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A LABORATORY STUDY OF THE BEHAVIOUR OF ADDED PHOSPHATE IN AN ALLOPHANIC SOIL

by

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I. A. Introduction.

A feature in the maintenance of high producing pastures, on the yellow-brown loam soils in Taranaki, is the need for high annual rates of phosphatic fertilizer application.

Burgess and Davies (I95I) in some early investigations into soil fertility problems in Taranaki noted that the yellow-brown loams could apparently accumulate large amounts of phosphate in a form which was difficult for plants to extract. Consequently to ensure adequate plant phosphate nutrition large annual dressings of superphosphate are recommended for high producing pastures on these soils.

This high phosphate-retaining property has been attributed to the presence of active aluminium supplied by allophane, the predominant clay mineral in these soils. (Saunders I959 (b)).

The only recent intensive study to be made on phosphate relationships in the yellow-brown loams is that of Saunders (I959 (a)(b)(c)) who carried out chemical fractionation of the phosphate in New Plymouth black loam, a soil which may be considered as representative of the group as a whole. His sampling sites were on areas of different topdressing histories, and although he was able to draw certain conclusions in respect of the trends of phosphate fixation this approach does not provide any information on the shorter term fate of applied phosphate. Information of this kind is, however essential if a rational explanation of the established need for substantial annual additions of phosphate to these soils, is to be forthcoming.

The present study was undertaken with the object of tracing,

in the laboratory, the course of the reaction of phosphate with New Plymouth black loam over approximately that period which would normally elapse between successive topdressing operations in the field both in respect of the forms of phosphate binding and the solubility and exchangeability ofthe reaction products. It was of interest alsc to determine whether the trends of fixation reported by Saunders (I959 (a)(b)(c)) in the field would be reproduced under laboratory conditions.

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B. Literature Review.

The literature relevant to the present study may be grouped as follows:-

I. The effects of time, and other factors, as influences on -

(a) the forms of phosphate binding in soils

(b) the solubility and exchangeability of fixed phosphate

2. The determination of isotopically exchangeable phosphate in soils.

I.(a) The forms of phosphate binding in soils.

Several workers have reported that the main fraction of soil responsible for the fixation of added phosphate is the clay component (Moschler et al I957, Fine and Bartholomew (I946).

The mechanisms for the reaction of soluble phosphate with soil constituents, and the identification of the products formed have been well documented (Wild I950, Haseman et al I950, Wright and Peech I960, Ellis and Truog I955, Coleman et al I960, Hemwall I957, Kittrick and Jackson I956, Lindsay et al I962, and Cho and Caldwell I959). However most of these reports have been made after using model systems in the laboratory. Identification of the various reaction products possible in soil systems is much more difficult and very often the evidence is only circumstantial.

In general it is agreed that calcium,iron and aluminium are the main elemental constituents of soils which are responsible for retention of phosphate. (Wild I950, Dean I949).

Fractionation techniques have been devised to categorise the inorganic fraction of soil phosphorus into three major forms - aluminium-bound, iron-bound and calcium-bound. (Dean I938, Ghani I943, Chang and Jackson I957 (I), Khin and Leeper I960, Fife I959). These techniques have enabled precise studies to be made on changes in phosphate binding in soils under a varying range of conditions.

The use of phosphate fractionation procedures for tracing soil/phosphate reactions has been criticised by several workers. Yuan, Robertson and Neller (I960) claim that chemical fractionation procedures give a low percentage recovery of the total phosphate applied to soils, whereas higher percentage recoveries can be obtained when an isotopic tracer method is employed.

Volk and McLean (I963), who do not support the findings of Yuan et al, were able to recover most of the phosphate, applied to soils, as the iron - bound and aluminium - bound fractions. Laverty and McLean (I96I) criticised the use of the fractionation procedure for studying soil phosphate binding, because it takes no account of the differences in solubilities between freshly formed phosphates and the more aged crystalline compounds. However they concluded that the method may be used empirically until such time as a better method emerges to enable studies in trends in phosphate fixation by soils.

One important factor governing the role of calcium, iron, and aluminium in the phosphate fixation process appears to be the pH of the system. Under neutral and slightly alkaline conditions, calcium and magnesium are probably responsible for phosphate retention, while under slightly acid conditions, manganese or aluminium may be more important in maintaining a low phosphate concentration in the soil solution. Iron would appear to be important under very acid conditions. (Teakle I928). Chiang (I963) showed that under waterlogging conditions in acid soils, the amount of the different forms of fixed phosphate was Fe - bound P > Al - bound P > Ca - bound P. However in alkaline soils the order was Ca - bound P > Fe - bound P > Al - bound P. When the pH of acid soils was raised, following the addition of organic matter, the amounts of Ca - bound P and Fe - bound P increased and Al - bound P decreased. In the alkaline soils, Ca - bound P and Al - bound P increased and Fe - bound P decreased after organic matter additions.

Saunders (I959 (a)) summarised the literature on the effects of pH on phosphate retention:-

(i) In iron and aluminium systems the phosphate in solution is at a minimum between about pH 2 and pH 7.

(ii) In calcium systems, the phosphate in solution is at its minimum above about pH 6.5.

(iii) The pH of minimum solubility in iron systems is about one pH unit lower than in aluminium systems.

Rathje (I960) presented a diagrammatic representation of the situation that could exist in the soil:-

$$Ca - P + \begin{matrix} Al \\ Fe \end{matrix} \text{ hydroxide} \rightleftharpoons \begin{matrix} Al \\ Fe \end{matrix} \text{ "hydroxide phosphate" } + CaOH$$

He suggested that the equilibrium was shifted to the left by an alkaline reaction and to the right by an acid reaction. However this is not the complete picture because some calcium-bound forms of phosphate can be formed under acid conditions.

Dean (I938) showed that much of the phosphate in the neutral soil appeared to be present as tri - calcium phosphate or apatite, and that in acid soils it was predominantly the iron -, aluminium- or mono - and di -, calcium -, phosphate forms.

Martin and Laudelout (I959), Ceccoui (I960) and Cho and Caldwell (I959) discussed the effects of pH on the form of phosphate retained by soils. However it is unlikely that pH alone is the only factor determining the distribution of applied phosphate between the calcium, iron and aluminium bound fractions in soil systems.

The amount of phosphate added may determine the form and quantity in which phosphate is fixed in soil. (Fiskell and Spencer I964)(Abdel-Samie, Hamdi and Barrada I962). Fiskell and Spencer (I964) showed that when a soil, whose native phosphate was largely in the form of iron - bound phosphate, was fertilised with

800 lbs phosphate/acre, most of the phosphate added accumulated as aluminium - bound phosphate with lesser amounts of the calcium - bound and iron - bound forms. However when the addition of phosphate was increased to I2,800 lbs phosphate/acre, there was considerably greater formation of iron - bound, and calcium - bound forms although the aluminium - bound form still showed the greatest increase.

Another important factor likely to affect the form in which phosphate is "fixed" in soils, appears to be the total fixation capacity of the soil. Laverty and McLean (I96I) showed that soils of low fixation capacity fixed 2½ times as much phosphate in the aluminium-bound fraction as in the iron - bound form, while the reverse was true for soils of high fixation capacity.

Volk and McLean (I963) showed a tendency to recover more than half of the applied phosphate as iron - bound phosphate in soils of high phosphate fixation capacity, and more than half as aluminium - bound phosphate in those soils of low phosphate fixation capacity.

Kaila (I963) showed that intensive phosphate fertilising led to accumulation of phosphate bound to iron and aluminium in the arable layer.

The above reports on the rates of phosphate fertilization and the fixation capacities of soils can be reconciled when it is remembered that the magnitude of the fixation process will depend largely on the mineral composition of the soil. Therefore a consideration of the total phosphate fixation capacity of a soil does not always allow predictions as to the form in which phosphate will be bound in that soil. It is generally accepted that where abundant aluminium is present as a soil constituent

the initial binding of added phosphate is likely to be in an aluminium-bound form. However a soil of high total fixation capacity but with a small percentage of aluminium sites available for fixation could conceivably bind phosphate in a form other than aluminium-bound phosphate. e.g. iron - bound P, or calcium - bound P.

Heck (I934) showed that if the ratio of active calcium to active aluminium and iron is high, the fixation of phosphate is largely in the calcium - bound form. If the reverse is true then iron - bound and aluminium - bound forms of fixed phosphate result.

It has been suggested that although the aluminium component of soils may be largely responsible for the magnitude of the phosphate sorption by soils, iron may be important in determining the strength of retention of the phosphate (Williams, Scott and McDonald I958).

Two types of phosphate adsorption were observed in volcanic ash soils by Onikura (I963) - one type had a soil phosphate system of low initial phosphorus concentration and the phosphate solid phase tended towards basic aluminium phosphate, while the other form had high initial phosphorus concentration and the solid phase was neutral and/or acidic aluminium phosphate.

Burgess and Davies (I95I) and Saunders (I959 (b)) found no increase in organic phosphorus in yellow - brown loams as a consequence of phosphate topdressing. In contrast, Jackman (I95I) on a yellow - brown pumice soil found that added phosphate accumulated largely in the soil in an organic form. Jackman produced evidence that no build up in organic phosphorus occurred if a virgin pumice soil was topdressed and left fallow for five

months. However, where clover and grass were grown, about I7% of the applied phosphate was recovered in the organic form in the soil.

Williams (I950) found that on a red - brown earth the application of superphosphate caused no increase in organic phosphorus content of the soil when the cover crop was a cereal. If the cover crop was pasture, the application of superphosphate fertilizer caused an increase in the organic phosphorus fraction of the soil phosphorus.

The lack of a universal method for the estimation of the organic fraction of soil phosphate could account for the anomalous results reported for changes in organic phosphorus following phosphate fertilization.

However some workers appear to neglect the organic fraction of soil phosphate during investigations into the fate of applied phosphate to soil. Fiskell and Spencer (I964) found that phosphate added to soil could not be accounted for in the calcium - bound, iron - bound and aluminium - bound forms of soil phosphate. They postulated the formation of occluded aluminium phosphate. Chang and Chu (I96I) did not take into account organic phosphorus when considering changes in soil phosphate following fertilizer application.

Several workers have demonstrated that under conditions of prolonged alternate wetting and drying of soil, there appeared a tendency for a reduction in the percentage of phosphate in the aluminium - bound fraction and an increase inthe percentage distribution of the iron - bound forms. (Mack and Barber I960) (Yuan, Robert and Neller I960) (Yuan I960) (Hsu I964) and (Chang and Chu I96I).

Mandal (1964) working with soils which were kept under waterlogged conditions in test - tubes showed that with time the control soils showed a slight increase in acetic - acid - extractable phosphate, a slight decrease in ferric - bound phosphate, but no change in either aluminium - bound or calcium - bound forms of phosphate.

In surface soils with an average phosphorus content of 675 $\pm$ 26 p.p.m. Gotoh et al (1963) showed the total phosphorus changed only slightly with increasing time. However they did show definite trends - organic phosphate (which represented 10.5% of the total phosphorus in the soil) increased gradually with time, aluminium - bound phosphate (5.9% of total) increased, as did iron - bound phosphate (19% of total). However calcium - bound phosphate (21.6% of total) decreased with time. In the soils used in this work, highly insoluble phosphate (43.5% of total) was the dominant form of fixed phosphate.

The apparent pK_{SP} value for aluminium - phosphate ranges from 28 - 32, and that for iron - phosphate from 33 - 35, indicating a much lower solubility of the latter. (Chang and Jackson 1957 (2)).

An explanation for the observed changes in distribution between the 3 categories of phosphate most commonly considered in these experiments, viz calcium - bound, aluminium - bound and iron - bound phosphate is offered by Chang and Chu (1961):- "initially the reaction of added soluble phosphate occurs on the surfaces of the solid phases with which it comes in contact in the soil. Therefore it is the specific surface area of the solid phases associated with the iron, calcium and aluminium irons, that determines the form and amount of the phosphate formed. Since

the main site of phosphate fixation is the clay fraction of the soil, and since the clay content of aluminium is higher than iron or calcium, the most likely initial form of phosphate is aluminium - bound phosphate. However, because the solubility product of iron - bound phosphate is lower than that of either aluminium - bound or calcium - bound phosphate, it is probable that as time progresses the aluminium - bound, and calcium - bound forms of phosphate in the soil will change to iron - bound forms."

In yellow - brown loams, where long and continued applications of phosphatic fertilizer have been practised, most of the increase in phosphate can be accounted for in the aluminium - bound fraction (Saunders I959(b)). Calcium binding of phosphate appears to play no part in the fixation of added phosphate in these yellow - brown loams.

Of particular importance in the study of phosphate fixation in these soils is the very high specific area of the clay particles, some 400 m^2/g (Birrell and Fieldes I952). This large surface area allows a high proportion of the aluminium to be present at the colloid surface where it is available for fixing phosphate. Fieldes and Swindale (I954) showed that the clay fraction of the yellow - brown loams had a C.E.C. of 80 - I00 meq/I00g. (Saunders (I956) quoted 30 - 50 m.e.%) and could fix I00 m.mol P_2O_5/I00g, in a form insoluble in I% citric acid. Most of the phosphate fixation capacity of these soils can be attributed to their allophanic content and various mechanisms for the actual fixation process have been postulated. Fieldes and Schofield (I960) suggested that phosphate was held in a difficultly available form at tetrahedral aluminium sites similar

to those found in montmorillonite and micaceous clay minerals, where aluminium substitutes extensively for silicon in silica tetrahedra. Saunders (I959 (b)) in a study on yellow - brown loams, which have a particularly high allophane content, showed that this soil had a capacity to retain large amounts of phosphate in an insoluble form. Wada (I959) showed that allophane was rapidly converted to the insoluble phosphate mineral "taranakite" following phosphate treatment of the soil with ammonium phosphate solution at pH4. On the yellow - brown loams (Saunders I959(c)) the retention of phosphate was at a maximum between pH 3.5 and pH 7.0. Wada (I959) showed the formation of taranakite from allophane proceeded faster at pH 4 than at pH 7.

Birrell (I96I) showed that by treating allophane with soluble ammonium phosphate, about 25% of the silica content of the soil was dissolved, but he concluded that the main reaction liable to occur was the solution of alumina followed by the precipitation of taranakite. This agreed with the mechanism proposed by Kittrick and Jackson (I956) for the retention of phosphate by kaolin.

Due to its extremely fine particle size and behaviour as a slowly reversible gel of high water content, allophane appreciably affects the physical properties of the clays in which it occurs(Gradwell and Birrell I954, Birrell and Fieldes I952).

According to the work of Chang and Jackson (I957 (2)) and Chang and Chu (I96I) it would be expected that given time phosphate initially bound as aluminium - bound phosphate in allophanic soils would be gradually converted into iron - bound phosphate.

(b) The solubility and exchangeability of fixed phosphate.

When soluble phosphate is added to a soil, the form in which it becomes initially bound is often prone to further changes. Many instances are reported where conspicuous changes occur between the forms of bound phosphate in soils as a result of environmental conditions, or the effects of time.

Wild (1950) noted that when soluble phosphate is added to a soil, its solubility in a variety of acids decreased with time.

Other workers have recorded similar changes in solubility, and rate of fixation, of added fertilizer phosphate.

Cecconi (1960) showed that the first products of phosphate fixation are often amorphous and possess a high ability to exchange the phosphate component. This capacity to exchange progressively decreases with the loss of amorphous characteristics during aging.

Benko, Hampl and Vnuk (1963) demonstrated that the fixation of added phosphate increases, and the proportion of water - soluble phosphate decreases, with increasing time of contact of the phosphate with the soil.

Smith and Simpson (1950) were able to show that, in general, the amount of phosphate soluble in water decreases rapidly with time, following phosphate additions over a variety of soil types.

Sell and Olson (1946) showed that available phosphate (i.e. soluble in 0.7N HCl + 0.3% ammonium molybdate) in a grazed pasture decreases with time when the phosphate was topdressed or incorporated into the soil. The depletion was greatest with the highest rate of phosphate application. However, Sell and Olsen could not decide whether the loss of valuable phosphate was due to removal by plant and animal, or to soil fixation.

Sillampaa (I96I) concluded that fixation of fertilizer phosphate was rapid immediately following its application to the soil, but progressively slowed down so as to exhibit a " double logarithmic function of time."

Chiang (I963) showed that when soils, both acidic and alkaline, were waterlogged, the amount of soluble phosphate increased as a result of hydrolysis of the difficultly-soluble aluminium-bound, and iron-bound, phosphates which were present before waterlogging.

There are few reports in the literature concerning the fraction of phosphate,added to soils, that remains in an exchangeable form for any length of time. This has probably been due to the lack of suitable techniques for a careful appraisal of the problem.

Mattingly, Russell and Jephcott (I963) showed that about one-half of the phosphate given in consecutive applications of superphosphate to the soil remained isotopically exchangeable, and about one-third still exchanged after phosphate additions had ceased for two years.