

THE UNIVERSITY OF MANITOBA

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

by

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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