"THE FATE OF APPLIED PHOSPHATE IN A NEW ZEALAND YELLOW-GREY EARTH, AS INFLUENCED BY PHOSPHATE CARRIER AND SOIL REACTION."

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PART I

A. INTRODUCTION

A considerable amount of evidence has been accumulated in support of the presence in soils of iron, aluminium, and calcium bound phosphorus, as products of the phosphorus fixation process, but the quantitative evaluation of these forms has been continuously hampered by the lack of suitable procedures for their separate and selective determination.

Although the separate determination of calcium bound phosphorus has been successful (Fraps, 1906; Fisher and Thomas, 1935; Ghani, 1943a) a procedure for the separate determination of iron and aluminium bound phosphorus was not available until recently when Chang and Jackson (1957) included such a method in their proposed scheme for the fractionation of soil phosphorus. Theirs is a definite advance on previous procedures as it has been generally considered that, at least in acid soils, these two forms represent the dominant products of phosphorus fixation, while their relative abundance may be expected to vary considerably in different soils and under different soil conditions. Fife (1959-I, 1959-II) modified the procedure of Chang and Jackson for the separate estimation of Al-P, and (priv.comm.) developed procedures for the selective determination of iron, calcium, and organic P.

The object of the present study was to investigate what information these methods could provide concerning the trends of P. fixation in a New Zealand Yellow-Grey Earth from a long term field experiment, embodying three forms of phosphate fertiliser, applied with or without lime.

B. REVIEW OF THE LITERATURE

1. The fractionation of soil phosphorus

The use of selective chemical extracting solutions, which offer the opportunity to define discrete forms of soil phosphorus are an advance over those chemical extractants which determine that portion of soil phosphorus which may be available to plants, as these methods are empirical and hence must be calibrated against field experiments before useful information can be obtained. On the other hand the selective determination of soil phosphorus fractions appears to produce less empirical results since a knowledge of the nature of the various phosphate compounds in a soil, together with a knowledge of the conditions under which these different forms are available to the growing crop, gives a much more general means of assessing availability.

Fraps (1906), and Fisher and Thomas (1935) employed an acetic acid-Sodium acetate buffer at pH 5.0 for various extracting periods. Dilute H_2SO_4 at pH 3.0 was also used. These workers classified their results as:

1. Ca, Mg, and Mn phosphates;
2. Fe and Al phosphates;
3. Absorbed P and apatite.

Williams (1937) introduced NaOH as a selective extractant, and divided the forms of soil phosphorus into:

1. Alkali soluble P, said to include organic P, exchangeable P, and the more soluble inorganic forms such as water soluble -, dicalcium -, and sesquioxide-P;

2. Alkali insoluble P, consisting of apatites, possibly Titanium -, and crystal lattice-P.

Alkali and acid extractions were combined by Dean (1938), who suggested three soil phosphorus fractions;

1. Organic compounds, soluble in 0.25 n NaOH;
2. Inorganic compounds, dissolved by 0.25 n NaOH and 0.5 n H_2SO_4;
3. Insoluble compounds.

When it was found that soluble and exchangeable Ca and Mg interfered in the alkali extractions, Ghani (1943a) modified

Dean's procedure by making a pre-extraction with 0.2 n acetic acid, which was then followed by a succession of extractions with 0.25 n NaOH, and finally by an extraction with 2 n H_2SO_4. Five fractions were thus obtained:

1. Acetic acid soluble P; mono-, di-, and tricalcium phosphates
2. Alkali soluble inorganic P; Fe- and Al- phosphates;
3. Alkali soluble organic P;
4. Strong acid soluble P of the apatite type;
5. Insoluble P.

It was noticed that some P was being resorbed during the acetic acid extraction, which would subsequently be extracted by NaOH. Thus Ghani (1943C) modified his procedure by employing 8-hydroxy quinoline as a sorption blocking agent.

The use of 8-hydroxy quinoline was further explored by Williams (1950). He adapted Ghani's procedure and made successive extractions with 2.5% acetic acid and 1% 8-hydroxy quinoline, followed this with 0.1 n NaOH, and omitted the final extraction with H_2SO_4.

A different scheme for the fractionation of soil P was proposed by Bray and Kurtz (1945).

1. Total P was determined by the perchlorate digestion method of Sherman (1942).

2. Organic P was determined by essentially the method of Dickman and De Turk (1938).

3. Available P was determined by an extractant which consisted of 0.5 n Hcl and neutral 0.5 M.NH_4F. After the acid soluble forms of P had been dissolved, the subsequently added NH_4F would dissolve the remaining forms. The acid soluble forms could then be calculated by difference. Baewin and Tyner (1954) adopted this procedure and classified the soil P fraction as;

1. Total P; as suggested by Bray and Kurtz;
2. Extractable P; the sum of organic, acid soluble, and adsorbed forms;
3. Non extractable P - as the difference between (1) and (2).

Since Turner and Rice (1954) found that neutral NH_4F would

isolate Al - P, but not Fe - P, Chang and Jackson (1957) concluded that the method for "available P" of Bray and Kurtz would largely be a determination of Al - P.

Chang and Jackson (1957) adopted the use of neutral NH_4F for the discrete delineation of Al - P, and included the method in their proposed scheme of soil-P fractionation. Briefly their procedure is as follows; using a single sample of soil throughout, and washing the residue after each extraction twice with saturated NaCl solution to remove the reagents;

1. Pre-extract for 30 minutes with 1 n NH_4Cl to remove water soluble P and exchangeable Ca,

2. Extract Al - P at a 1:50 soil/solution ratio with neutral 0.5 M.NH_4F for 1 hour.

3. Extract Fe-P (1: 50 ratio) with 0.1 n NaOH for 17 hours.

4. Extract Ca-P (1: 50 ratio) with 0.5 n H_2SO_4 for 1 hour.

5. Extract "reductant soluble Fe-P" by the citrate-dithionite method of Aguilera and Jackson (1953). This time the washings are combined with the extract.

6. Extract "r.s. Al-P" with neutral 0.5 M.NH_4F, as under (2), or alternatively extract "r.s. Fe-Al-P" with 0.1 n NaOH, as under (3

7. Organic P is determined by the method of Bray and Kurtz (1945).

It has been suggested by Saunders (1959) and Yuan and Fiskell (1959) that the citrate-dithionite method is not specific for "reductant soluble Fe-P", but that appreciable amounts of 'r.s. Al-P" may be removed also.

Several modifications have been suggested by Aung Khin and Leeper (1960);

a. Extract Al-P with 0.5 M.NH_4F at pH 8.5 as proposed by Fife (1959-I).

b. Extract organic P after a more drastic treatment with H_2O_2 than employed by Bray and Kurtz.

c. Subject at least two separate samples to the procedure; one for the stages (1) to (4), the other for the stages (5) to (7), executing stage (7) first.

The modified procedure for the extraction of Al-P has been further refined by Fife (priv. comm.), and is included in a scheme for the fractionation of soil phosphorus developed by him (priv. comm.).

2. The fate of applied phosphate

From evidence in the literature it appears that the phosphate, liberated during the decomposition of fertiliser particles, is fixed in the top inch of an undisturbed soil, (Fiskell et al, 1953) and that the greatest proportion of fixed P may be accounted for in the clay fraction (Fine and Bartholomew, 1946; Moschler et al, 1957). Variations in the penetration of P down the soil profile are due to such factors as texture (Stephenson and Chapman, 1931; Pathak et al, 1950), drainage (McGregor, 1953; Lawton and Vomocil, 1954), the amount of P applied (Smith and Simpson, 1950; Heslep and Black, 1954) and its solubility in water (Haasjes and Sissingh, 1953, the sesquioxide content of the soil (Heck, 1934), and the pH, controlling cationactivity (Chang and Jackson, 1958); but the accumulation of P below the upper soil layer appears mainly due to biological activity distributing P in the organic form (Williams, 1950; Sandal and Garey, 1954; Jackman, 1955). The major inorganic complexes concerned with P fixation are calcium, aluminium, and iron (Dean, 1949; Wild, 1950; Williams, 1952).

From his studies on the fixation of applied P in an acid soil from Rothamsted, and a neutral soil from the Woburn plots, Dean (1938) concluded that, whereas in the acid soil P occurred mainly as Fe-P and Al-P, in the neutral soil P would be found mainly fixed as apatite or tri-Ca-P, and that many neutral and calcareous soils contained much P not fixed as apatite, while in acid soils P would also be present as apatite or tri-Ca-P.

For their studies on corn belt soils Bray and Kurtz (1945) found that both "adsorbed" and "acid soluble" P occurred. They showed that in soils of pH < 6 added soluble phosphates and acid soluble (rock-) phosphate tended to change into the relatively more

abundant adsorbed forms; an opposite trend was found to occur in soils of pH > 6 where adsorbed forms and added soluble phosphates changed into acid soluble forms while added acid soluble phosphates did not. They regarded pH 6 as the critical boundary between adsorbed and acid soluble forms of P in these soils. Williams (1950-I, 1950-II), in a study of some Australian pasture soils, also found that soil acidity had a considerable effect on the forms in which added P was fixed; at a high pH more P was retained in an acid soluble form (Ca-P) whereas at a low pH the alkali soluble forms were more abundant. (Fe-P and Al-P) Williams also found that phosphate topdressing would increase both organic and inorganic P forms in the soil, and also non extractable P. The accumulation of organic P was found to be disproportional to the amounts of P applied, and tended to approach a constant value irrespective of the amount and nature of the fertiliser applie Although the accumulation of inorganic P was directly proportional to the amounts applied, the use of Super, Basic Slag, or Rock phosph ate would lead to different distributions of inorganic P fractions. Where Super was applied the increase in inorganic P was equally divided between the acetic acid and alkali soluble fractions. Where Rock phosphate was applied most of the phosphorus was extracted in the acetic acid soluble fraction. The application of Basic Slag resulted in a greater increase in the acetic acid soluble fraction and a smaller increase in the alkali soluble fraction than in the soils to which Super had been applied.

Chang and Jackson (1958) subjected a number of samples, representing some widely different major soil groups, to their fractionation procedure. From this study they concluded that the formation of the various discrete chemical forms of phosphate in the soil apparently depended on such soil factors as pH, cation activity, solubility product of the various phosphates, degree of chemical weathering, and fertiliser practice. Immediately after the application of phosphate fertiliser Ca-P and Al-P were more likely to be formed than Fe-P due to the relatively higher activities in the soil of Ca and Al ions than Fe ions. Al-P at

first would increase more than Fe-P. As time elapsed, Ca-P and Al-P would change gradually into Fe-P, the least soluble form of these three. These three forms were found to occur not only in acid soils but also at neutral soil reactions, according to the principle of solubility product (Kittrick and Jackson, 1955 B, 1955 C, 1956; Chang and Jackson, 1957 C). Since Ca-P is more soluble than the other forms it would more easily be removed by crops, or shifted to the less soluble forms. However, an increase in the calcium activity and pH by liming would appear to favour the formation of Ca-P and the release, through repression of Fe and Al activity (Cole and Jackson, 1951), of P from the Al-P and Fe-P forms for plant use.