlier (page 18 Sect. i).

The rate of phosphate fixation by all soils was very rapid during the first four hours of reaction (Table VI and Figure 1). The initial rapid reaction was complete in 24 hours when phosphorus was added to the East African soils. This rapid fixation reaction was followed by a slower reaction which continued for the entire period studied. The rate of phosphorus fixation by all the East African soils was similar but much greater than that of the Keld B soil. The Keld B soil appeared to attain equilibrium after eight hours of shaking. This equilibrium was maintained up to 48 hours of shaking. It is possible that a reaction other than adsorption of phosphorus was operative after the 48 hours shaking period. It is also possible that the value obtained for the 96 hours shaking period was in error.

Table VI

Rate of phosphorus adsorption or fixation by soils

Soil	Check		Mulch		Phosphate		Mulch + Phosphate		Keld B	
	P remain- ing in solution ($\mu\text{gP/ml}$)	P adsor- bed ($\mu\text{gP/g}$ soil)	P remain- ing in solution ($\mu\text{gP/ml}$)	P adsor- bed ($\mu\text{gP/g}$ soil)	P remain- ing in solution ($\mu\text{gP/ml}$)	P adsor- bed ($\mu\text{gP/g}$ soil)	P remain- ing in solution ($\mu\text{gP/ml}$)	P adsor- bed ($\mu\text{gP/g}$ soil)	P remain- ing in solution ($\mu\text{gP/ml}$)	P adsor- bed ($\mu\text{gP/g}$ soil)
Shaking										
Time (hr)										
$\frac{1}{4}$	38.6	570	37.4	630	34.8	660	36.0	700		
$\frac{1}{2}$	28.0	1,100	31.0	950	27.0	1,150	25.6	1,220	41.0	450
4	21.6	1,420	* -	-	21.0	1,450	17.7	1,615	34.0	800
8	20.2	1,490	17.25	1,637.5	19.5	1,525	14.3	1,785	33.0	850
24	12.0	1,900	11.5	1,925.0	11.7	1,915	12.0	1,900	33.0	850
48	9.9	2,005	10.0	2,000.0	9.7	2,015	9.9	2,005	30.0	1,000
96	9.25	2,037.5	6.6	2,170.0	9.25	2,037.5	7.2	2,140	15.0	1,750

* Sample lost during shaking

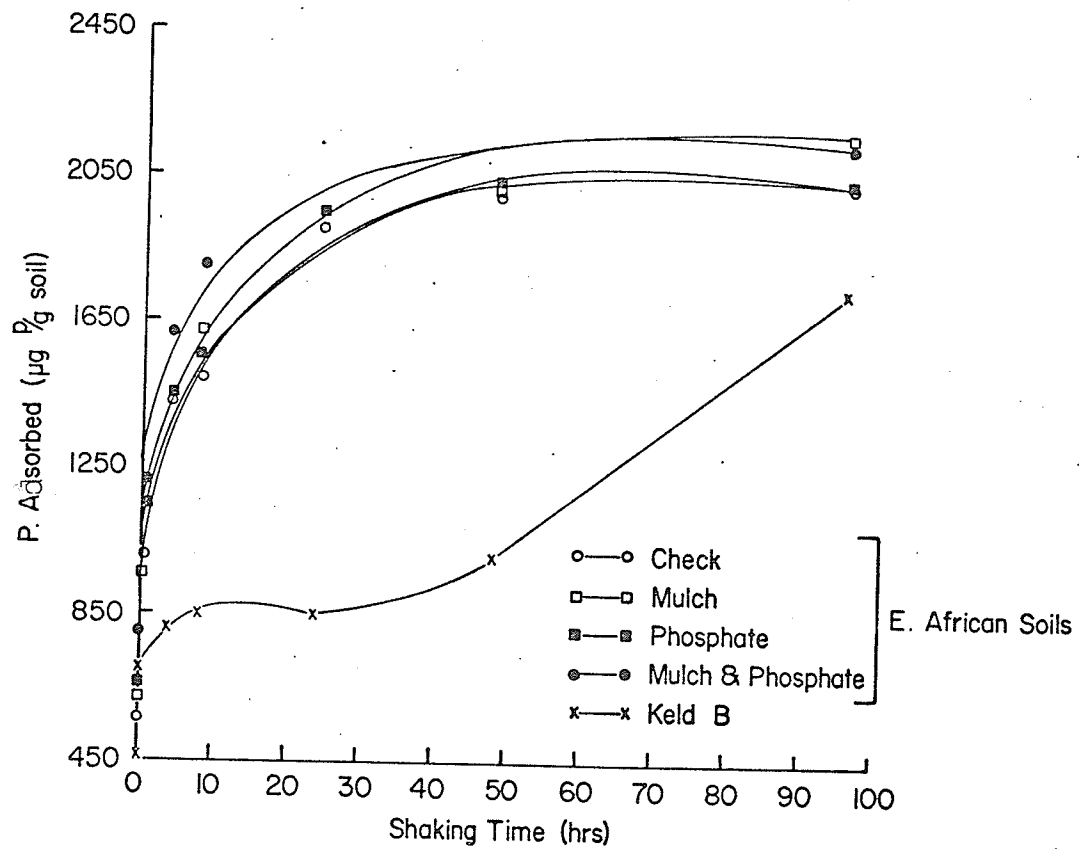


Figure 1. Rate of phosphorus adsorption or fixation by soils.

(b) The nature and form of phosphorus adsorbed on Soil Surfaces.

(1) Adsorption isotherm studies. The East African soils obtained from the 0 to 5 cm depth were bulked into mulched and unmulched samples. The bulked soils and the two Keld soils were used in this experiment. Five g soil samples, passed through a 2 mm sieve, were shaken in 50 ml of KH_2PO_4 solutions varying from 10 to 1,000 $\mu\text{gP/ml}$. The suspensions were shaken for 24 hours at $25 \pm 1^\circ\text{C}$. After shaking, the suspensions were centrifuged at 2,000 rpm for 10 minutes and filtered through a Whatman No. 42 filter paper. The amount of phosphorus remaining in the solutions was determined and the amount of phosphorus adsorbed calculated.

A twenty-four hour shaking period was selected since the previous study had indicated that the initial adsorption reaction was complete after 24 hours of shaking. The adsorption isotherms (Table VII and Figure 2) showed that the East African soils retained about the same amount of phosphorus when low concentrations of phosphorus was added. However, the mulched soil adsorbed more phosphorus than the unmulched soil when the phosphorus concentrations were increased. The differences in the amount of phosphorus adsorbed between mulched and unmulched soils increased with increases in the amount of phosphorus added. The Keld A soil, containing 9.00% organic matter, had an adsorption maximum pattern which was similar to the East African soil (Table VIII and Figure 2). The Keld B soil, containing 2.96% organic matter, adsorbed less phosphate than did the soil containing 9.00% organic matter. The high adsorptive

Table VII

Adsorption of phosphorus by Mulched and
Unmulched East African Soils

Soil P added ($\mu\text{gP/g soil}$)	Mulched			Unmulched		
	P remaining in solution ($\mu\text{gP/ml}$)(c)	P adsorbed ($\mu\text{gP/g soil}$) $\left(\frac{x}{m}\right)$	$\frac{c}{x} \times 10^3$	P remaining in solution ($\mu\text{gP/ml}$)(c)	P adsorbed ($\mu\text{gP/g soil}$) $\left(\frac{x}{m}\right)$	$\frac{c}{x} \times 10^3$
100	0.00	100.0	0.00	0.00	100.0	0.00
500	0.08	499.2	0.16	0.12	498.8	0.24
1,000	0.68	993.2	0.69	1.30	987.0	1.34
2,000	5.04	1,949.6	2.68	11.00	1,890.0	5.82
4,000	50.00	3,500.0	14.28	80.00	3,200.0	18.65
5,000	120.00	3,800.0	28.10	132.00	3,680.0	36.05
6,000	152.00	4,480.0	33.92	195.00	4,050.0	48.15
7,000	220.00	4,800.0	45.84	270.00	4,300.0	62.80
10,000	474.00	5,260.0	90.00	525.50	4,745.0	110.00

Table VIII

Adsorption of phosphorus by the Keld Soils

Soil	Keld A (9.00% O.M.)			Keld B (2.96% O.M.)			
	P added ($\mu\text{gP/g soil}$)	P remaining in solution ($\mu\text{gP/ml}(c)$)	P adsorbed ($\mu\text{gP/g soil}$) $\left(\frac{x}{m}\right)$	$\frac{c}{x} \times 10^3$	P remaining in solution ($\mu\text{gP/ml}(c)$)	P adsorbed ($\mu\text{gP/g soil}$) $\left(\frac{x}{m}\right)$	$\frac{c}{x} \times 10^3$
100		0.58	94.2	6.16	0.20	98.0	2.04
500		1.60	484.0	3.31	0.98	490.2	2.00
1,000		2.20	978.0	2.25	5.41	945.9	5.66
1,500		- *	-	-	19.00	1,310.0	14.51
2,000		8.50	1,915.0	4.26	41.60	1,584.0	25.63
4,000		75.00	3,250.0	23.08	159.10	2,409.0	66.04
5,000		137.00	3,630.00	37.74	225.00	2,750.0	85.46
7,000		250.00	4,500.0	55.56	343.00	3,570.0	97.08
10,000		450.00	5,500.0	81.82			

* sample lost during shaking

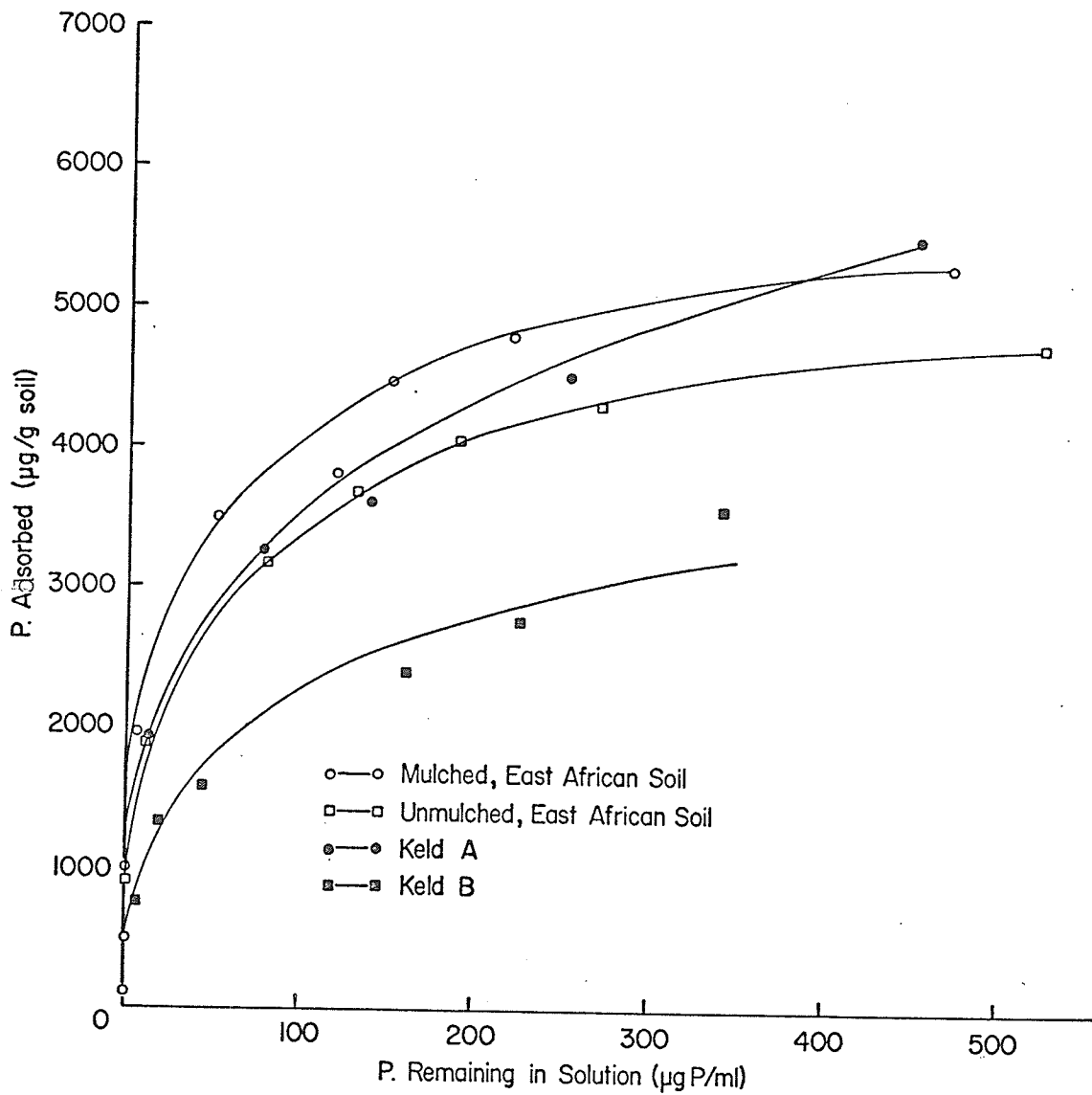


Figure 2. Phosphorus adsorption isotherms for the East African and Keld soils.

capacity of soil organic matter for phosphorus is extremely well demonstrated by these results.

The adsorption data in Tables VII and VIII were plotted according to the Langmuir equation (Figure 3). Phosphorus adsorption by the East African soils followed that described by the Langmuir equation up to a concentration of about 200 to 300 $\mu\text{gP/ml}$ remaining in solution. Phosphorus adsorption by the Keld A and Keld B soils followed that described by the Langmuir equation up to a concentration of 40 and 137 $\mu\text{gP/ml}$ remaining in solution, respectively. The Keld soil with the low organic matter content (Keld B), showed a second reaction which obeyed the Langmuir equation between 40 and 225 $\mu\text{gP/ml}$ remaining in solution. This second reaction could be a true adsorption or a precipitation reaction. The adsorption maxima for the various soils are also shown in Figure 3. The East African mulched soil showed a higher adsorption maximum than the East African unmulched soil. Similarly, the Keld A soil with the high organic matter content had a higher adsorption maximum than the Keld B, with the low organic matter content. The organic matter contents of the East African soils were found to be 12.96 and 8.39% for the mulched and unmulched soils, respectively.

Since the fixation of phosphorus by the soils could be described by the Langmuir equation, it is probable that an adsorption reaction was operative. However, it is possible that some precipitation reactions may have occurred. Therefore, the results presented do not exclude the possibility that

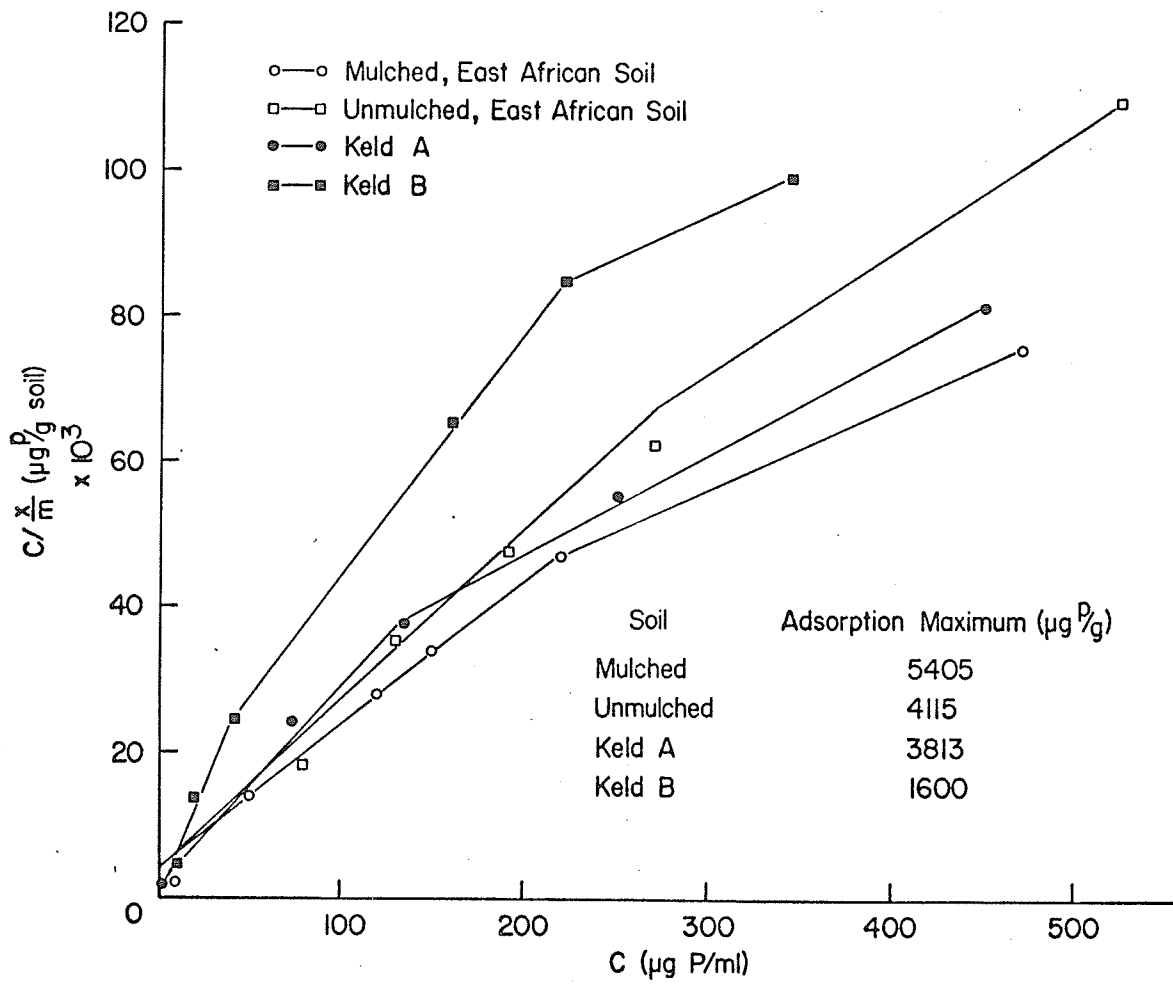


Figure 3. Langmuir plot of adsorption data for the East African and Keld soils.

inorganic phosphate compounds may have formed and that these compounds behaved in a manner that could be described by the Langmuir equation. The advantage of applying the Langmuir equation to phosphorus adsorption is that it provides a method for characterising the behaviour of the added phosphorus. Furthermore an adsorption maximum can be calculated which has been used in assessing phosphate fertilizer requirements of soils (40).

(2) Amounts of adsorbed phosphorus extractable by NH_4F , NaOH and H_2SO_4

The soils treated with varying amounts of phosphorus during the adsorption studies were saved and air-dried at $21 \pm 1^\circ\text{C}$. The dry soils were ground to pass through a 1 mm sieve.

The amount of phosphorus extracted by NH_4F , NaOH and H_2SO_4 was then determined as follows: A 0.5g sample of soil was placed into a 100 ml plastic centrifuge tube. The soils were then fractionated according to a modified Chang and Jackson (9) procedure as described in section III of Methods and Materials.

The results, corrected for initial phosphate levels, are presented in Table IX. Eighty to ninety percent of the phosphorus adsorbed by the soils was extracted by NH_4F and NaOH . Thus, most of the added phosphorus fixed by the soils was present as aluminum and iron phosphates. At low concentrations of added phosphorus, iron adsorbed as much phosphorus

as aluminum in the East African soils. A linear relationship between the amount of phosphorus held by aluminum and phosphorus adsorbed was observed (Figure 4). More than 80 percent of the adsorbed phosphorus was held by aluminum when 10,000 $\mu\text{gP/g}$ of soil was added. Iron held less than 10 percent of the phosphorus adsorbed by the East African soils when large amounts of phosphorus was added. The adsorbed phosphorus in the Keld A soil was more equally distributed between aluminum and iron bound forms than for the East African soils. However, as was noted for the East African soils, a linear relationship between aluminum bound phosphorus and amount of phosphorus adsorbed was observed. The greater retention of phosphate by iron in the Keld A soil as compared to the East African soils suggests that the Keld A soil had a greater number of adsorption sites associated with iron than did the East African soils.

It has been shown that the clay minerals provide sites for phosphate adsorption. The aluminum content of clays is much higher than the iron or calcium content. Therefore, aluminum would be expected to fix more phosphate than would iron or calcium.

The equal retention of phosphate by iron and aluminum at low phosphate concentrations may be attributed to the relative number of adsorption sites associated with aluminum and iron. It is possible that at low phosphorus concentrations the number of adsorption sites associated with iron were not limiting. Since the iron content of clay minerals is usually less than the aluminum content, the number of adsorption sites

Table IX Amounts of adsorbed Phosphorus Extracted by NH_4F , NaOH and H_2SO_4

Soil	Mulched				Unmulched				Keld A			
	P added ($\mu\text{gP/g}$)	P adsorbed ($\mu\text{gP/g}$)	NH_4F - Ext. P ($\mu\text{gP/g}$)	NaOH - Ext. P ($\mu\text{gP/g}$)	H_2SO_4 - Ext. P ($\mu\text{gP/g}$)	P adsorbed ($\mu\text{gP/g}$)	NH_4F - Ext. P ($\mu\text{gP/g}$)	NaOH - Ext. P ($\mu\text{gP/g}$)	H_2SO_4 - Ext. P ($\mu\text{gP/g}$)	P adsorbed ($\mu\text{gP/g}$)	NH_4F - Ext. P ($\mu\text{gP/g}$)	NaOH - Ext. P ($\mu\text{gP/g}$)
500	499	202	269	24	499	218	252	23	484	174	296	- *
1,000	993	522	432	33	987	578	366	37	978	554	516	-
2,000	1,950	1,322	570	35	1,890	1,258	556	46	1,915	849	1,076	-
5,000	3,800	2,842	761	53	3,680	3,058	613	64	3,250	1,099	866	-
10,000	5,260	4,492	481	80	4,745	4,018	315	85	5,500	2,589	866	-

* not determined

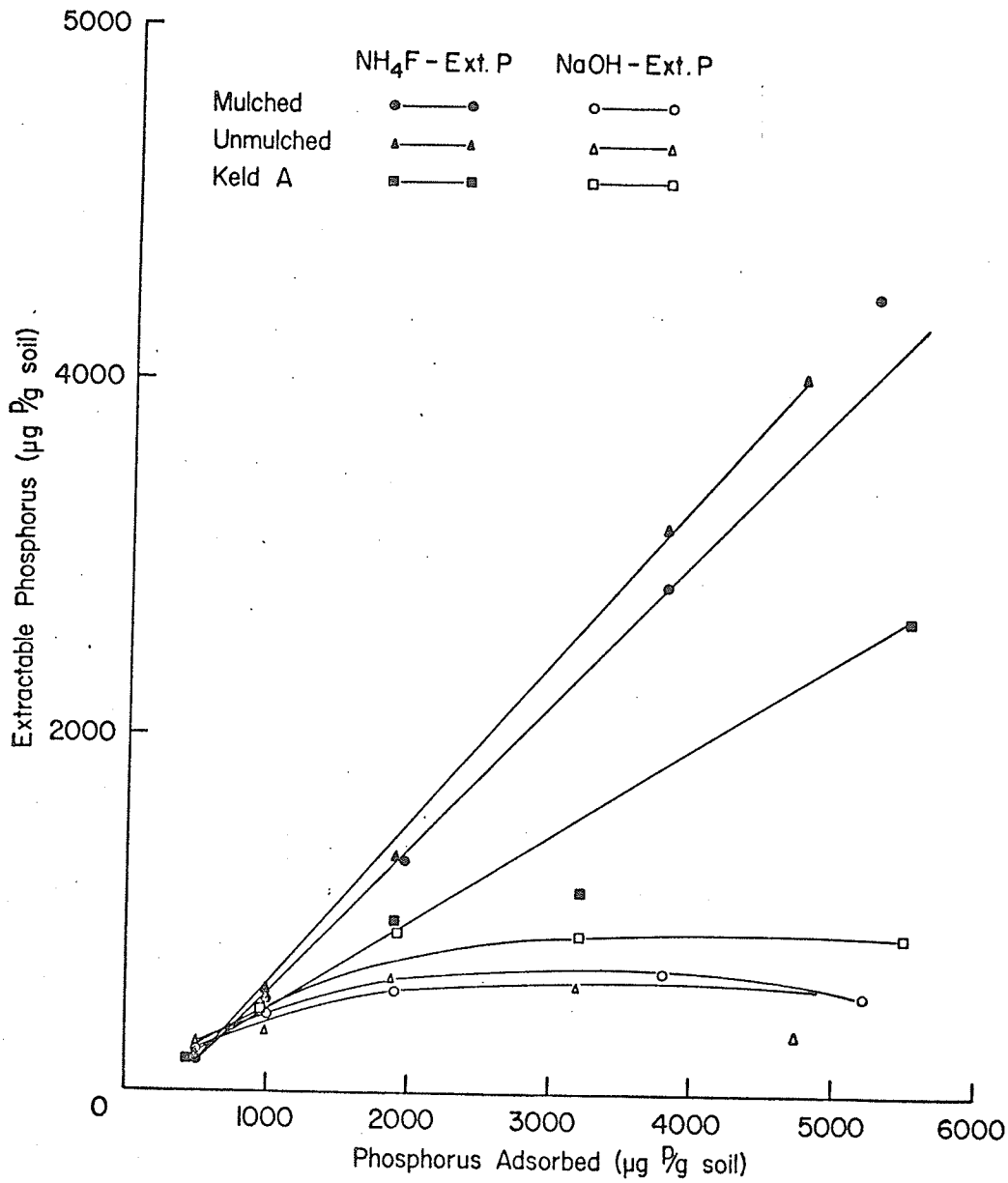


Figure 4. Amounts of adsorbed P extracted by NH_4F or NaOH .

associated with iron could be limiting adsorption of phosphorus at high phosphorus concentration. It is also possible that the affinity for phosphorus by adsorption sites associated with aluminum is greater than those associated with iron. Thus, aluminum would fix more phosphate than iron.

The phosphorus held by iron in the untreated soils was several fold higher than the phosphate held by aluminum (Table III). The East African soils (Table III) obtained from the plots which received annual dressings of phosphate at a rate of 22.4 kgP/ha for 15 years also contained larger amounts of NaOH extractable phosphate than NH_4F extractable phosphorus. Therefore, it is possible that a continuous shift from aluminum bound to iron bound phosphate takes place in the soils after the addition of phosphorus. This reaction has been found to occur in acid soils by several workers (1, 8, 12, 51, 56).

(c) Isotopic exchangeability of adsorbed phosphorus

(1) The amount and rate of exchangeability.

The exchangeability of the adsorbed phosphorus with ^{32}P was studied on the samples remaining from the previous adsorption studies. Only the East African soils were used in this study. 0.5 g samples were shaken with 49 ml of H_2O for 48 hours at $25 \pm 1^\circ\text{C}$. One ml of water containing 10 μc carrier-free ^{32}P was added to the soils and shaking continued for 4, 48 or 96 hours. The suspensions were centrifuged and filtered. ^{32}P and ^{31}P in the filtrates were determined

as previously outlined (page 20).

The amount of isotopically exchangeable phosphorus was calculated from the isotope-dilution law:

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

^{32}P (surface) was calculated from the activities (cpm) of the ^{32}P standard solution (10 μc ^{32}P in 50 ml H_2O) and ^{32}P remaining in solution as follows:

$$^{32}\text{P} \text{ (surface)} = \left\{ 1 - \frac{^{32}\text{P} \text{ remaining in solution (cpm)}}{^{32}\text{P} \text{ in standard solution (cpm)}} \right\}$$

There was a rapid initial exchange of the fixed phosphorus with ^{32}P , (Table X), particularly in the samples previously treated with large amounts of phosphorus. Equilibrium was usually attained with less than 48 hours of shaking for the mulched soils. The soils without mulch failed to reach equilibrium even after shaking for 96 hours. It is possible that the slow exchange of ^{32}P with the adsorbed phosphorus, noted between the 48 and 96 hours shaking periods, could have continued for a period of time greatly in excess of 96 hours.

The results also showed that phosphate adsorbed by these soils was only partially exchangeable with ^{32}P . As the amount of added phosphorus increased, the fraction of the adsorbed phosphate that was exchangeable with ^{32}P decreased. It is possible that some of the adsorbed phosphate became non-

Table X

Isotopic exchangeability of adsorbed phosphorus

Soil P Added ($\mu\text{gP/g}$)	P adsorbed ($\mu\text{gP/g}$)	—— Mulched ——			P added ($\mu\text{gP/g}$)	P adsorbed ($\mu\text{gP/g}$)	—— Unmulched ——		
		Exchangeable P ($\mu\text{g/g}$)					Exchangeable P ($\mu\text{g/g}$)		
		4 hr	48 hr	96 hr			4 hr	48 hr	96 hr
500	499	134	290	280	500	499	121	175	240
1,000	993	172	622	589	1,000	987	137	479	569
2,000	1,950	182	856	836	2,000	1,890	241	819	948
5,000	3,800	134	802	876	5,000	3,680	179	1,110	1,324
10,000	5,260	172	1,080	1,719	10,000	4,745	175	1,327	1,879

exchangeable as a result of drying or was fixed in a form not exchangeable with ^{32}P .

In a preliminary experiment conducted to determine the amount of surface phosphorus initially present in these soils, it was observed that almost all the ^{32}P (carrier-free) disappeared from the equilibrating solutions. The ^{31}P content of the extracts was extremely low and could not be measured. Only 7.3 and 13.7 percent of the added ^{32}P remained in the extracts for the unmulched and mulched soils, respectively. Since it was not possible to measure the ^{31}P content in the extracts, it was not possible to calculate the exchangeable phosphorus content of the untreated soils.

(2) Exchangeability of NH_4F , NaOH and H_2SO_4 extractable phosphorus

The soils used for studying the exchangeability of adsorbed phosphorus in the previous experiment were saved after equilibration with ^{32}P .

Only the soils initially treated with phosphorus solutions containing 1,000 and 5,000 $\mu\text{gP/ml}$ and equilibrated with ^{32}P for 48 hours were studied. After the equilibration with ^{32}P , the soils were fractionated by a modified Chang and Jackson (9) procedure as described previously. The ^{32}P contents of the soil extracts were then determined.

It was assumed that the ^{32}P recovered in the NH_4F , NaOH and H_2SO_4 extracts represented the total ^{32}P in the soils. Table XI shows the percent ^{32}P recovered by NH_4F , NaOH and H_2SO_4 extraction as a percentage of the total

Table XI Recovery of ^{32}P and ^{31}P by NH_4F , NaOH and H_2SO_4 extraction (%)

Soil	P added ($\mu\text{gP/g}$)	P adsorbed ($\mu\text{gP/g}$)	Exch. P ($\mu\text{gP/g}$)	^{32}P			^{31}P		
				NH_4F Ext. (%)	NaOH Ext. (%)	H_2SO_4 Ext. (%)	NH_4F Ext. (%)	NaOH Ext. (%)	H_2SO_4 Ext. (%)
Mulched	1,000	993	622	59.7	36.2	4.1	52.6	43.5	3.3
	5,000	3,800	802	75.0	22.6	2.4	74.8	20.0	1.4
Un- mulched	1,000	987	479	57.2	39.2	3.6	58.6	37.1	3.8
	5,000	3,680	1,110	71.8	26.6	1.6	83.1	16.7	1.7
		Mean		65.92	31.15	2.93	67.28	29.32	2.55

^{32}P recovered. At low concentrations of phosphorus, about 60 and 40 percent of the total ^{32}P recovered was held by aluminum and iron, respectively. At high phosphorus concentrations about 70 to 75 percent and 22 and 30 percent of the ^{32}P recovered was held by aluminum and iron, respectively. Less than 5 percent of the ^{32}P recovered from the soils was held by calcium. The percent of ^{32}P recovered in the aluminum, iron and calcium phosphate fractions was related to the amounts of phosphorus adsorbed or held by these cations. The mean percentages of adsorbed phosphorus (^{31}P) extracted by NH_4F , NaOH and H_2SO_4 from these soils were 67.28, 29.32 and 2.55%, respectively (values are percentages of the total amount extracted by NH_4F , NaOH and H_2SO_4). The mean percentage of ^{32}P recovered by NH_4F , NaOH and H_2SO_4 extraction was 65.92, 31.15 and 2.93%, respectively. Thus it appears that the phosphate adsorbed by the various cations were equally exchangeable.

(d) The effect of humic acid on phosphorus fixation by soils.

Humic acid was extracted from the organic mulch, described in Table II, as outlined by Weir and Soper (66). Ten g of mulch, passed through a 2 mm sieve, was treated for six hours with 100 ml of 0.1 N NaOH in a 250 ml centrifuge tube. The suspension was centrifuged and the supernatant acidified to a pH of 1.5 by the addition of 1:1 HCl . The acidified solution was left to stand for 10 minutes. The precipitated humic acid was then centrifuged and washed with

water. After several washings with water, the suspension of humic acid was treated slowly with 2 N NaOH until the pH was about 7.0 and evaporated to dryness at 70°C. The humic acid was finely ground.

Five g of soil was placed in a 100 ml plastic centrifuge tube and 0, 5, 10, 20, 50, 75 or 100 mg of humic acid added. The materials were mixed thoroughly and 2 ml of water added to wet the soils to field moisture content. Two drops of chloroform were added and the tubes stoppered. The soil - humic acid mixture was incubated for one week at $25 \pm 1^\circ\text{C}$. The unmulched East African and Keld A soils were studied.

After incubation, the soils were shaken with 50 ml of 100 ppm P solution for 24 hours at $25 \pm 1^\circ\text{C}$. After shaking, the suspensions were left to stand for 15 minutes and the pH of the supernatant measured. The suspensions were centrifuged and the phosphorus content of the extracts determined.

The increases in pH for each level of humic acid added was usually higher for the Keld A soil than for the East African soil (Table XII). The pH of the soil increased only slightly with increases in the amount of humic acid added. The pH increased by 0.35 and 0.49 for the East African and Keld A soils, respectively, when 100 mg of humic acid was added. However, the amount of phosphorus remaining in solution increased two fold for both soils when 100 mg of humic acid was added. Phosphorus fixation by the soils was reduced by 12.4 and 90.1 $\mu\text{gP/g}$ soil for the East African and Keld A soils, respectively. The East African soil adsorbed more

Table XII

Effect of a Humic acid on the pH and
phosphorus fixed by soils

Soil	Unmulched			Keld A		
	pH	P remaining in solution ($\mu\text{gP/g}$)	P adsorbed ($\mu\text{gP/g}$)	pH	P remaining in solution ($\mu\text{gP/g}$)	P adsorbed ($\mu\text{gP/g}$)
Humic Acid (mg)						
0	4.69	.94	990.6	3.99	11.60	884.0
5	4.71	.98	990.2	4.02	13.61	863.9
10	4.75	.98	990.2	4.05	13.62	863.8
20	4.77	1.02	989.8	4.11	14.80	852.0
50	4.85	1.20	988.0	4.26	16.43	835.7
75	4.92	1.44	985.6	4.36	17.44	825.6
100	5.04	2.18	978.2	4.48	20.61	793.9

phosphate than the Keld A soil. These results indicate that humic acid can reduce the amount of phosphate fixed by these soils and increase the amount of phosphorus remaining in solution. It is possible that the mechanism whereby organic acids block the phosphorus fixation sites (54) on soil colloids was operative. The results also suggest that the use of organic mulches may reduce phosphate fixation by acid soils. In the process of mulch decomposition humic substances are released which may block phosphorus adsorption sites.

Solubility of native and applied phosphates in acid soils

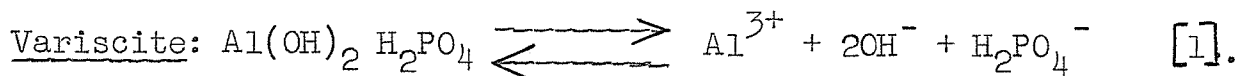
The preceding studies showed that nearly all of the inorganic phosphate in the soils studied was held by aluminum and iron. A determination of the apparent solubility product of a phosphate compound present in the soil is another method of determining if a particular compound exists. To confirm the existence of such a compound in soils, the solubility of phosphorus in the soil is related to the solubility of a known pure phosphate compound. Information on the availability of fertilizer and soil phosphate is also obtained.

It is proposed that in acid soils, variscite ($\text{AlPO}_4 \cdot 2\text{H}_2\text{O}$) and strengite ($\text{FePO}_4 \cdot 2\text{H}_2\text{O}$) are the principal crystalline phosphate compounds formed (10,14). Solubilities of these compounds in pure systems have been studied.

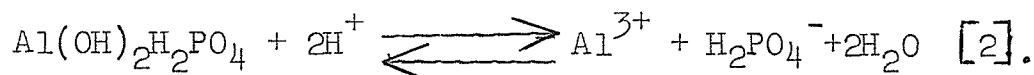
The objective of the study reported here was to gain further information on the nature of native and applied phosphate in these soils.

The composition of variscite and strengite can be written as follows (14): $\text{Al}(\text{OH})_2 \text{H}_2\text{PO}_4$ and $\text{Fe}(\text{OH})_2 \text{H}_2\text{PO}_4$.

The two compounds dissolve according to the equations:

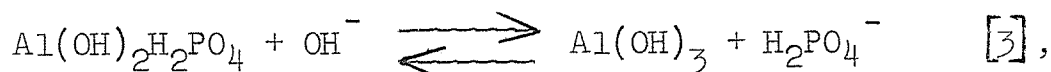


In suspensions with pH values less than 4.0, the suspensions approach equilibrium according to the reaction:

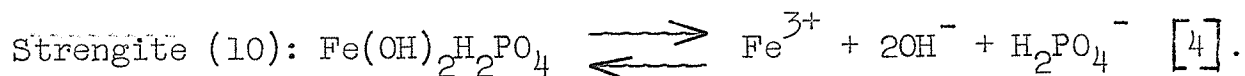


and all the products are soluble. In a system with pH values

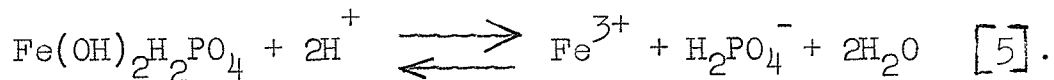
greater than 4.0, there is a downward shift in pH as a result of the reaction:



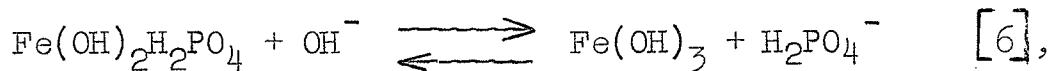
in which Al(OH)_3 , gibbsite, remains as a solid phase.



In suspensions with pH values less than 2.75, the system approaches equilibrium according to the reaction:



In suspensions with pH values greater than 2.75, there is a downward shift of pH as a result of the reaction:



in which Fe(OH)_3 , goethite, remains as a solid phase.

Calculations of the solubility products of variscite and strengite become possible using equations [1] and [4].

By taking the negative logarithms of all ionic species in equations [1] and [4] the following equations were obtained:

$$\text{pK} = \text{pAl}^{3+} + \text{pH}_2\text{PO}_4^- + 2\text{pOH}^- \text{ for variscite} \quad [7].$$

$$\text{pK} = \text{pFe}^{3+} + \text{pH}_2\text{PO}_4^- + 2\text{pOH}^- \text{ for strengite} \quad [8].$$

The values for pH_2PO_4^- , pAl^{3+} and pFe^{3+} can be determined from their concentrations in solution. The activit-

ies of the various ions in solution were obtained from the following relationships:

Phosphate: Since the pH of the systems varied from 3.61 to 7.28, the total concentration of phosphorus in solution,

$$[P_T] = [H_2PO_4] + [HPO_4] \quad [9].$$

Substitution of activities for concentrations results in the following equation

$$[P_T] = \frac{(H_2PO_4^-)}{f^-} + \frac{(HPO_4^{2-})}{f^{2-}} \quad [10],$$

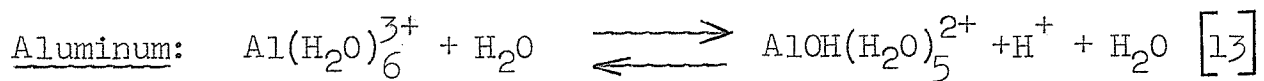
where f^- and f^{2-} represents the activity coefficients of the $H_2PO_4^-$ and HPO_4^{2-} ions, respectively. The brackets and paranthesis represent concentrations and activities, respectively. The (HPO_4^{2-}) can be expressed as follows:

$$\frac{K_2 (H_2PO_4^-)}{(H^+)} \quad [11].$$

Where K_2 represents the second dissociation constant of phosphoric acid ($pK_2 = 7.22$ (52)).

Combining equation [10] and [11] and solving for the $(H_2PO_4^-)$ results in the following equation:

$$(H_2PO_4^-) = \frac{[P_T]}{\frac{1}{f^-} + \frac{K_2}{f^{2-} \cdot H}} \quad [12].$$



From equation 13, the total aluminum concentration in solution,

$$[\text{Al}_T] = [\text{Al}^{3+}] + [\text{AlOH}^{2+}] \quad [14]$$

Substitution of activities for concentrations results in the following equation

$$[\text{Al}_T] = \frac{(\text{Al}^{3+})}{f^-} + \frac{(\text{AlOH}^{2+})}{f^{2-}} \quad [15]$$

Where f^- and f^{2-} are the activity coefficients for Al^{3+} and AlOH^{2+} , respectively.

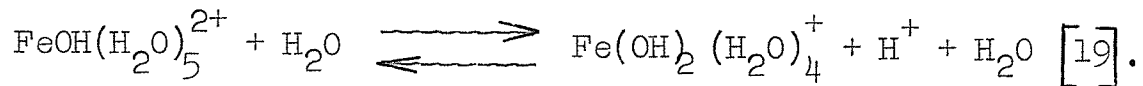
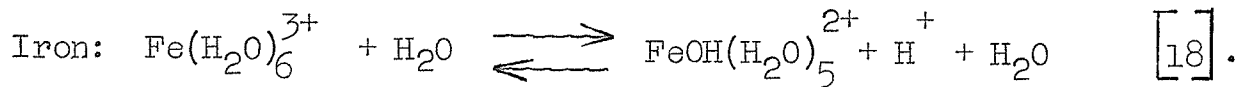
The (AlOH^{2+}) can be expressed as follows:

$$(\text{AlOH}^{2+}) = \frac{K (\text{Al}^{3+})}{(\text{H}^+)} \quad [16]$$

Combining equations [15] and [16] and solving for (Al^{3+}) gives:

$$(\text{Al}^{3+}) = \frac{[\text{Al}_T]}{\frac{1}{f^-} + \frac{K}{f^{2-} \cdot H}} \quad [17]$$

Where $K = 1.05 \times 10^{-5}$ (48)



From equations [18] and [19] the total Fe concentration,

$$[\text{Fe}_T] = [\text{Fe}^{3+}] + [\text{FeOH}^{2+}] + [\text{Fe}(\text{OH})_2^+]. \quad [20].$$

Substitution of activities for concentrations results in the following equation:

$$[\text{Fe}_T] = \frac{(\text{Fe}^{3+})}{f^-} + \frac{(\text{FeOH}^{2+})}{f^{2-}} + \frac{(\text{Fe}(\text{OH})_2^+)}{f^{3-}} \quad [21].$$

Where f^- , f^{2-} and f^{3-} are activity coefficients for Fe^{3+} , FeOH^{2+} and $\text{Fe}(\text{OH})_2^+$, respectively.

The (FeOH^{2+}) and $(\text{Fe}(\text{OH})_2^+)$ can be written as:

$$(\text{FeOH}^{2+}) = \frac{K_1 (\text{Fe}^{3+})}{(\text{H}^+)} \quad [22]$$

and

$$(\text{Fe}(\text{OH})_2^+) = \frac{K_1 K_2 (\text{Fe}^{3+})}{(\text{H}^+)^2} \quad [23], \text{ respectively.}$$

Combining equations [21], [22] and [23], and solving for the (Fe^{3+}) gives:

$$(\text{Fe}^{3+}) = \frac{[\text{Fe}_T]}{f^- + \frac{K_1}{f^{2-} \cdot H} + \frac{K_1 K_2}{f^{3-} \cdot (H)^2}} \quad [24]$$

$$\text{Where } K_1 = 8.1 \times 10^{-4} \text{ and } K_2 = 5.50 \times 10^{-4} \quad (52)$$

Values for the activity coefficients of the various ions were calculated from the simplified Debye - Huckel equation:

$$\log f_i = \frac{-Az^2 \sqrt{I}}{1 + \sqrt{I}} \quad [25]$$

where A = a constant equal to 0.509 when water is used as the solvent, z the valency of the ion and I the ionic strength. I is defined by:

$$I = 1/2 \sum C_i z_i^2 \quad [26]$$

where C_i represents the molar concentration of the ion and z_i the valency of the ion. The concentrations of Ca^{2+} plus Mg^{2+} in solution determined by titration with EDTA (59) was used to calculate the ionic strength of the solution. A monovalent anion concentration equivalent to the concentration of Ca plus Mg found in the solution was used in the calculation of I .

The ionic concentrations and activities of phosphate and calcium plus magnesium in solution were determined as

described by Racz and Soper (43).

(a) Native soil phosphate. The soils described in Table II were used. A 1:2 soil : solution ratio was used. Preliminary studies showed that, at higher soil : solution ratios, the phosphorus concentration in the extracts was very low and difficult to determine. A soil : solution ratio lower than 1:2 was avoided due to the limited supply of soil.

Fifty g of soil, passed through a 2 mm sieve, was shaken in 100 ml of 0.01 M CaCl_2 solution for 96 hours at $25 \pm 1^\circ\text{C}$. One ml of chloroform was added to inhibit microbial activity during equilibration. Thirty minutes after removal from a shaker, the pH of the suspensions was measured. The solutions were then centrifuged at 2,000 rpm for 10 minutes and filtered through Whatman filter paper No. 42. The aluminum and iron concentrations of the filtrate was determined by the use of an Atomic Absorption Spectrophotometer (41). The phosphorus concentrations of the filtrates was determined by the phosphomolybdo blue color method with chlorostannous reductant reagent (26).

Table XIII(a) shows the ionic concentrations and activities, and aluminum, iron and phosphate potentials of the soil extracts. The pH of the extracts from the mulched East African soils were higher than the pH of the extracts from the soils not mulched. There was no difference in phosphate

Table XIII(a)

Ionic concentrations and activities, and aluminum,
iron and phosphate potentials of soil extracts

Soil	pH	P Mx10 ⁶	Fe Mx10 ⁶	Al Mx10 ⁴	p(H ₂ PO ₄ ⁻)	p(Fe ³⁺)	p(Al ³⁺)	pH-	pH-	p(H ₂ PO ₄ ⁻)	p(H ₂ PO ₄ ⁻)
								1/3 p (Fe ³⁺)	1/3 p (Al ³⁺)	1/3 p (Fe ³⁺)	1/3 p (Al ³⁺)
Mulched	4.56	4.03	4.30	3.33	5.49	8.24	4.08	1.81	3.20	8.24	6.85
Unmulched	4.39	4.03	3.90	3.04	5.50	7.76	3.79	1.79	3.13	8.09	6.76
Keld A	4.33	6.93	64.80	5.75	5.26	6.58	3.75	2.14	3.08	7.45	6.51
Keld B	3.61	4.03	6.80	3.20	5.39	6.48	3.20	1.46	2.55	7.54	6.46

Table XIII(b)

Solubility product values for soil extracts

Soil	pKsp FePO ₄ ·2H ₂ O	pKsp AlPO ₄ ·2H ₂ O
Mulched	32.61	28.45
Unmulched	32.48	28.51
Keld A	31.12	28.25
Keld B	32.63	29.37

concentrations in the extracts of the East African soils. The concentrations of aluminum and iron in the extracts increased with increased organic matter content and pH of the soils. The Manitoban soils showed trends similar to that of the East African soils. The Keld A soil, with the high organic matter content and pH, had a high concentration of phosphorus, aluminum and iron in the extracts. The results indicated that as organic matter content and pH of the Keld soil increased, the solubility of the aluminum and iron phosphate compounds in the soil also increased (Figures 5 and 6). The high concentrations of aluminum and iron in the extracts of soils with high organic matter contents may be due to formation of water soluble organo-metallic complexes (54).

With the exception of the Keld A soil in Figure 5 the solubility values for all soils were within the aluminum and iron hydroxide bands (Figures 5 and 6). This suggests a possibility of a coexistence of phosphate compounds with these metals and with their hydroxides.

It has been shown that variscite and strengite probably do not exist in temperate soils, regardless of their acidity (7). The Keld B soil, however, had a pK_{sp} value of 29.37 for variscite (Table XIII(b)). This value is very close to 29.5 found as the pK_{sp} value for a variscite crystal species (13). Therefore, it is possible that variscite existed in this soil.

The East African soils and Keld A behaved as though they were supersaturated with respect to variscite.

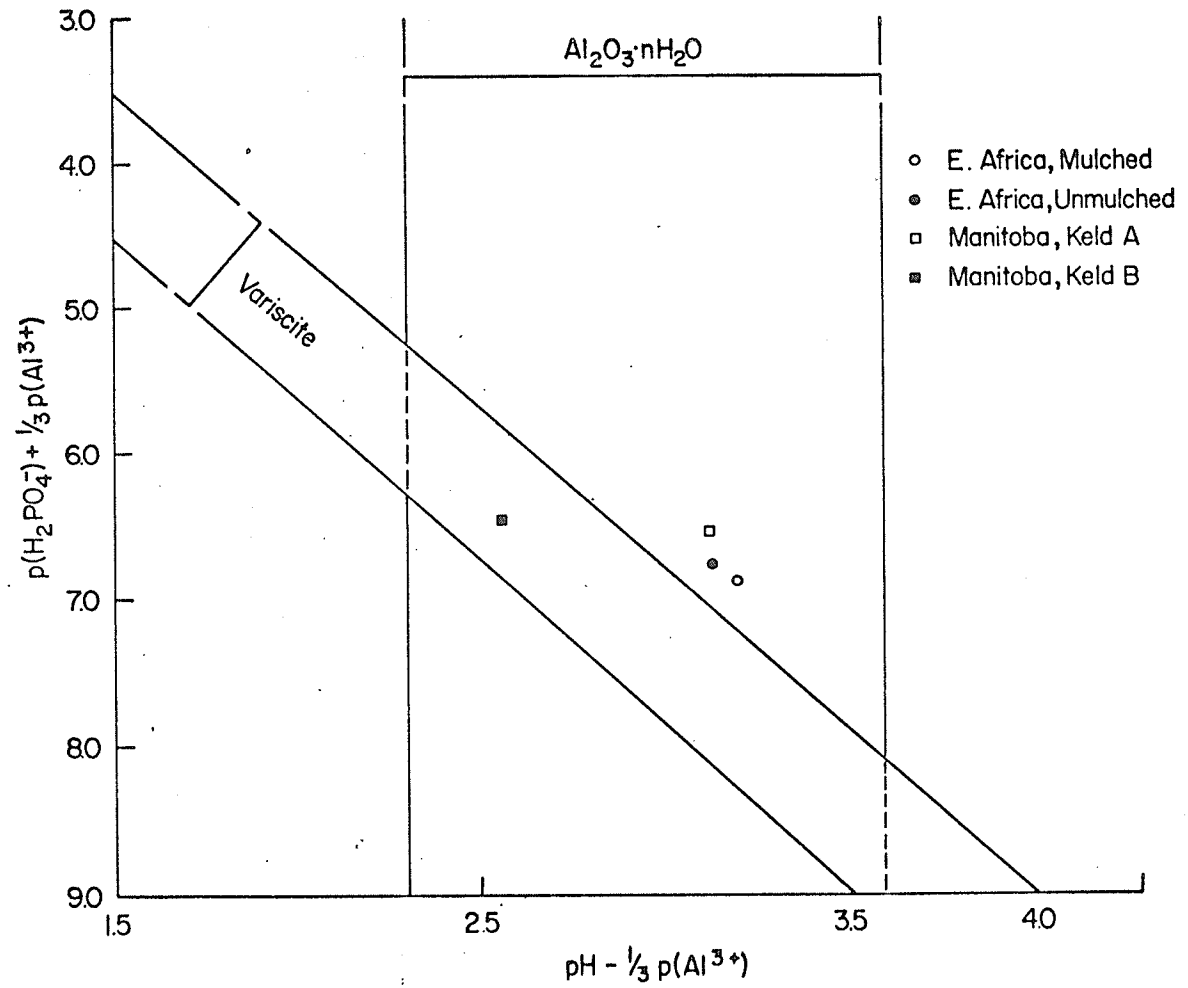


Figure 5. Solubility diagram for variscite showing the aluminum and phosphate potentials of soil extracts.

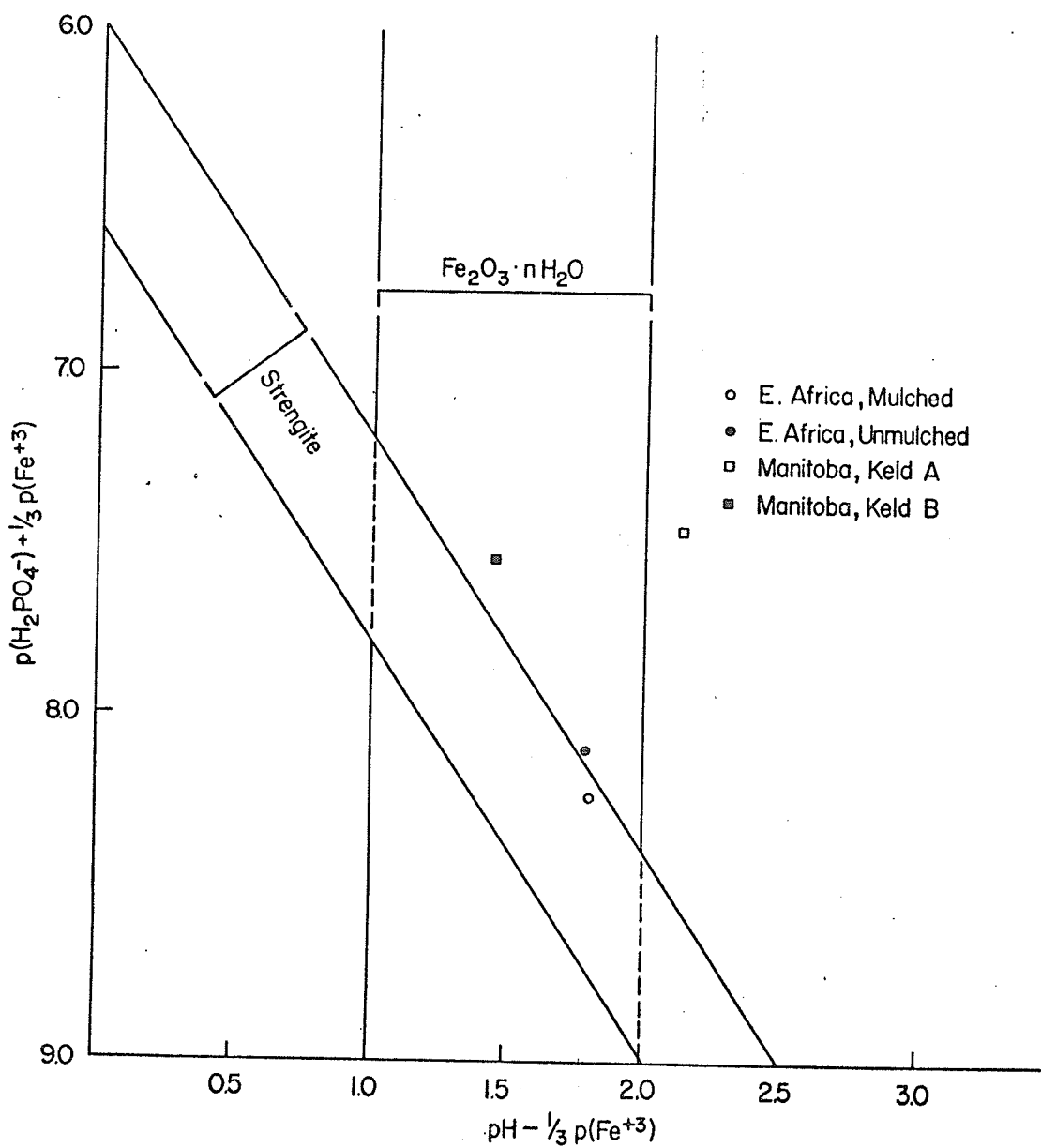


Figure 6. Solubility diagram for strengite showing the iron and phosphate potentials of soil extracts.

All four soils studied showed greater solubility values than that of strengite and thus the soils appeared to be supersaturated with respect to strengite.

(b) Applied phosphorus. (i) The solubility of added phosphorus in the two East African and Keld B soils (Table II), were determined by equilibrating 5g soil with various amounts of phosphorus. Concentrations of phosphorus approximating those which occur in soils near a phosphorus fertilizer pellet were selected (43). One tenth, 0.2, 0.4 and 0.6 g of KH_2PO_4 and K_2HPO_4 were added to 5 g of soil in 50 ml of 0.01 M CaCl_2 and equilibrated by shaking for 120 hours at $25 \pm 1^\circ\text{C}$. One ml of chloroform was added to inhibit microbial activity during equilibration. A CaCl_2 solution rather than water was used as a preliminary study showed that soil suspensions shaken with water for 120 hours would become highly deflocculated. It was impossible to get clear extracts from suspensions without the use of a rigorous flocculant. The pH of the suspensions were measured and the suspensions centrifuged at 2,000 rpm for 10 minutes. The supernatants were filtered, and their phosphorus, aluminum, iron and calcium plus magnesium contents determined as outlined previously.

A second study on the solubility of applied phosphorus consisted of incubating soils with various amounts of added phosphorus for various periods of time. Five g of soil was placed in 100 ml plastic centrifuge tubes. One tenth, 0.2,

0.4 or 0.6 g of $\text{NH}_4\text{H}_2\text{PO}_4$ was added and mixed thoroughly. Two ml of water was added to bring the moisture content of the soils to about 40 percent (F.C.). One ml of chloroform was added to inhibit microbial activity during incubation. The soils were incubated at $25 \pm 1^\circ\text{C}$ for zero, one and two months. At the end of each incubation period, the soils were extracted with 48 ml of 0.01 M CaCl_2 . The extraction consisted of shaking the soil suspensions for 24 hours at $25 \pm 1^\circ\text{C}$. The pH of the suspensions were measured and the suspensions centrifuged and filtered. The phosphorus and calcium plus magnesium concentrations of the filtrates were determined.

(ii) The pH of the soil extracts usually decreased slightly with increased amounts of added KH_2PO_4 in all soils (Table XIV). The phosphorus concentrations in the soil extracts increased with increased amounts of KH_2PO_4 added. The phosphorus concentrations in the extracts of the East African soils varied slightly within each level of KH_2PO_4 added. The phosphorus concentrations of the extracts of the Keld B soil were greater than that of the East African soils. The concentrations of aluminum and iron in the extracts of soils treated with KH_2PO_4 , were variable. However, the concentrations of iron and aluminum in the extracts of the mulched soils was usually higher than that from the unmulched soil. The extracts from the Keld B soil contained higher concentrations of aluminum and iron than the extracts obtained from the East African soils. There was a general tendency for the aluminum and iron concentrations in the extracts to increase with increased amounts of added KH_2PO_4 when 0.2 and/or 0.4 g or less was added. The concentrations

Table XIV Ionic concentrations and activities, and aluminum, iron and phosphate potentials obtained by equilibrating soils with KH_2PO_4

Soil	KH_2PO_4 added (g)	pH	P $\text{M} \times 10^2$	Fe $\text{M} \times 10^6$	Al $\text{M} \times 10^5$	$\text{p}(\text{H}_2\text{PO}_4^-)$	pH-		$\text{p}(\text{H}_2\text{PO}_4^-)$		$\text{p}(\text{H}_2\text{PO}_4^-)$	
							$1/3_p$ (Fe^{3+})	$1/3_p$ (Al^{3+})	$1/3_p$ (Fe^{3+})	$1/3_p$ (Al^{3+})	$1/3_p$ (Fe^{3+})	$1/3_p$ (Al^{3+})
Mulched	0.1	4.99	0.049	0.806	0.85	3.36	3.27	1.92	1.72	3.07	6.63	5.28
	0.2	4.91	0.625	0.627	1.85	2.23	3.25	1.80	1.66	3.11	5.48	4.03
	0.4	4.81	2.865	1.522	1.85	1.61	3.05	1.82	1.76	2.99	4.66	3.43
	0.6	4.80	5.805	1.074	1.48	1.32	3.10	1.89	1.70	2.91	4.42	3.21
Unmulched	0.1	4.98	0.057	0.448	0.74	3.32	3.35	1.93	1.63	3.05	6.67	5.25
	0.2	4.94	0.722	0.537	0.74	2.19	3.33	1.94	1.61	3.00	5.62	5.13
	0.4	4.93	2.839	0.358	2.22	1.61	3.38	1.79	1.59	3.14	4.99	3.40
	0.6	4.89	5.805	0.448	3.14	1.30	3.36	1.47	1.53	3.42	4.66	2.77
Keld (B)	0.1	4.03	0.113	0.358	0.22	2.95	2.75	2.08	1.28	1.95	5.70	5.03
	0.2	3.96	1.131	0.711	2.63	1.95	2.65	1.74	1.31	2.22	4.60	3.69
	0.4	3.91	3.613	1.701	3.26	1.44	2.49	1.75	1.42	2.16	3.93	3.60
	0.6	3.90	6.500	2.417	5.55	1.62	2.48	1.71	1.42	2.19	4.10	3.33

of iron and aluminum usually decreased when more than 0.4 g KH_2PO_4 was added to the East African soils.

Equilibration of the soils with amounts of KH_2PO_4 corresponding to those which may occur in a fertilizer pellet zone, resulted in high phosphorus concentrations in the extracts. Therefore, the soils appeared to be highly supersaturated with respect to variscite and strengite (Figures 7 and 8). The solubility values for the East African soils were within the aluminum and iron hydroxide bands. As was found for native phosphorus, the phosphate compounds formed when KH_2PO_4 was added probably coexisted with the hydroxides of aluminum and iron. It is interesting to note that when the values on the variscite and strengite diagrams are connected, the resulting curves have shapes similar to those reported by Chakavarti and Talibudeen (7). These workers treated Kaolinite with 10^{-5} to 10^{-1} M KH_2PO_4 for $4\frac{1}{2}$ months. They found that the optimum phosphate concentration for variscite at pH 3.0 to 3.5 was 10^{-4} to 10^{-5} M. Clay minerals treated with 10^{-5} M KH_2PO_4 solution and incubated for 9 months at pH values of 3.0 to 8.0 showed that variscite formed only between pH values of 4.3 and 5.5.

It has been shown (23) that the first step in the reaction of soluble phosphorus with the various cations occurs on the surfaces of the solid phases with which the phosphate comes in contact. Therefore, it is not the relative ionic activities of aluminum, iron and calcium plus magnesium in the solution but rather the specific surface area of the solid phases associated with aluminum, iron and calcium plus magnesium ions that determines the relative amounts and kinds of

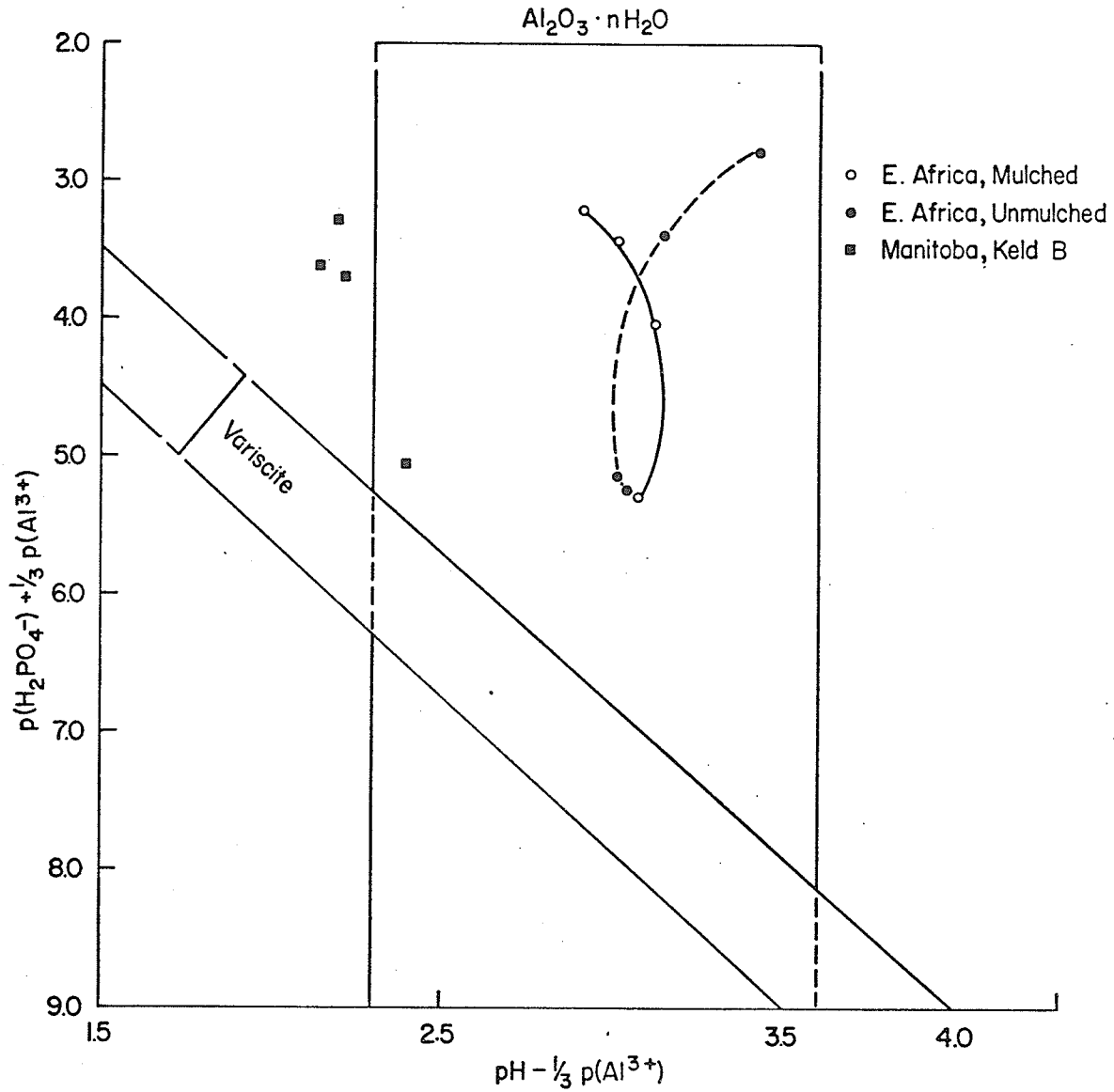


Figure 7. Solubility diagram for variscite showing the aluminum and phosphate potentials obtained by equilibrating soils with KH_2PO_4 .

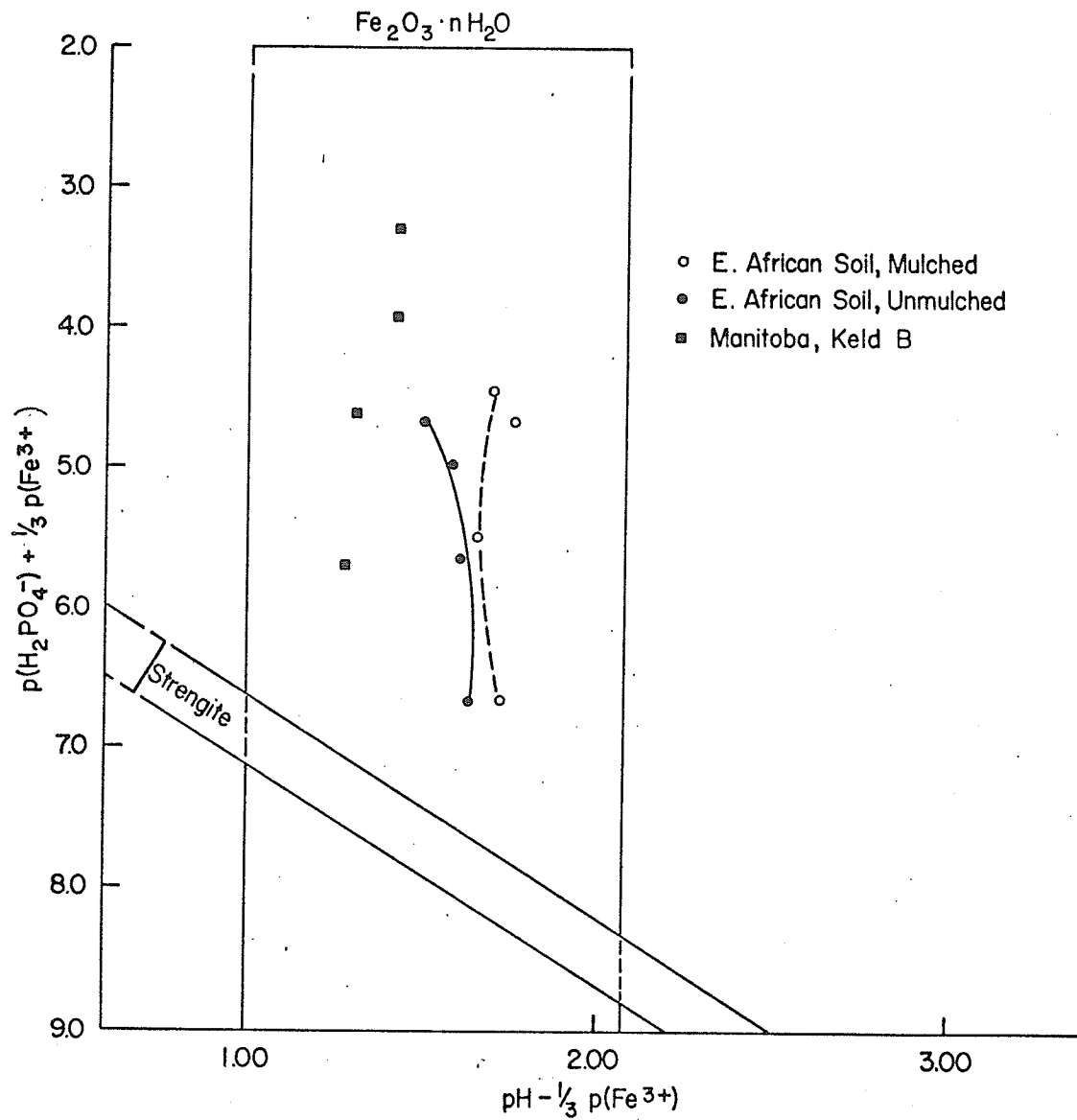


Figure 8. Solubility diagram for strengite showing the iron and phosphate potentials obtained by equilibrating soils with KH_2PO_4 .

phosphate formed. In the second step of phosphorus reaction with soil cations, however, ionic activity becomes appreciable, and the principle of solubility products governs the amount and kinds of phosphate formed. The time required for reaction to go from the first step to the second reaction will depend on soil characteristics, equilibration conditions, concentrations of phosphorus and the kind of phosphate used. Thus, the difference between the solubility values obtained and those of the pure phosphates may be due to a variety of reasons.

The calcium plus magnesium concentrations in the soil extracts did not consistently vary with increases in amounts of KH_2PO_4 added (Table XV). The concentration of Ca + Mg in the extracts from the Manitoba soil were higher than those obtained for the East African soils. Figure 9 shows that the solubility of the phosphate added to the East African soils approximated that of hydroxyapatite (HA) - $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ and dicalcium phosphate dihydrate (DCPD) - $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ when 0.1 and 0.2 g of KH_2PO_4 were added, respectively. When more than 0.2 g of KH_2PO_4 was added to the East African soils, the phosphate compounds formed were more soluble than DCPD. The solubility of phosphorus in the Keld B soil did not approximate that of any of the calcium phosphates and thus it is doubtful if the phosphate (KH_2PO_4) added to this soil reacted with calcium.

The pH of the soil suspensions increased with increasing amounts of K_2HPO_4 added (Table XVI). The phosphorus concentrations of the soil extracts increased whereas calcium plus magnesium concentrations decreased with increased

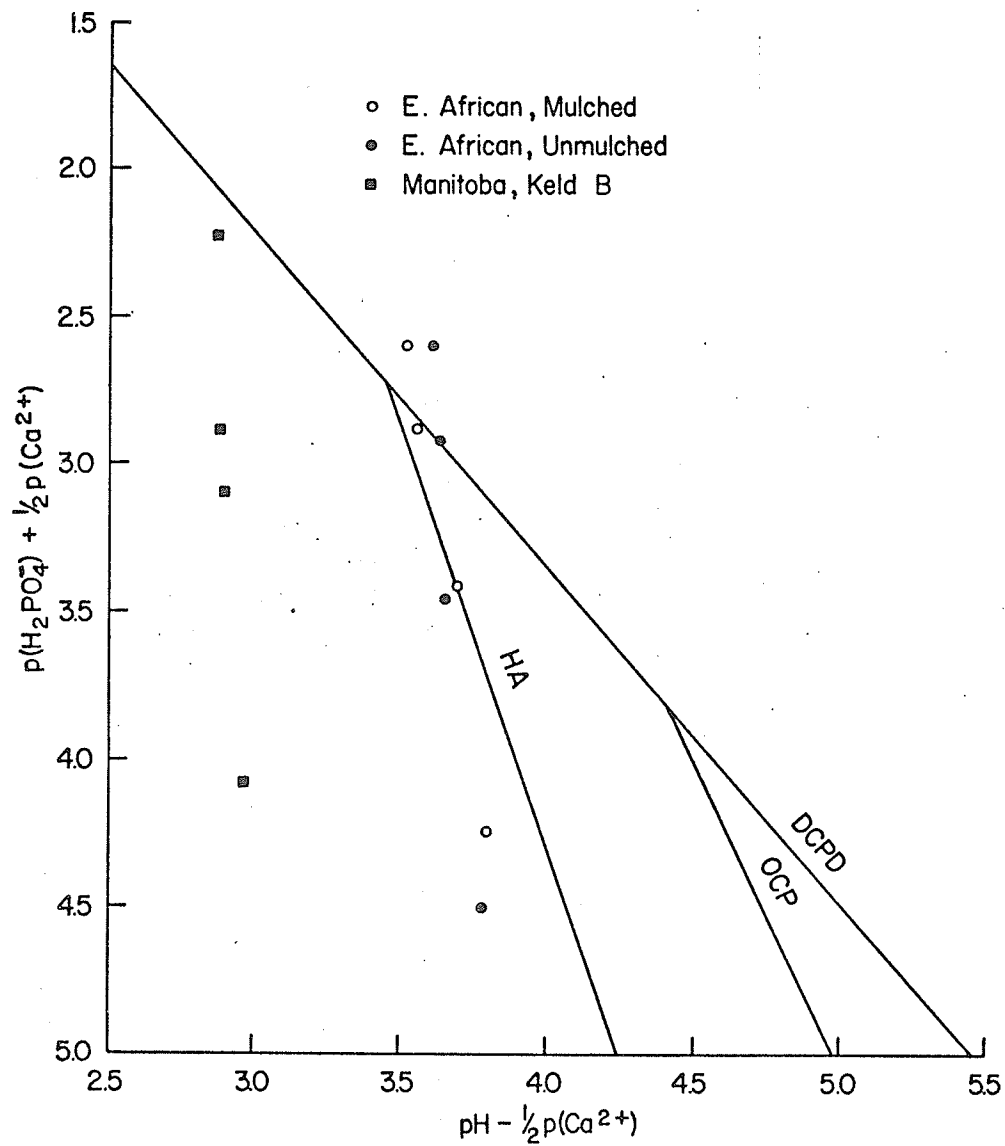


Figure 9. Solubility diagram for the calcium phosphates showing the phosphate and lime potentials obtained by equilibrating soils with KH_2PO_4 .

Table XV Ionic concentrations and activities, and phosphate and lime potentials obtained by equilibrating soils with KH_2PO_4

Soil	KH_2PO_4 added (g)	pH	P $\text{Mx}10^2$	Ca+Mg $\text{Mx}10^3$	$\text{p}(\text{H}_2\text{PO}_4^-)$	1/2 $\text{p}(\text{Ca}^{2+})$	$\text{pH} -$ + $\text{p}(\text{H}_2\text{PO}_4^-)$ + 1/2 $\text{p}(\text{Ca}^{2+})$	
							1/2 $\text{p}(\text{Ca}^{2+})$	1/2 $\text{p}(\text{Ca}^{2+})$
Mulched	0.1	4.99	0.049	6.00	3.37	1.21	3.79	4.58
	0.2	4.91	0.625	6.70	2.26	1.19	3.72	3.45
	0.4	4.81	2.865	5.00	1.61	1.26	3.54	2.87
	0.6	4.80	5.805	5.00	1.31	1.29	3.51	2.60
Unmulched	0.1	4.98	0.057	6.30	3.30	1.20	3.78	4.50
	0.2	4.94	0.722	4.30	2.19	1.27	3.64	3.46
	0.4	4.93	2.840	4.10	1.61	1.31	3.63	2.92
	0.6	4.89	5.805	5.10	1.31	1.29	3.60	2.60
Keld B	0.1	4.03	0.113	9.60	3.01	1.12	2.91	4.13
	0.2	3.96	1.131	6.70	2.01	1.18	2.78	3.19
	0.4	3.91	3.613	9.40	1.52	1.13	2.78	2.65
	0.6	3.90	6.500	8.70	1.26	1.17	2.73	2.43

Table XVI Ionic concentrations and activities, and phosphate and lime potentials obtained by equilibrating soils with K_2HPO_4

Soil	KH_2PO_4 added (g)	pH	P $M \times 10^2$	Ca+Mg $M \times 10^3$	$p(H_2PO_4^-)$	$1/2 p(Ca^{2+})$	pH- $1/2 p(Ca^{2+})$	$p(H_2PO_4^-)$ + $1/2 p(Ca^{2+})$
Mulched	0.1	5.57	0.020	4.10	3.75	1.28	4.29	5.03
	0.2	6.20	0.323	1.70	2.59	1.47	4.73	4.06
	0.4	6.97	2.221	0.70	2.05	1.91	5.06	3.96
	0.6	7.22	5.565	0.30	1.82	2.28	4.94	4.10
Unmulched	0.1	5.65	0.023	4.10	3.71	1.28	4.37	4.99
	0.2	6.61	0.361	2.30	2.66	1.43	5.18	4.09
	0.4	7.05	1.987	1.10	2.08	1.83	5.22	3.91
	0.6	7.28	5.987	0.90	1.86	2.05	5.23	3.91
Keld B	0.1	4.74	0.034	5.70	3.53	1.21	3.52	4.74
	0.2	5.38	0.370	1.70	2.46	1.45	3.93	3.91
	0.4	6.46	2.221	0.30	1.82	2.01	4.45	3.83
	0.6	6.78	5.565	0.30	1.55	2.21	4.57	3.76

amounts of added K_2HPO_4 . The decrease in calcium plus magnesium concentrations of the extracts with increased amounts of K_2HPO_4 added may be due to the lower solubility of the calcium phosphates at higher pH values.

Solubility of phosphate in all soils was near that of Hydroxyapatite when 0.1 g K_2HPO_4 was added (Figure 10). Dicalcium phosphate dihydrate was most likely the phosphate compound formed when 0.2 g K_2HPO_4 was added to the soils. When more than 0.2 g K_2HPO_4 was added, the soils appeared to be supersaturated with respect to DCPD and a compound more soluble than DCPD was probably formed. It is also possible that adsorbed phosphorus and not precipitated phosphorus was governing the concentration of phosphorus in the soil extracts.

Results of incubating the East African soils for various periods of time with increasing amounts of added $NH_4H_2PO_4$ are presented in Tables XVII and XVIII. The pH and phosphorus concentrations of the soil extracts increased with increased amounts of phosphate added for each particular time of incubation. The pH of the extracts, also increased with increases in time of incubation. The calcium plus magnesium concentrations of the soil extracts decreased with increased amounts of phosphate added for each incubation period. The phosphorus and calcium plus magnesium concentrations in the extracts decreased with increases in time of incubation. The above trends were observed for both the mulched and unmulched

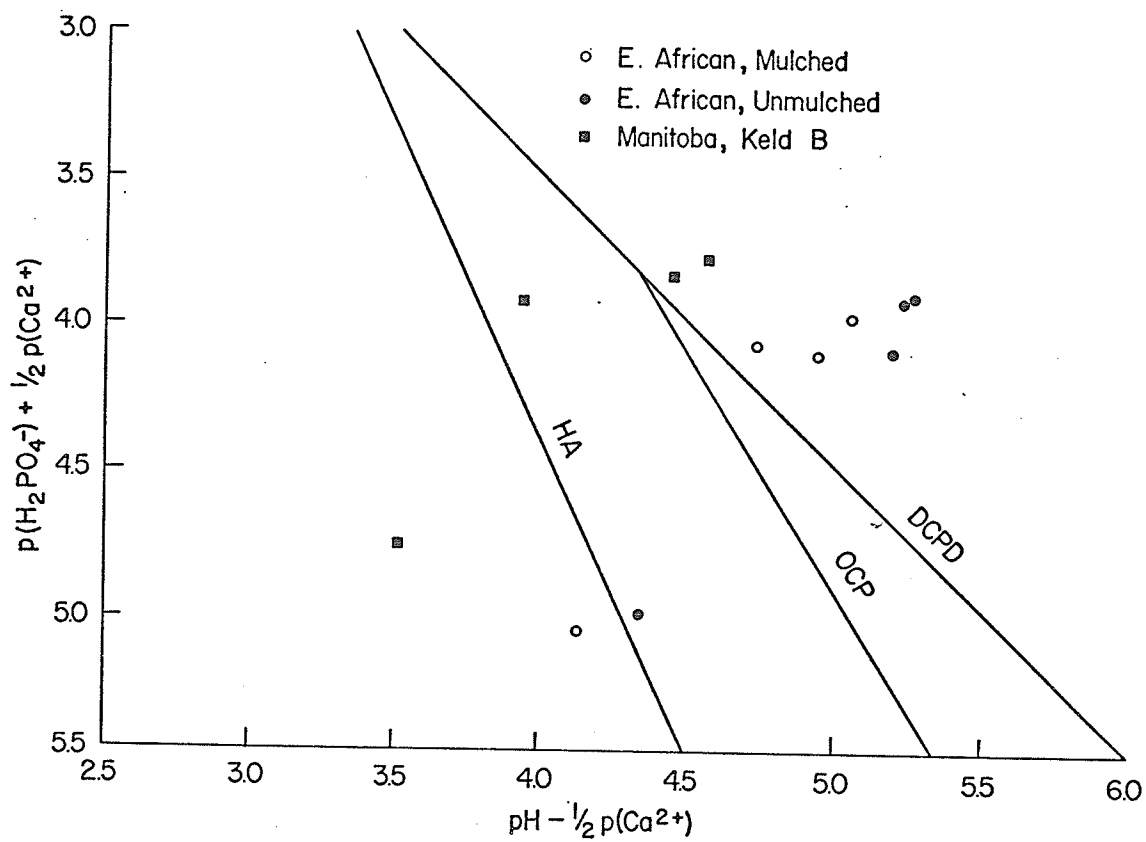


Figure 10. Solubility diagram of the calcium phosphates showing the phosphate and lime potentials obtained by equilibrating soils with K_2HPO_4 .

Table XVII Ionic concentrations and activities, and phosphate and lime potentials obtained by incubating the mulched soil with $\text{NH}_4\text{H}_2\text{PO}_4$

Soil	Incubation period (months)	$\text{NH}_4\text{H}_2\text{PO}_4$ added (g)	pH	P	Ca	$p(\text{H}_2\text{PO}_4^-)$	$1/2 p(\text{Ca}^{2+})$	pH - $1/2 p(\text{Ca}^{2+})$	$p(\text{H}_2\text{PO}_4^-)$
									$1/2 p(\text{Ca}^{2+})$
					$\text{M} \times 10^3$				
Mulched	0	0.1	4.50	2.00	10.30	2.77	1.11	3.39	3.88
		0.2	4.50	12.90	10.10	1.96	1.11	3.39	3.07
		0.4	4.60	37.10	8.70	1.50	1.16	3.34	2.66
		0.6	4.70	67.10	8.00	1.26	1.20	3.50	2.46
	One	0.1	5.40	.06	5.00	4.29	1.24	4.16	5.53
		0.2	5.44	2.90	4.60	2.61	1.26	4.18	3.87
		0.4	5.73	12.74	2.10	1.97	1.45	4.28	3.42
		0.6	5.80	25.60	1.30	1.67	1.60	4.20	3.27
	Two	0.1	5.75	.013	3.70	4.97	1.29	4.46	6.26
		0.2	5.97	1.03	1.50	3.06	1.47	4.50	4.53
		0.4	5.93	9.10	1.10	2.11	1.58	4.35	3.69
		0.6	6.01	17.10	.90	1.85	1.67	4.34	3.52

Table XVIII Ionic concentrations and activities, and phosphate and lime potentials obtained by incubating the unmulched soil with $\text{NH}_4\text{H}_2\text{PO}_4$

Soil	Incubation period (months)	$\text{NH}_4\text{H}_2\text{PO}_4$ added (g)	pH	P M x 10^3	Ca	$\text{p}(\text{H}_2\text{PO}_4^-)$	$1/2 \text{ p}(\text{Ca}^{2+})$	pH - $1/2\text{p}(\text{Ca}^{2+})$	$\text{p}(\text{H}_2\text{PO}_4^-)$ $1/2\text{p}(\text{Ca}^{2+})$
Unmulched	0	0.1	4.30	3.00	10.14	2.57	1.11	3.19	3.68
		0.2	4.45	13.50	8.00	1.93	1.15	3.30	3.18
		0.4	4.50	41.90	7.80	1.45	1.18	3.32	2.63
		0.6	4.60	71.00	7.80	1.23	1.20	3.40	2.43
	One	0.1	5.06	.07	5.70	4.19	1.22	3.84	5.41
		0.2	5.47	3.70	3.10	2.49	1.33	4.14	3.82
		0.4	5.85	15.20	1.10	1.89	1.60	4.25	3.49
		0.6	5.95	22.00	.70	1.74	1.74	4.21	3.48
	Two	0.1	5.70	.014	6.50	4.95	1.19	4.51	6.13
		0.2	5.82	1.70	3.70	2.86	1.30	4.52	4.16
		0.4	5.98	7.90	1.50	2.18	1.51	4.47	3.69
		0.6	6.21	14.20	1.00	1.96	1.66	4.58	3.62

soils. The phosphate compounds formed when 0.1 g $\text{NH}_4\text{H}_2\text{PO}_4$ was added to the soils and incubated for one or two months were slightly less soluble than HA (Figures 11 and 12). The solubility of phosphorus decreased with increased time of incubation. Dicalcium phosphate dihydrate was the most likely compound formed when 0.2 g of $\text{NH}_4\text{H}_2\text{PO}_4$ was added to the soils and incubated for one or two months. When greater than 0.2 g $\text{NH}_4\text{H}_2\text{PO}_4$ was added, the soils appeared to be supersaturated with respect to DCPD. It is possible that phosphate compounds, more soluble than DCPD, were formed when greater than 0.2 g $\text{NH}_4\text{H}_2\text{PO}_4$ were added to the soils and incubated for one or two months. It is also possible that adsorbed phosphorus rather than precipitated phosphorus was governing the concentrations of phosphorus found in the extracts.

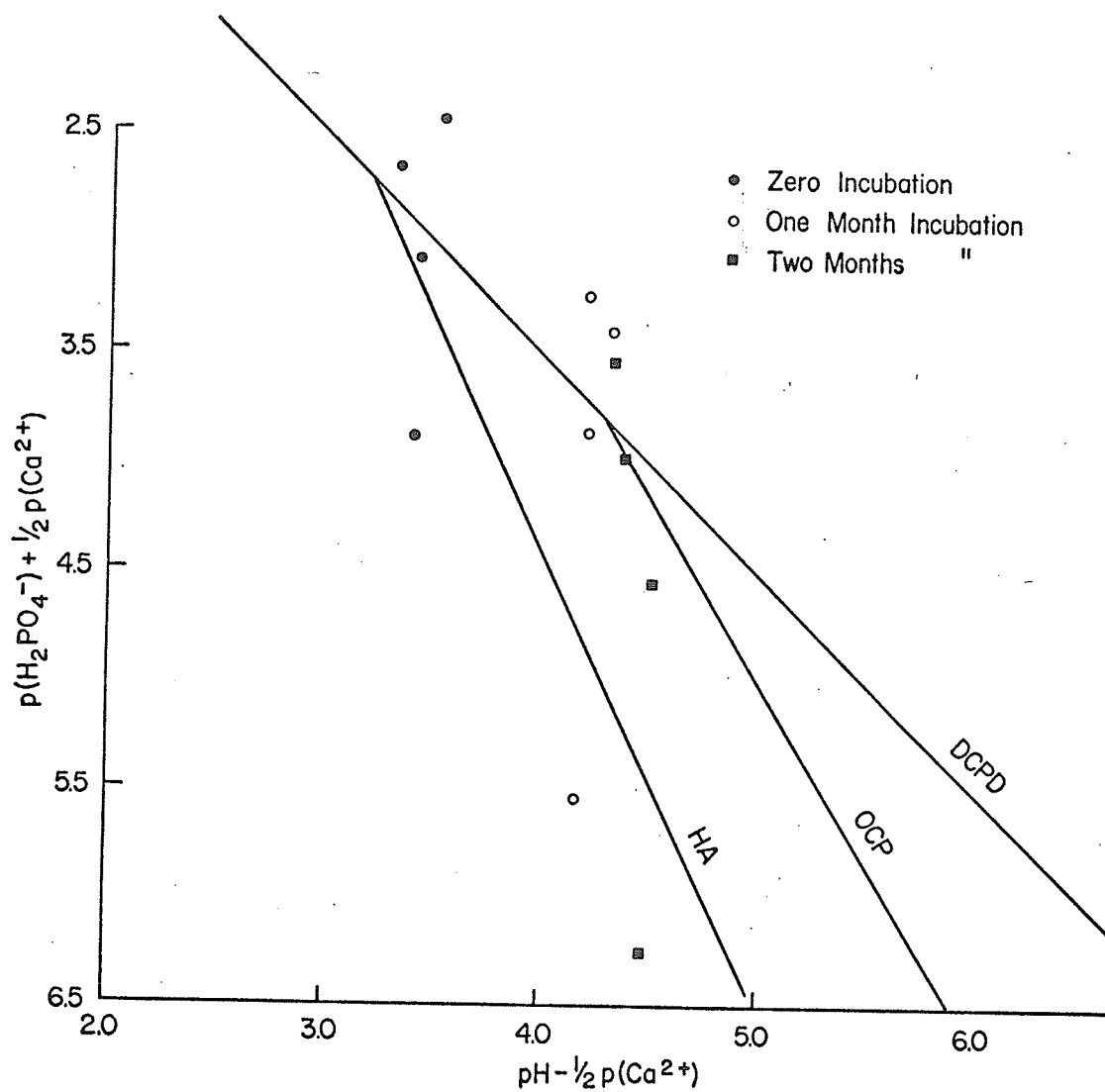


Figure 11. Solubility diagram of the calcium phosphates showing the phosphate and lime potentials obtained by incubating the mulched soils with $\text{NH}_4\text{H}_2\text{PO}_4$.

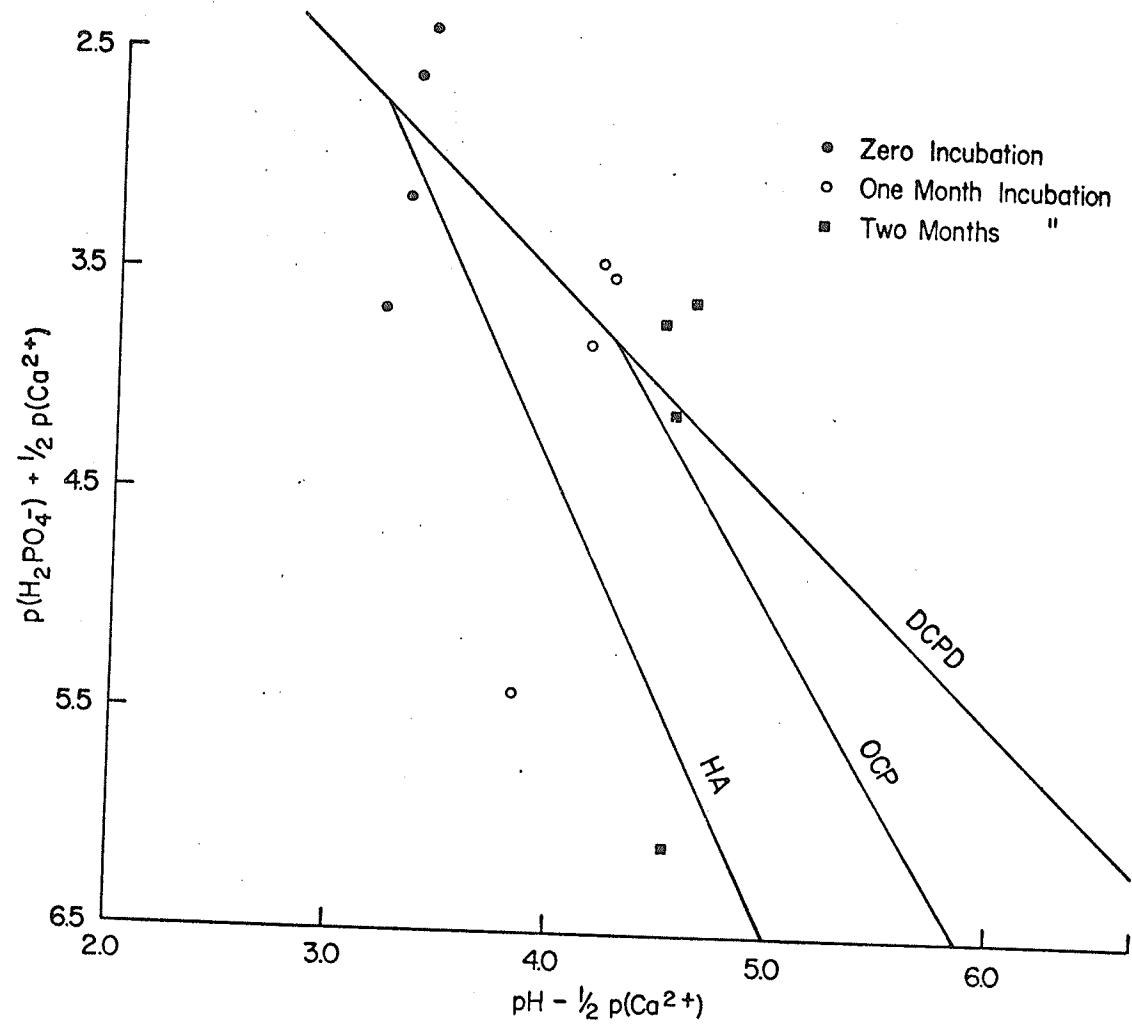


Figure 12. Solubility diagram of the calcium phosphates showing the phosphate and lime potentials obtained by incubating the unmulched soils with $\text{NH}_4\text{H}_2\text{PO}_4$.

Effects of an organic mulch on crop yields and phosphorus utilization by plants grown in an acid soil

The greenhouse experiments were conducted to study:

- (a) The effects of an organic mulch on the availability of added phosphate to plants, and
- (b) the chemical and physical effects of mulch on plant growth and phosphate uptake.

The first experiment was conducted to test the field observation that organic mulches increase the availability of soluble orthophosphate added to acid soils. The experiment was also designed to evaluate the efficiency of different orthophosphate carriers.

Three and five tenths Kg of air-dry Keld A soil, passed through a 0.6 cm sieve, was placed in 6.8 liter plastic pots. Twenty wheat seeds (Triticum aestivium L. var. Manitou) were placed at a soil depth of about 1.2 cm. The pots were arranged in a split-plot design with four replicates. The main plots consisted of no mulch and mulch treatments. The main plots were split for different phosphate carriers. A few days after emergence, the plants were thinned and eight plants left to grow in each pot.

Nitrogen at a rate of 1,000 mg per pot was added two weeks after planting by pipetting 25 ml of a solution containing 114.29 g/l NH_4NO_3 onto the surface of the soil.

Two hundred g of organic mulch, passed through a 0.6 cm sieve, was applied to one half of the pots. This rate gave a 2.5 cm layer of mulch above the soil surface.

The phosphate applications were made three weeks after planting. One hundred mg of ^{32}P labelled phosphate was added to the soil surface by pipetting 25 ml of solution containing 16.28 g $\text{Ca}(\text{H}_2\text{PO}_4)_2/1$, 17.57 g $\text{KH}_2\text{PO}_4/1$, 22.49 g $\text{K}_2\text{HPO}_4/1$ or 17.05 g $(\text{NH}_4)_2\text{HPO}_4/1$. Six days after the application of phosphate, CaCl_2 , KCl , and NH_4Cl were added in amounts such that the amounts of added Ca, K or NH_4 were equal for all pots.

The above ground portion of the plants were harvested for total and radioactive phosphorus analyses 41 days after planting.

The second and third experiments were conducted to compare the effects of mulch with other means of making surface applied phosphate more available to plants. An attempt was also made to separate the mulch effects on crop yields and phosphorus utilization by plants into physical and chemical factors. The procedure followed for experiment 2 and 3 differed from that for experiment 1. However, the size of pots, and quantities of soil and mulch used were the same as in experiment 1.

The procedure for experiment 2 and 3 was the same, except that buckwheat (Fagopyrum esculentum, L. var. Tokio) and rape (Brassica napus, L. var. Tanka) were used for experiments 2 and 3, respectively. These two plant species were selected because of their contrasting tolerance to soil acidity (20).

The experiments were arranged in a split-plot

design with three replicates. The main plots consisted of no phosphate and phosphate treatments. The main plots were split for check (no treatment), mulch (surface), mulch (leachate), humic acid and lime as sub-treatments. Humic acid was extracted as outlined on page 54.

The mulch leachate was obtained as follows: Two hundred g of mulch was placed in separate pots of the same size as those for planting. The bottom of the pots were perforated and lined with a 2 mm mesh plastic screen. A pre-determined amount of water was passed through the mulch each time the plants were watered. The leachate was collected and applied to the pots which received the mulch leachate sub-treatment. The pots containing the mulch were covered to keep the mulch moist. It was assumed that the effect of mulch on crop yield and phosphorus utilization by plants resulting from this sub-treatment, would be strictly due to chemical factors. Mulch applied to the surface of the soils was assumed to combine both physical and chemical factors.

Three and a half Kg air-dry soil was mixed thoroughly with 2.875 g NH_4NO_3 to give 1,000 mg N per pot. The soils were placed into the pots. The soils in the pots, receiving lime as a sub-treatment, were mixed thoroughly with 10.5 g CaCO_3 per pot (3.4 tonnes per hectare). A representative sample of the limed soils was taken for a pH determination. Twenty seeds were planted. Immediately after planting the mulch was applied. Humic acid, at the rate of 100 mg per

pot, was applied as a surface broadcast treatment to the soils which received this sub-treatment. One hundred mg of ^{32}P labelled phosphate was added onto the surface of the soil by pipetting 25 ml of solution containing 17.57 g $\text{KH}_2\text{PO}_4/1$. Phosphate was also applied to the mulch in the pots used for extraction of the mulch leachate.

A study was conducted (Table XXII) which showed that the mulch did not retain the added phosphate. Phosphorus in excess of the amount of added phosphate was released from the mulch.

Seven days after phosphate application, KCl was added to the soils without added phosphate. Thus, the amount of potassium added to all soils was the same.

A few days after germination, the plants were thinned and eight plants left to grow in each pot.

The above ground portion of the plants were harvested for analyses of total and radioactive phosphorus 40 and 50 days from planting of buckwheat and rape, respectively.

The wheat was grown in the summer months and although the experiment was conducted in a greenhouse, the plants suffered from excessive summer heat. Because of the high temperatures and high soil acidity, the plants were thin and stunted. The plants reached heading stage earlier than expected for a wheat crop. At harvesting time the plants showed an average of eight kernels per head. The plants in the check (no mulch no phosphate) treated soils showed the least number of kernels per head while plants in the mulched plus $(\text{NH}_4)_2\text{HPO}_4$ treated soils showed the highest numbers of kernels per head.

In some cases the growth of the mulched plants appeared to be suppressed. It is possible that applying mulch after the wheat plants was germinated was detrimental to the plants. A latter study showed that plants grew better in mulched soils when the mulch was applied immediately after seeding.

Moisture loss measurements, taken by weighing the pots daily in the last two weeks before harvesting, showed that the mulched soils lost approximately one half as much water as the unmulched soils. Soil temperature taken at the soil surface and at depths of 2.5 and 5.0 cm showed no differences between mulched and unmulched soils.

Table XIX shows the effect of mulch and phosphate addition on crop yields and phosphorus utilization by wheat plants. With few exceptions, mulched plants contained a higher percent total phosphorus and utilized significantly more phosphorus per pot than did unmulched plants. Fertilizer phosphorus absorbed by the plants was significantly greater when grown in mulched soils than when grown in unmulched soils. The efficiency of $\text{Ca}(\text{H}_2\text{PO}_4)_2$, KH_2PO_4 and K_2HPO_4 were similar. However, $(\text{NH}_4)_2\text{HPO}_4$, when combined with mulch, gave the highest crop yields and provided the greatest amount of phosphorus to the plants.

Since 100 mg of phosphorus was added per pot, the amounts fertilizer phosphorus absorbed (last column in Table XIX) represent the percentage of fertilizer phosphorus recovered by the plants. The low recovery of fertilizer

Table XIX

Effect of mulching and phosphate addition on yield and phosphorus utilization by wheat

Treatment	Yield of forage (g)		Total P in tissue (%)		Total P uptake per pot (mg)		P in tissue from fertilizer (%)		Fertilizer uptake per pot (mg)	
	Mulched	Un-mulched	Mulched	Un-mulched	Mulched	Un-mulched	Mulched	Un-mulched	Mulched	Un-mulched
Check	1.59	1.37	0.41	0.27	6.37	3.72				
Ca(H ₂ PO ₄) ₂	1.44	1.60	0.35	0.33	5.13	5.28	11.16	4.14	0.56	0.19
KH ₂ PO ₄	1.32	1.54	0.42	0.29	5.52	4.49	11.90	3.46	0.48	0.23
K ₂ HPO ₄	1.73	1.71	0.36	0.30	5.04	4.90	10.76	2.00	0.55	0.10
(NH ₄) ₂ HPO ₄	2.07	1.46	0.38	0.35	7.45	5.05	17.57	3.44	1.33	0.19

LSD (0.05P)

Between mulch treat.	NS	NS	NS	6.51	0.28
Between phosphate treat.	NS	NS	NS	NS	NS
Mulch x Phosphate	NS	NS	NS	NS	NS

NS = not significant

phosphorus by the crop was probably due to poor crop growth. Also, the fertilizer was applied only three weeks prior to harvest. Therefore, the plants probably did not have adequate time to absorb the added phosphate.

The greater absorption of phosphate by mulched plants than by unmulched plants may be attributed to the enhanced mobility of the added phosphate. The upward growth of feeder roots when plants were mulched, as observed by others (5, 6, 11, 16, 24, 53, 55, 58, 70) was not evident in this study.

Despite the poor crop and recovery of added phosphate by the plants, the experiment demonstrated the beneficial effects of organic mulches in increasing the utilization of added phosphate by plants.

The buckwheat plants showed a high tolerance to soil acidity and produced a better crop than did wheat or rape (Tables XIX, XX and XXI). Except for the soils treated with humic acid, the phosphate fertilized soils produced significantly greater crop yields of buckwheat than did the unfertilized soils. The soils treated with humic acid produced the lowest crop yields. It is possible that the amount of humic acid added was too high and hence, suppressed the growth of the plants.

Total phosphorus absorption by the plants was highest in the surface mulched soils followed by the limed and mulch leachate treated soils. The plants in the soils treated with humic acid absorbed less phosphorus than did the plants in the untreated soils. Utilization of added phosphate was greatest in the surface

Table XX

Yield and phosphorus utilization by buckwheat

Treatment	Yield of forage (g)		Total Phosphorus in tissue (%)		Total Phosphorus uptake per pot (mg)		P in tissue from fertilizer (%)	Fertilizer P uptake per pot (mg)
	No Phos- phorus	Phos- phorus	No Phos- phorus	Phos- phorus	No Phos- phorus	Phos- phorus		
Check	3.38	4.73	0.213	0.260	7.10	11.76	19.31	2.32
Mulch (surface)	6.12	7.35	0.253	0.375	15.45	27.14	65.40	17.73
Mulch (leachate)	4.07	5.43	0.262	0.315	10.68	17.05	41.06	6.97
Humic Acid	2.66	3.18	0.218	0.245	5.86	7.79	22.72	1.58
Lime	4.87	6.41	0.215	0.272	11.13	17.27	40.87	6.74
LSD (.05P)							15.71	1.26
Between P treatments		1.08		NS		2.80		
Between subtreatments		1.45		NS		5.75		
PX Subtreatments		NS		NS		NS		

NS = Not significant

mulched soils. Plants in the limed soils utilized slightly lower amounts of added phosphorus than did the plants grown in the soils with the mulch leachate. Thus, indicating that although liming increased the crop growth more than the addition of mulch leachate, it did not increase the phosphorus utilization by the plants. The lime application increased the pH of the soil from 4.30 to about 5.50.

In the early stage of growth, the moisture loss from the surface mulched soils was less than from the other soils. The plants in the surface mulched soils, however, grew faster than in the other soils. Thus, in the late stages of growth, when there was complete plant cover over the surface of the soils, the moisture loss from the surface mulched soils was greater than from the other soils. This was due to increased transpiration as a result of increased growth.

A review of the literature showed that many workers attributed the effects of mulches on increasing crop yields and phosphate uptake by plants to either physical or chemical factors. No attempt was made to separate these effects. By assigning physical plus chemical factors to the effect of surface applied mulch, and chemical to the effect of mulch leachate, it was possible to separate the effects into these two factors. The results showed that with or without added phosphate, about 75 percent of the increase in crop yield could be attributed to physical factors. About 65 and 60 percent of the increases in total phosphorus absorbed by the plants in the soils with and without added phosphate, respectively, could be attributed to the effects of mulch per se. About 75 percent of the

increases in the fertilizer phosphorus absorbed by the plants could be attributed to physical factors. Thus, approximately 25 to 40 percent of the effects noted were due to the chemical changes resulting from the addition of mulch.

The rape crop followed a pattern similar to that of buckwheat, despite the poor yield (Table XXI). Surface mulched soils produced the greatest crop yield, followed by soils treated with lime and mulch leachate. Limed soils produced a greater crop than did the soils treated with mulch leachate. Plants grown in the soils treated with humic acid had the lowest yield, but was better than the check treatment when phosphate was added. Yield, when phosphate was added, was greater than without phosphate. In spite of the poor yield, rape responded to phosphate fertilization to a greater degree than did buckwheat. The phosphate addition increased yields of rape by about 18, 8, 8, 2 and less than 2 times for the humic acid, check, mulch leachate, lime and surface mulch treatments, respectively. It is evident from the data that surface applied mulch has an extremely large beneficial effect on yield.

Plants grown in the soils with added phosphate had a higher percent total phosphorus in their tissues than plants grown in the unfertilized soils. The total phosphorus adsorbed per pot by the plants showed a similar pattern to that noted for buckwheat. Utilization of added phosphorus by rape also followed a pattern similar to that noted for buckwheat. Utilization of the added phosphate decreased in the order: surface mulch, lime, mulch leachate, humic acid and check.

Table XXI

Yield and phosphorus utilization by rape

Treatment	Yield of forage		Total Phosphorus in tissue		Total Phosphorus uptake per pot		P in tissue from fertilizer (%)	Fertilizer uptake per pot (mg)
	No Phosphorus	Phosphorus (g)	No Phosphorus	Phosphorus (%)	No Phosphorus	Phosphorus (mg)		
Check	0.08	0.64	0.075	0.165	0.06	1.06	29.4	0.31
Mulch (surface)	3.48	4.36	0.240	0.320	8.35	13.94	47.7	6.65
Mulch (leachate)	0.16	1.30	0.215	0.230	0.34	2.99	34.5	1.03
Humic Acid	0.05	0.91	0.110	0.165	0.06	1.50	29.9	0.45
Lime	1.38	3.11	0.180	0.260	2.51	8.09	39.4	3.19

The rape crop from the various replicates were bulked according to sub-treatments in order that enough plant material would be available for weighing and analyses. Therefore, the data was not analysed statistically.

The physical effect of mulch on crop yield and phosphorus utilization by plants could be attributed to an improvement in the environment near the plant root zone. It was observed that roots, particularly fine roots, grew profusely into the mulch layer immediately near the soil surface. The higher root density in the surface mulched soils, therefore, enabled plants to explore the soil surface to which the phosphate was added. Thus, there was increased nutrient uptake, particularly phosphorus which was fixed at or near the soil surface.

The chemical effects of mulch (leachate) was probably due to the effect of organic acids released from the decomposing mulch. It was shown previously that humic acid, extracted from the mulch material, reduced phosphorus fixation by the soils (Table XII). It was also found that mulch increased the mobility of added phosphate in the soil (Table XXIII). Therefore, it is possible that humic substances released from the mulch may have blocked phosphate fixation sites thereby increasing the availability and mobility of added phosphate. It is also possible that an organo-phosphate complex may form which may render the phosphate less susceptible to fixation.

Phosphate - Mulch studies

Studies were conducted to gain information on the retention of added phosphate by mulch and the effect of mulch on the mobility of added phosphate.

(a) Phosphate retention by an organic mulch

A 20 g sample of mulch was placed in columns 5.0 cm long and 4.4 cm inner diameter cut from acrylic tubing. One end of the columns were fitted with a 1 mm mesh plastic screen and lined with a filter paper. The mulch was wetted to bring the amount of water to near water holding capacity. Ten mg of phosphorus as KH_2PO_4 or K_2HPO_4 was added to the mulch and left to stand overnight. Water was passed through until 200 ml was collected as leachate. Leaching was continued until a total of 600 ml of leachate was collected. The latter was collected in 100 ml portions. The pH, phosphorus and organic carbon contents in the leachates were determined. Table XXII shows the pH, phosphorus and organic carbon contents of the leachates. The results show that mulch did not retain the added phosphate. There was more phosphorus leached from the mulch than was initially added. All the added phosphorus was recovered in the first 200 ml of leachate collected. Phosphorus was leached by the subsequent leachates, but the amount decreased with increased leaching. Most of the readily soluble phosphorus was leached after 500 ml of leachate was collected. There was very little phosphorus in the last 100 ml of the leachate collected. More phosphorus was leached in the first 200 ml of leachate collected when

Table XXII pH, Phosphorus and Organic carbon contents of mulch leachates

Leachate No.	Volume of H ₂ O collected	Phosphate added (10 mg P)	pH	Phosphorus in solution (ppm)	Organic carbon (%)
1	200	KH ₂ PO ₄	5.35	60.00	0.023
		K ₂ HPO ₄	5.48	55.00	0.029
2	100	KH ₂ PO ₄	5.83	6.32	0.010
		K ₂ HPO ₄	5.88	6.80	0.016
3	100	KH ₂ PO ₄	5.94	2.76	0.005
		K ₂ HPO ₄	6.03	3.58	0.012
4	100	KH ₂ PO ₄	5.99	3.58	0.012
		K ₂ HPO ₄	6.13	2.96	0.013
5	100	KH ₂ PO ₄	6.18	0.48	0.002
		K ₂ HPO ₄	6.51	0.66	0.002

KH_2PO_4 rather than K_2HPO_4 was added. This trend was not evident in the subsequent leachings.

The pH of the leachates increased with increased leaching. This was probably due to the removal of easily soluble organic acids by the first few leachings. The pH of the leachate from the mulch treated with K_2HPO_4 was usually higher than that of the mulch treated with KH_2PO_4 .

The organic carbon content of the leachates decreased with increases in leaching. There was more organic carbon leached from the mulch treated with K_2HPO_4 than from that treated with KH_2PO_4 .

- (b) The effect of an organic mulch on the movement of phosphate added to acid soils

Rings 6 mm thick and with inner diameters of 4.4 cm cut from acrylic tubing were joined together to form columns 10.0 cm long. One end of the columns was fitted with a 1 mm mesh plastic screen and lined with a filter paper. Sixty g air-dry Keld A soil was placed into the columns and wetted to field capacity moisture content. The moist soils were covered with a filter paper. Eight g of air-dry mulch was added to the surface of the soil in one of the columns and then covered with a filter paper. The depth of the mulch layer was about 2.5 cm.

One ml of labelled phosphate, containing 4 mg P as KH_2PO_4 and about 10 μC ^{32}P was added to the soil or mulch surface. The soils were left to stand overnight. The

soils were leached slowly with water until 400 ml of H_2O was passed through the columns. The columns were dismantled and the soils in the columns sectioned and air-dried. The radioactivity of the various sections were measured by placing a one g sample of soil in aluminum planchets on an end window of Geiger Muller counter.

Table XXIII: Radioactivity (cpm) of ^{32}P in the soil sections

Soil Section No.	No Mulch	Mulch	
1	1,562	71	} Mulch layer
2	61	82	
3	4	43	
4	3	884	
5	3	316	
6	51	119	
7		49	
8		15	
9		43	

The results show that nearly all of the added phosphate was held in the first soil section when the soil was not mulched. There was very little movement of phosphate into the soil when mulch was not added. There was some phosphate remaining in the mulch layer. However, most of the added phosphate was leached through into the soil. The results show that phosphate moved farther down into the soil when the soil was mulched than when not mulched. This is further evidence that organic mulch increases the downward movement of added phosphate in acid soils.

V SUMMARY AND CONCLUSION

Acid soils, such as those of East Africa on which tea is grown, are inherently low in phosphorus. These soils have very high contents of aluminum and iron and thus have a very high capacity for fixing added phosphate. Due to fixation, the availability of added phosphate is generally limited by the very low solubility and/or mobility of the added phosphate. It has been shown that the availability of surface applied phosphate was increased when organic residues such as leaf-fall and pruning litter are left to accumulate on the surface of the soils. Workers who have studied the effects of organic mulches on plant growth in acid soils have attributed the beneficial effects of the mulch to various factors. These factors included the enhanced uptake of applied phosphate by plants. No attempts, however, have been made to study the effects of organic mulches on the behaviour of phosphate in acid soils.

Several studies were conducted to determine the effects of organic mulches on the fixation and forms of phosphate in acid soils. A study was conducted using East African soils which had received mulch and phosphate treatments over a period of 15 years. It was found that mulching increased the organic matter and total phosphorus contents of the soils. However, the application of mulch with phosphate increased the amounts of soil phosphorus to a greater extent than did mulching alone. The increases in organic matter, total phosphorus

contents, and the NH_4F , NaOH and H_2SO_4 extractable phosphorus contents of the mulched soils was probably due to the mulches and the phosphates released from the mulches. These increases were very marked in the surface soil but were less pronounced in the subsurface soil. The application of mulch was also found to increase the mobility of phosphorus. Long-term mulching also increased the calcium and potassium contents of the surface soil.

Experiments, using samples of East African soils and an acid Manitoba soil (Keld), were conducted to study the nature and amounts of phosphorus fixed by acid soils. The phosphorus adsorption or fixation characteristics of the Keld soils were similar to those of the East Africa soils. The soils with a high organic matter content adsorbed more phosphate than did the soils with a low organic matter content. It was found that over 80 percent of the adsorbed or fixed phosphate was extracted as aluminum and iron phosphates. However, aluminum was found to be the most active adsorber of phosphate added to the soils. The phosphate adsorbed by aluminum showed a linear relationship with the total amount of phosphate adsorbed by the soils. The adsorbed phosphate was found to be only partially exchangeable with ^{32}P . The fraction of the adsorbed phosphate that exchanged with ^{32}P was found to decrease with increases in the amounts of total adsorbed phosphate. The aluminum, iron and calcium phosphate fractions were found to be equally exchangeable with ^{32}P .

Humic acid, extracted from an organic mulch and

added to the soils, was found to decrease the amount of added phosphate fixed and increase the amounts of phosphorus remaining in solution.

Experiments were also conducted to determine the solubility of native and applied phosphorus. The solubility of native phosphorus in the soil with a high organic matter content was greater than in the soil with a low organic matter content. The solubility of the native phosphorus in the Keld B soil was very close to that of variscite; thus suggesting that this phosphate compound probably existed in this soil. The solubility product values obtained for the other three soils studied were greater than that of variscite and appeared to be supersaturated with respect to variscite. The solubility product values for all four soils was greater than that of strengite. When the soils were equilibrated for 120 hours with amounts of KH_2PO_4 and K_2HPO_4 approximating that found in a fertilizer pellet zone, the phosphorus concentrations in the soil extracts was usually very high. It was found that the solubility of phosphorus approximated that of hydroxyapatite or dicalcium phosphate dihydrate when low amounts of phosphorus were added. The soils appeared to be supersaturated with respect to dicalcium phosphate dihydrate when large amounts of phosphorus were added to the soils. The solubility of phosphorus in the soils was usually greater than the solubility of the aluminum or iron phosphates thought to occur in soils.

The solubility of phosphorus was found to decrease

with increases in incubation time when the soils were treated with increasing amounts of $\text{NH}_4\text{H}_2\text{PO}_4$. Hydroxyapatite or dicalcium phosphate dihydrate probably formed when the soils were treated with small amounts of $\text{NH}_4\text{H}_2\text{PO}_4$ and incubated for one or two months. When large amounts of $\text{NH}_4\text{H}_2\text{PO}_4$ were added, the solubility of phosphorus in the soils was greater than that of hydroxyapatite or dicalcium phosphate dihydrate. The solubility of phosphorus in the mulched and unmulched East African soils was similar in all studies. The results also suggested that adsorbed phosphorus and not precipitated phosphorus may have governed the concentrations of phosphorus in the soil extracts.

The effect of an organic mulch on the availability of phosphate applied to the Keld A soil was determined using a variety of crops. The crops utilized a greater portion of applied phosphate when the soil was mulched than when not mulched. The increased utilization of applied phosphate by the plants grown in the mulched soils appeared to be due to two factors. First, mulching resulted in a better root distribution near the soil surface enabling the plants to utilize the surface applied phosphate. Approximately 70 percent of the effect of mulch on phosphate utilization could be attributed to the above factor. Secondly, mulching increased the mobility of phosphorus and decreased the amount of phosphorus fixed by the soils. It was found that mulch application increased the downward movement of phosphate applied to the soils. It has also been shown by other workers

that during decomposition, organic mulches release organic acids which block phosphate fixation sites on the soil colloids.

The studies reported in this manuscript certainly indicate that the role of organic mulches in increasing the availability and/or ^{movement} mobility of added phosphate in acid soils is an important one. The application of mulches not only provides a suitable media for root growth near the soil surface enabling the roots to utilize surface applied phosphorus, but increases the ^{movement} mobility and retard the fixation of the added phosphorus as well.

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