# LABORATORY STUDY ON THE
# FATE AND REACTIVITY OF PHOSPHATE
# ADDED TO YELLOW BROWN PUMICE SOILS.

Thesis

presented at Massey University of
Manawatu in part fulfilment of the
requirements for the Degree of Master
of Agricultural Science.

By

Hong-hee Chuah.

- 1965 -

# TABLE OF CONTENTS

# LIST OF TABLES.

TABLE PAGE

# LIST OF PLATES AND FIGURES.

PLATE

FIGURES

# I. INTRODUCTION

Volcanic ash blankets almost two-thirds of the North Island (Baumgart 1954). Of the volcanic ash soils, rather more than one third are classified as yellow brown pumice soils (Baumgart 1954) derived from rhyolitic pumiceous ash having clay fractions made up principally of allophane (Fieldes and Taylor 1961). This mineral shows a considerable capacity for fixing phosphate (Jackman 1951). Yellow brown pumice soils present an interesting field of research for the soil scientist, since they are among the most dynamic of soils - their equilibrium with the environment is quite unstable (Baumgart 1954). An attempt is being made in New Zealand to bring the yellow brown pumice soils to a high level of production through both foresting and agriculture. Phosphate topdressing is essential for establishment and maintenance of improved pastures. It appears from the results of Jackman (1955) that a substantial proportion of fertilizer phosphate becomes converted to organic forms and accumulates as such. He has shown also that these soils in the virgin state contain a high proportion of their total phosphorus in the organic form.

Less information is available on the trend of inorganic fixation of phosphate in these soils and the laboratory studies reported herein, were undertaken with a view to elucidating these trends. In particular, in-

information was sought on the relative significance of aluminium-,iron- and calcium-binding of phosphate as influenced by time of contact between added phosphate and soil, and on changes in the solubility and exchangeability of phosphate occuring throughout the time of contact.

To these ends use was made of

(a) The phosphate fractionation procedures developed by Fife (Fife 1959a,b; 1962; 1963; priv. comm.),

(b) Truog's procedure for the determination of available phosphate (Truog 1930),

(c) An anion exchange resin technique (Saunders and Metelerkamp 1962, Cooke and Hislop 1963, Saunders 1964, Fife and Spedding priv. comm.)

(d) A radio-isotopic exchange procedure (Furkert 1962, Shao 1963, Spedding priv. comm.).

## 11. REVIEW OF LITERATURE

### THE MECHANISM OF PHOSPHATE RETENTION

The general field of phosphate fixation has been the subject of a number of comprehensive reviews (Midgley 1940, Dean 1949, Wild 1950, Hemwall 1957) and it is proposed to limit the present discussion to a review of literature considered to have a direct bearing on the work being undertaken.

It has been shown that iron and aluminium oxides and hydroxides and clay minerals are capable of removing large amounts of phosphate from solution. This phenomenon has been well reviewed and studied (Midgley 1940, Dean 1949, Wild 1950, Hemwall 1957).

The relationship between phosphate retention and pH in the presence of aluminium, iron and calcium has been investigated by many workers (Teakle 1928, Gaarder 1930, Mattson et al 1957, Miller 1954). From the consideration of this literature Saunders (1959) concluded that three generalization can be made,

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

(b) In calcium systems the phosphate in solution is at a minimum about pH 6.

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

The effect of the removal of iron or aluminium or both from clays or soils on their ability to retain phosphorus has been used to evaluate the role of iron and aluminium compounds in the fixation of phosphorus (Toth 1937, Romine and Metzger 1939, Metzger 1940, Chandler 1941, Black 1949, Coleman 1942). Treatments which remove a part of the iron or aluminium, result in a reduction in phosphate retention. Such treatments do not completely eliminate significant retention by the residual materials.

Allophane, which has an approximate mineral composition represented by $Al_2O_3$, $SiO_2$,$nH_2O$, is the predominant mineral in the clay fraction of soils derived from rhyolitic and andesitic volcanic ash. In soils from rhyolitic ash, the amount present may be only a few per cent of the soil, but in those from the andesitic members it may reach 60% (Birrell 1954). The Si:Al ratio of allophane may vary from 1.01-1.78(Birrell and Fieldes 1952) to 0.8-2.0 (Fieldes 1955). Taylor (1953) suggested that the reason for the generally low ratio of silica to alumina was due mainly to early loss of silica during the initial breakdown of clays. Fieldes (1955) showed that allophane B was dominant in yellow brown pumice soils and allophane A in yellow brown loam. In allophane B the amorphous hydrous oxides of aluminium and silica are discrete and with increasing age grow together to form allophane A where very few small particles of solid hydrous Al-oxides are randomly cross-linked by tetrahedral Si (Fieldes and Taylor 1961). Because of its high content of aluminium and very small particle size (less than 100 Å), these minerals have been regarded as important fixers of soil phosphate.

Saunders (1959c) studied the retention of phosphate by a soil derived from andesitic volcanic ash and containing allophane as the dominant colloidal constituent. He found the retention to be greatest between pH 3.5 and pH 7, falling off rapidly above and below this range. He also found that allophane is rapidly converted to taranakite, an insoluble phosphate, following treatment with 1M ammonium phosphate at pH4. Fieldes and Schofield (1960) suggested that phosphate was held in a difficultly available form at tetrahedral aluminium sites similar to montmorillonite where aluminium substitutes extensively for silicon in tetrahedral positions. Birrell (1961), showed that Tirau ash clay fraction, when treated with either ammonium or potassium dihydrogen phosphate at pH 4, formed the phosphate mineral taranakite.

The explanation by Birrell (1961) and Fieldes (1962) of phosphate fixation by allophane is that anionic groups containing $O_2$ can coordinate at tetrahedral aluminium sites; anions like phosphate with pentavalent elements in tetrahedral coordination are most strongly retained because the valence contribution (+$\frac{3}{4}$ from Al and 5/4 from P) balance the -2 from oxygen, resulting in structural stability, thus $(\text{-SiO})_{3}\equiv\text{Al}\overset{\frac{3}{4}}{\text{——}}\text{O}\overset{5/4}{\text{——}}\text{P}$.

Birrell (1961) showed that by treating allophane with soluble $NH_4$-phosphate about 25% of the silica content was dissolved. He concluded that the main mechanism likely to occur would be solution of alumina followed by precipitation of taranakite. He also showed that allophane type soils develop a considerable negative charge in the range pH 6-7.5 and are strongly buffering in this range. This effect appears to be related to the Al which is in tetrahedral form.

Hemwall (1957) in an extensive review concluded that the formation of insoluble iron and aluminium compounds of the nature of $M(H_2O)_x(OH)_y.H_2PO_4$, is governed by the solubility product principle (Kittrick and Jackson 1955a,c; 1956), the common ion effect and salt effects. Under certain conditions a precipitate is formed, whereas under other conditions the phosphate is adsorbed.

Chang and Chu (1961) reported that added soluble phosphate is mainly fixed as aluminium phosphate followed by iron phosphate and then by calcium phosphate regardless of soil pH. They found that when the time of contact was prolonged the amount of iron phosphate increased with corresponding decrease in the amounts of aluminium and calcium phosphates. The rate of change increased with the moisture content of the soil.

They further suggested that the first stage of fixation of added soluble phosphate by cations would occur at the surface of the solid phase and that the relative amounts and kinds of phosphate formed would depend of the specific surface area of the solid phase associated with aluminium, iron and calcium. Since the major constituent of clay is aluminium, the most likely initial form of phosphate fixed would be aluminium-bound. However, because the solubility product of iron-bound phosphate is lower than that of either aluminium-or calcium-bound-phosphate, they concluded that as time elapsed the aluminium-and calcium-bound forms of phosphate in the soil would probably change to iron-bound forms.

Lavety and McLean (1961) showed that soils of low fixation capacity tied up 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 phosphate fixation capacity.

Volk and McLean (1963) showed a tendency for the recovery of more than half the applied phosphate as iron-bound phosphate in soils of high phosphate-fixing capacity and more than half as aluminium-bound phosphate in soils of low phosphate—fixing capacity.

Hsu (1964) studied the adsorption of phosphate by aluminium and iron in soil. He found that in slightly acid soils treated with dilute phosphate solution at pH 7, two reactions were operating at different rates. The one that proceeded more rapidly was believed to be due to surface adsorption of phoshate by the amorphous aluminium hydroxide and iron oxide in the soil. The subsequent slow reaction was due to similar surface reactive components developed during the ageing process.

Lindsay, Frazier and Stephenson (1962) used X-ray, petrographic and chemical analysis methods to identify the reaction products following the addition of various fertilizer solutions to soils and soil constituents. They demonstrated the formation of approximately 30 crystalline phosphate compounds as well as several colloidal precipitates of variable composition.

Saunders (1965) studied phosphate retention from $KH_2PO_4$ solution at pH 4.6 in some New Zealand soil profiles, from sedimentary and volcanic parent materials, arranged in sequences of increasing weathering and leaching. He found that phosphate retention from $KH_2PO_4$ solution correlated closely with P retention measured by adding solid $Ca(H_2PO_4)_2H_2O$ to moist soil. He also found that P retention by topsoils correlated closely with organic carbon, total nitrogen, loss in ignition, organic phosphorus, Tamm Al and Fe and neutral citrate-dithionite Fe. Subsoil P retention correlated closely with Tamm Al and Fe and citrate-dithionite Fe. Soil organic matter was not considered to be directly concerned in P retention; the correlation with P retention followed from a close correlation between soil organic matter and Tamm Al-Fe. He also pointed out that on each parent material, Tamm Al and Fe and P retention increased with degree of weathering to a maximum in moderately weathered soils of silt texture and then decreased in strongly weathered soils of clay texture. With increasing degree of leaching within the profile P retention and Tamm Al and Fe decreased in topsoils and increased in subsoils. P retention per unit of Tamm Al and Fe was similar in topsoils and in subsoils. Where allophane lowered the P retention per unit of Tamm Al and Fe, the soils were found to contain appreciable Tamm Si. He explained this behaviour on the grounds that Tamm Si combined with Tamm Al and Fe, thereby preventing P retention by the Al and Fe.

The retention of phosphate by the non-living organic matter in soil is believed to be small (Burd 1948), (Pierre 1948). Doughty gave evidence that such retention as there is due to a reaction of the phosphate with Fe, Al and Ca ions which are associated with the organic matter (Doughty 1930, 1935). Chaminade (1946) reported that humus forms a complex with phosphate ions which is not readily precipitated by Ca ions, even at high pH values. Other workers have shown that the humate ion can replace the phosphate ions that are adsorbed by clay minerals and by artifical alumino-silicates (Mattson 1931, 1950). In laboratory studies, organic anions, such as oxalate, citrate and tartrate, which complex iron and aluminium, reduce phosphate retention by aluminium and iron compounds (Swenson, Cole and Seiling 1949). Jackman (1955) had reported that fertilizer phosphorus topdressed on permanent pastures, is partly converted into organic form in the soil especially in soils derived from rhyolitic pumice which were found to contain up to 80% of their total phosphate in organic form and to accumulate fertilizer phosphorus in this form. He quoted evidence from Goring and Bartholomew (1952) that aluminium may be important insofar as nucleic acids are held by phosphate bounds to bentonite and kaolinite, and that adsorption, together with the formation of insoluble aluminium organic phosphates, could well account for the stabilization of organic phosphate by allophane.

Dixon (1954) showed in one experiment on a pumice soil, that 50 per cent of the phosphorus applied to a 12-year old pasture was recovered; of this, 80-90 per cent was in organic form. He suggested three alternative explanations, (1) phosphorus occuring in the organic matter is bound through protein groups to allophane,(2) the organic phosphorus is unbound and not decomposed because of inactivation of phosphatase by allophane,(3) allophane itself fixes the phosphorus. The third possibility is open to question since Saunders (priv. comm. with Dixon) has found relatively low absorption of phosphate from solution by an allophane sample separated from a geological specimen.

Microorganisms also play a part in phosphate retention. Pierre(1948) suggested that microorganisms may immobilize a large amount of phosphate when a source of nitrogen and energy is available. Taylor (1946) found that the fixation of phosphate by a garden soil was substantially increased by the addition of peptone, urea and blood meal. Sterilization of the soil by heat and by certain chemicals prevented this increase, but did not reduce the amount of phosphate retained when no organic supplements had been given. Wild (1950) concluded that inorganic phosphate is unlikely to be metabolized by microorganisms in the soil unless phosphate supply is a limiting factor.

## THE FRACTIONATION OF SOIL PHOSPHORUS

The chemical methods for the estimation of the different forms of phosphate in soils are based on the use of a series of selective extracting solutions.

Fisher and Thomas (1935), by extracting separate samples of soil with acetic acid-sodium acetate buffer at pH 4.98-5.02 for different periods of time, and also with dilute sulphuric acid at pH 2, attempted the fractionation of soil phosphates into three groups comprising:

(a) Amorphous and finely divided crystalline phosphates of calcium, magnesium and manganese,

(b) Amorphous phosphates of aluminium and iron,

(c) Phosphorus absorbed upon hydrous oxides and that present in the apatite forms.

Williams (1937) using boiling sodium hydroxide as an extractant divided the soil phosphorus into:

(a) An alkali soluble fraction, said to include organic phosphorus, exchangeable phosphate and the more soluble inorganic phosphate such as sesquioxide-bound phosphate, dicalcic phosphate and any water soluble phosphate,

(b) Possibly titanium phosphate and crystal lattice phosphate, and

(c) the alkali-insoluble fraction consisting of apatite.

Dean (1937,1938), extended this fractionation by following the 0.25 N sodium hydroxide extractant at 95°C with an extraction with dilute (0.5 N) sulphuric acid. He suggested that the sodium hydroxide extraction removed mainly iron and aluminium phosphate and mono- and di-calcium phosphate as an inorganic fraction. The sulphuric acid extraction then removed mainly tricalcium phosphate and apatites. A fourth fraction was that part insoluble in either of these extractants.

Dean also stressed that exchangeable calcium had a marked effect on the solubility of inorganic phosphorus in sodium hydroxide. Alkali extraction of soils requires pretreatment of the soil with a sodium salt solution (such as sodium acetate) in order to eliminate interference from soluble or exchangeable calcium and magnesium.

Ghani's modification of Dean's method incorporates an initial extraction with 0.5N acetic acid followed by successive extractions with 0.25N NaOH and finally with sulphuric acid. Ghani claimed that the acetic acid extracted principally mono-,di- and tri-calcium phosphate, the sodium hydroxide extracted the organic phosphorus and the combined iron and aluminium phosphates, while the sulphuric acid extracted principally apatites.

The main disadvantage of Ghani's method is that some of the phosphate brought into solution by the acetic acid is readsorbed by the soil and is then extracted during the sodium hydroxide extraction. To overcome this, Ghani (1943b) suggested the use of 8-hydroxy-quinoline as a means of blocking readsorption or precipitation of phosphate by active iron and aluminium during the acetic acid extraction.

This suggestion was further explored by Williams (1950a, b,c). He employed successive single extraction with 2.5% acetic-acid-1%-8-hydroxy-quinoline solution (which has a pH of 3.9) and 0.1N sodium hydroxide.

In some of these methods (Ghani 1943, Williams 1950), the acid extractions which preceded the alkali extraction was shown to remove not only calcium phosphate but also considerable aluminium and iron phosphate. Further, in these methods no separation of iron and aluminium phosphate is achieved.

Turner and Rice (1954) found that neutral ammonium fluoride can dissolve aluminium phosphate but not iron phosphate. Chang and Jackson (1957) suggested that the method used for the determination of available phosphate by Bray and Kurtz (1945) should be selective for aluminium phosphate.

Chang and Jackson (1957) put forward an analytical scheme for identifying each of several kinds of phosphorus compounds in soils. This was based on the selective solubility of phosphate in various extractants. They classified the soil phosphorus into the discrete chemical forms: calcium phosphate, aluminium phosphate, iron phosphate, reductant soluble (iron oxide coated) iron phosphate and occluded aluminium-iron phosphate. Briefly, their methods of fractionation are as follows:

(a) Pretreat soil sample with 1N $NH_4Cl$ for 30 minutes to remove water soluble, loosely bound phosphate and the exchangeable calcium.

(b) Extract Al-phosphate from the $NH_4$-soil with 0.5N $NH_4F$ one hour.

(c) Extract Fe-phosphate from residue with 0.1N NaOH for 17 hours.

(d) Extract Ca-phosphate from residue with 0.5 N $H_2SO_4$ for 1 hour (Dean 1938). (NaCl solution is used to wash soil residues after treatments b,c,d.)

(e) Extract the reductant soluble Fe-phosphate with citrate-dithionite at pH 7 (adapted from the method of Aguilera and Jackson, 1953).

(f) Extract again with (1) neutral $NH_4F$ as in (b) for occluded Al-phosphate or (2) with 0.1 N NaOH as in (c) for occluded Al-, and Fe-phosphate.

(g) Determine organic phosphate on a separate sample by the method of Bray and Kurtz (1945).

These procedures have been criticized and modified, (Fife 1959a,b; 1962, 1963; Glean et al 1959; Saunders 1959; Yuan and Fiskell 1959; Khin and Leeper 1960).

Saunders (1959) and Yuan and Fiskell (1959) suggested that the citrate-dithionite attacked iron and aluminium indiscriminately. Therefore it should not be used to distinguish the so-called reductant soluble iron phosphate.

Khin and Leeper (1960) made the modification:

(a) Extracting Al-phosphate with 0.5 N $NH_4F$ at pH 8.5 as proposed by Fife instead of pH7.

(b) Using stronger $H_2O_2$ and longer period of disgestion for organic phosphate.

Fife (1959a,b, 1962,1963) carried out critical studies in soil and non-soil systems of the solubility characteristics of iron-bound phosphate and aluminium-bound phosphate in 0.5N $NH_4F$ over a range of pH. His results were consistent with iron-bound phosphate possessing considerable resistance to alkaline hydrolysis in 0.5N $NH_4F$ and showed that the most general selective delineation of aluminium-bound phosphate by this extractant is likely to be attained at approximately pH 8.5. He has also advanced (priv.comm.) a method for fractionating soil phosphate; the detail of this procedure is given under "Methods".

## THE ISOTOPIC EXCHANGE KINETIC METHODS.

Russel, Rickson, Adams and Seatz (1954) suggested that all inorganic phosphate fractions in soil must be regarded as undergoing exchange although at very different rates. Depending on the nature of the soils, on the exchangeable cation present and on the surface development of the precipitated phosphate present, the rate of the process may vary widely.

It is through the use of the radio-isotope, $^{32}P$, as a tracer for the phosphate exchange reaction between solid-liquid phase that the studies of the exchange reaction are possible. Many workers such as McAuliffe, Hall, Dean and Hendricks (1948); Wiklander (1950) and Russel, Rickson, Adams (1954) and Seatz (1954) have used $^{32}P$ in the study of phosphate exchange reactions.

McAuliffe et al (1948) considered that the basic soil reactions involving $^{32}P$ phosphate were:

$$\text{Surface phosphate-P}^{31} + \text{solution phosphate-P}^{32} \rightleftharpoons \text{Surface phosphate-P}^{32} + \text{solution phosphate-P}^{31}$$

The extent of surface reaction can be estimated at equilibrium for the above reaction, namely

$$\frac{\text{Surface phosphate-}P^{32}}{\text{Solution phosphate-}P^{32}} = \frac{\text{Surface phosphate-}P^{31}}{\text{Solution phosphate-}P^{31}}$$

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

They applied $P^{32}$ to study the exchange between solution and solid phase phosphate. They allowed soils to equilibrate with water for 4 days then added a quantity of carrier free $P^{32}$ which was considered would cause no significant change in the phosphate content of the solution. Exchange was measured by observing the disappearance of $P^{32}$ from the solution. A part of the soil phosphate was found to equilibrate rapidly by exchange with the solution. The amount of this rapidly equilibrating surface phosphate was found to parallel other estimates of phosphate availability. A slower, less reversible exchange of phosphate was also recognized.

The mechanism of phosphate sorption and kinetics of phosphate exchange in soil was investigated with the aid of $^{32}P$ by Wiklander (1950). He used another approach. Samples of soil were shaken with labelled phosphate for 3 days, following which the bathing solution was replaced by a solution of unlabelled phosphate of equal concentration and the return of $P^{32}$ to the solution was observed.

According to Wiklander, the exchange seemed to be composed of 2 separate reactions: the primary rapid ion exchange between solution phosphate ($P_s$) and the micellar phosphate ($P_m^*$), the main part being exchanged in 10 minutes;

and the secondary exchange between the micellar $(P_m)$ and the fixed phosphate $(P_f^*)$, the latter progressing slowly. The rapid exchange can be written:

$$P_s + P_m^* \; = = = = = = = = = = = \; P_m + P_s^* \quad \ldots\ldots\ldots\ldots\ldots \quad (1)$$

and the secondary process as;

$$P_m + P_f^* \; = = = = = = = = = = = \; P_f + P_m^*$$

This reaction is of a chemical nature and the law of mass action can therefore be applied,

$$\frac{(P)_f \cdot (P^*)_m}{(P)_m \cdot (P^*)_f} = K \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (2)$$

By combining equation (1) and (2) the micellar phosphate is cancelled out which gives:

$$\frac{(P)_f \cdot (P^*)_s}{(P)_s \cdot (P^*)_f} = K \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (3)$$

He also further stressed that, from this evidence, the law of mass action governs the reaction between the phosphate in the soil solution and the phospate fixed by the soil.

He also commented that if the exchange reaction is allowed to proceed until equilibrium is reached, the ratio $P^*_{\text{solution}}/P^*_{\text{soil}}$ must be equal to the same ratio of P. This implies that the thermodynamic constant K has the value 1. To express the momentary or apparent equilibrium state, K has to be multiplied with a coefficient, $\beta$, the magnitude of which grows to the limit value 1 as the reaction approaches true equilibrium; thus $0 < \beta K < 1$. If the relation between $\beta$ and the reaction time were known, then the time required to reach equilibrium could be determined.

Russell et al (1954) indicated the nature of exchange reaction by showing that if an aliquot of soil is suspended in a solution containing $(x)P^{31}$ and $(y)P^{32}$ and isotopic exchange occurs, then, $\frac{y}{x + E_t} = \frac{y_t}{x_t}$ ................ (1)

where $(x_t)$ and $(y_t)$ are the amount of $p^{31}$ and $P^{32}$ in the solution after time $(t)$ and $(E_t)$ is the quantity of soil phosphate which has undergone exchange. Hence,

$$E_t = \frac{x_t}{y_t} y-x \text{ ......................(2)}$$

They stated that if an attempt is made to estimate the exchange capacity of a natural soil by this procedure, difficulty arises from the fact that, if the concentration of labelled phosphate used is sufficiently large for accurate colorimetric measurements to be made, sorption will occur simultaneously with isotopic exchange. Thus the effect of sorption on the validity of the calculated result will depend on the rapidity of exchange between the bathing solution and the phosphate sorbed during the experiment. Should exchange be so rapid that the sorbed phosphate remains virtually in equilibrium with the bathing solution the value of $x_t/y_t$ will be unaffected by sorption and no error in the estimation of $E_t$ will result. However, the rate of the process may be affected and the kinetics of exchange cannot therefore be studied. If the phosphate sorbed during the experiment exchanges slowly or not at all with that in the bathing solution, its specific activity will exceed $y_t/x_t$ at time t since exchange necessarily causes the specific activity of solution to decrease during the experiment. The value $x_t/y_t$ will therefore be increased by sorption and isotopic exchange will be overestimated by equation(2).

Russell et al also commented that the validity of the procedure of McAuliffe et al (1948) depends on the two conditions, that the $p^{32}$ is added after equilibtium has been attained and that the carrier added with the $p^{32}$ does not affect the phosphate balance of the system.

The validity of Wiklander's method for estimating the exchangeable phosphate content of the soil clearly depends on equilibrium between the initial labelled solution and all forms of exchangeable phosphate in the soil having been attained before the labelled solution is removed. That this condition was satisfied in Wiklander's investigation appears most improbable since as his results show, equilibrium between the treated soil and the second solution was not reached in 4 days. This suggests that the procedure may give rise to errors which are not readily detectable.

Russel et al (1954) suggested a method that involved shaking aliquots of soil with solutions containing known quantities of $p^{31}$ and $p^{32}$ and observing the change in these quantities. If it could be proved that at the end of the experiment the phosphate which had been sorbed by the soil was isotopic equilibrium with bathing medium, it appeared that an unequivocal estimate of the exchangeable soil phosphate could be made.

Talibudeen (1960) examined the specific activity (S.A.) data for over a hundred arable soils from England and Wales by observing the curvilinear decay in log.(SA) with time. The results show that at least 3 groups of exchanging sites are involved with half-time of exchange 10-30 minutes, 5-15 hours and 40-60 hours. The phosphate in the equilibrium solution, which is removed from the soil during equilibrium, is a part of the more rapidly exchanging category of the total isotopically exchangeable phosphate.

Shao (1962) using $p^{32}$ and mathematical calculation was able to analyse the curve of log. count rate versus time into a number of straight lines (for systems in chemical equilibrium) representing the number of different types of exchangeable inorganic phosphate that were present on the solid phase. He was able to calculate the specific rate constants for all these types of exchangeable inorganic phosphate. By comparing these rate constants, he reached conclusions in respect of:

(a) the numbers of types of exchangeable inorganic phosphate on clay minerals, soils, and ion exchange resins.

(b) the nature of bonding of these phosphates.

(c) relationship between specific rate constants and phosphate availability in soils.

# III. MATERIALS

## Description of soils:

Descriptions of the soils used are presented in Tables 1 and 2. The soil samples were collected from the sites established as modal by New Zealand Soil Bureau and for which complete descriptions were available. (Data on soil profiles 1962).

TABLE 1.

## Description of soils

| Serial No. | Depth ( inch) | Soil Type | Parent Material | Genetic No. | Genetic classification | Predominant sand and clay mineral | Location of soil | Slope and aspect | Altitude ft. | Rain-fall in. |
|---|---|---|---|---|---|---|---|---|---|---|
| 1<br>and<br>2 | 0-8½<br>8½-12½ | Taupo sandy silt | Rhyolitic pumic (Taupo ash) erupted 1700 years ago | 13a. | Moderately leached yellow brown pumice soil | Allophane, glass, andesine, pyroxenes. | Wharepaina, west side of Rotorua-Taupo highway, 5 miles south of Waiotopu | Flat | 1080 | 50 |
| 3<br>and<br>4 | 0-10<br>10-13 | Ngaroma sandy silt | Same as No.1 above | 13a. | Very strongly leached yellow brown pumice soil | Allophane. | Summit Turangakuma Hill | Easy rolling plateau, deeply dissected | 1500 | 70 |
| 5<br>and<br>6 | 0-3<br>3-5½ | Kaingaroa loamy sand | Same as No.1 above | 13a. | Same as No.2 above | Allophane, glass, pyroxenes. | Waimihia road, Kaingaroa forest, 450 yards north from Napier-Taupo highway | 3 degree, North. | 2300 | 55 |
| 7<br>and<br>8 | 0-5½<br>5½-12 | Tirau silt loam | Tirau ash. The top soil includes thin contributions of Taupo and Kaharoa ash | 14a. | Moderately leached central yellow brown loam. | Allophane, glass, andesine. | Hetherington road, Tirau, on roadside 1½ miles east of Tirau and ½ miles south of cemetery | 2 degree, East, near crest of easy rolling ridge. | 400 | 55 |

Table 2

Soil chemistry

chemistry

| Soil Type | Taupo Sandy Silt | | | | | Ngaroma Sandy silt | | | | Kaingaroa Loamy Sand | | | | Tirau Silt Loam | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Depth (inch.) | 0-3 | 5-7 | 7-10 | 14-17 | 17-20 | 0-5 | 7-10 | 16-19 | 24-27 | 0-3 | 5-8 | 8-9½ | 9-15 | 0-3 | 3-7½ | 8-12 | 13-20 | 24-30 |
| Horizon | A | AB | B | C | C | A | B | C1 | C2 | A1 | B2 | BhFe | C1 | A11 | A12 | AB | B | C |
| pH | 4.9 | 5.9 | 5.9 | 6.1 | 6.0 | 5.4 | 5.8 | 6.00 | 6.00 | 4.00 | 5.00 | 5.10 | 5.20 | 5.70 | 5.80 | 5.90 | 6.30 | 6.70 |
| Cation exchange | | | | | | | | | | | | | | | | | | |
| C.E.C. me% | 31.30 | 8.70 | 6.90 | 4.20 | 3.40 | 52.60 | 17.50 | 8.10 | 10.90 | 27.10 | 11.70 | 13.00 | 3.20 | 36.80 | 28.10 | 15.60 | 15.10 | 14.10 |
| T.E.B. me% | 9.60 | 2.10 | 1.90 | 1.80 | 1.90 | | | | | 0.80 | 0.3 | 0.30 | 0.20 | 17.80 | 7.70 | 1.50 | 3.60 | 5.60 |
| B.S. me% | 30.00 | 24.00 | 28.00 | 43.00 | 56.00 | 50.00 | 10.00 | 0.00 | 3.00 | 3.00 | 3.00 | 2.00 | 6.00 | 48.00 | 27.00 | 10.00 | 24.00 | 40.00 |
| Ca me% | 6.80 | 0.90 | 0.70 | 0.60 | 0.30 | 17.90 | 1.00 | 0.20 | 0.10 | 0.40 | 0.20 | 0.20 | 0.10 | 11.80 | 5.20 | 1.20 | 2.50 | 2.40 |
| Mg me% | 2.00 | 0.40 | 0.30 | 0.30 | 0.30 | 7.50 | 0.40 | 0.10 | 0.10 | 0.40 | 0.10 | 0.10 | 0.20 | 4.60 | 1.50 | 0.40 | 0.50 | 2.10 |
| K me% | 0.78 | 0.53 | 0.65 | 0.60 | 0.72 | 1.10 | 0.30 | 0.10 | 0.10 | 0.27 | 0.22 | 0.09 | 0.14 | 1.37 | 0.90 | 0.49 | 0.73 | 0.86 |
| Na me% | 0.20 | 0.20 | 0.30 | 0.40 | 0.50 | 0.30 | 0.30 | 0.10 | 0.10 | 0.20 | 0.20 | 0.30 | 0.30 | 0.20 | 0.10 | 0.00 | 0.10 | 0.30 |
| Organic matter | | | | | | | | | | | | | | | | | | |
| C % | 10.10 | 2.30 | 1.40 | 0.60 | 0.20 | 19.80 | | | | 10.10 | 3.60 | 3.40 | 0.50 | 10.60 | 7.20 | 2.30 | 1.10 | 0.50 |
| N % | 0.52 | 0.14 | 0.10 | 0.05 | 0.02 | 0.69 | | | | 0.42 | 0.18 | 0.14 | 0.03 | 0.87 | 0.60 | 0.24 | 0.12 | 0.06 |
| C/N | 19 | 16 | 14 | 12 | 10 | 29 | | | | 24 | 20 | 24 | 17 | 12 | 12 | 10 | 9 | 9 |
| Phosphorus | | | | | | | | | | | | | | | | | | |
| Total mg P% | 92.00 | | | 31.00 | | | | | | 62.00 | 45.00 | | 28.00 | 143.00 | | 98.00 | 60.00 | 34.00 |
| Organic mg P% | 67.00 | | | 10.00 | | | | | | 36.00 | 22.00 | | 3.00 | 101.00 | | 45.00 | 17.00 | 7.00 |
| Inorganic mg P% | 25.00 | | | 21.00 | | | | | | 26.00 | 23.00 | | 25.00 | 42.00 | | 53.00 | 43.00 | 27.00 |
| Truog mg P% | 0.50 | | | 0.20 | | | | | | 0.70 | 0.20 | | 0.20 | 0.50 | | 0.20 | 0.20 | 0.20 |
| P retention % | 63.00 | | | 43.00 | | | | | | 70.00 | 80.00 | | 45.00 | 95.00 | | 98.00 | 95.00 | 92.00 |
| N/Organic P | 8 | | | 5 | | | | | | 12. | 8 | | 10 | 9 | | 5 | 7 | 9 |
| Tamm oxalate | | | | | | | | | | | | | | | | | | |
| Aluminium % | 0.60 | | | 0.78 | | | | | | 0.61 | 1.09 | | 0.83 | 3.23 | | 4.26 | 4.24 | 2.75 |
| Iron % | 0.30 | | | 0.22 | | | | | | 0.45 | 0.37 | | 0.27 | 0.63 | | 0.85 | 1.10 | 1.08 |

## IV. METHODS

### 1. Preparation of soil samples.

The soil samples employed had been air-dried and ground to pass a 2 mm. sieve. For analysis, sub-samples were ground to pass an 80-mesh sieve.

### 2. Calorimetric determination of phosphate.

Total phosphate was determined on the perchloric acid digests by the method recommended by Bray and Kurtz (1945).

Colour development for all remaining phosphate determinations (apart from Truog values) was carried out by the method of Dickman and Bray (1940). In the determination of Al-bound phosphate, the boric acid procedure of Kurtz (1942) was employed to eliminate interference in colour development by fluoride. Colour measurement was made on a Beckman spectrophotometer at $815 m\mu$.

### 3. Fractionation procedures to determine iron-, aluminium-, calcium- and organically-bound phosphate.

The scheme in outline is as follows:

(a) Iron- and aluminium - bound phosphate were determined together by extracting 0.5 M NaCl preleached samples with 1 N NaOH

(b) Iron-, aluminium- and calcium-bound phosphate were determined by two stage extraction as follows,

(i) 0.01 N HCl solution,

(ii) 1 N NaOH on the residue from the above after 0.5 M NaCl washing and acetone drying.

(c) Calcium-bound phosphate was determined by difference (b - a)

(d) Aluminium bound phosphate was extracted with 0.5 N $NH_4F$ at pH 8.5. Fife (1959a,b,1962, 1963.) has recommended no particular soil: extractant ratio for this extraction but suggests that, for routine study, as high as possible a dilution should be used to offset as much as possible the tendency for phosphate liberated by the 0.5 M $NH_4F$ to recombine with free iron oxides. In the present investigation a ratio of 1:100 was adopted on the basis of the following preliminary experiments.

Taupo sandy silt (mg P/100 g. soil)

| Dilution | 1:100 | | 1:200 | | 1:400 | |
|---|---|---|---|---|---|---|
| Soil layer / Time | Top-soil | Sub-soil | Topsoil | Subsoil | Topsoil | Subsoil |
| 3(hours) | 2.1 | 3.3 | 2.5 | 3.8 | 2.6 | 3.9 |
| 7 | 2.5 | 3.5 | 2.7 | 3.9 | 2.7 | 3.9 |
| 16 | 2.6 | 3.8 | 2.7 | 3.9 | 2.7 | 3.9 |
| 25 | 2.5 | 3.8 | 2.7 | 4.0 | 2.8 | 3.9 |
| 40 | 2.5 | 3.8 | 2.8 | 4.0 | | |

Ngaroma sandy loam (mg P/100 g.soil)

| Dilution | 1:100 | | 1:200 | | 1:400 | |
|---|---|---|---|---|---|---|
| Soil layer / Time | Top-soil | Subsoil | Topsoil | Subsoil | Topsoil | Subsoil |
| 3(hours) | 2.1 | 1.2 | 2.4 | 2.0 | 2.9 | 2.5 |
| 7 | 2.4 | 1.6 | 2.6 | 2.6 | 2.9 | 2.5 |
| 16 | 2.6 | 1.9 | 2.7 | 2.7 | 3.1 | 2.6 |
| 25 | 2.7 | 1.8 | 2.7 | 2.7 | 3.1 | 2.6 |
| 40 | 2.7 | 1.8 | 2.7 | 2.7 | | |

Kaingaroa loamy sand (mg P/100 g.soil)

| Dilution | 1:100 | | 1:200 | | 1:400 | |
|---|---|---|---|---|---|---|
| Soil layer / Time | Topsoil | Subsoil | Topsoil | Subsoil | Topsoil | Subsoil |
| 3(hours) | 3.3 | 1.2 | 3.7 | 1.7 | 3.8 | 1.7 |
| 7 | 3.5 | 1.4 | 3.9 | 1.7 | 4.2 | 1.7 |
| 16 | 3.7 | 1.5 | 4.1 | 1.7 | 4.2 | 1.7 |
| 25 | 3.8 | 1.4 | 4.1 | 1.7 | 4.2 | 1.7 |
| 40 | 3.8 | 1.5 | 4.1 | 1.6 | | |

Tirau silt loam (mg P/100 g. soil)

| Dilution | 1:100 | | 1:200 | | 1:400 | |
|---|---|---|---|---|---|---|
| Soil layer / Time | Topsoil | Subsoil | Topsoil | Subsoil | Topsoil | Subsoil |
| 3(hours) | 36.7 | 17.1 | 41.7 | 21.3 | 44.5 | 25.0 |
| 7 | 41.2 | 22.8 | 44.9 | 27.0 | 46.2 | 29.0 |
| 16 | 41.0 | 24.6 | 46.3 | 28.8 | 47.0 | 29.0 |
| 25 | 41.5 | 24.3 | 46.2 | 28.1 | 47.0 | 29.4 |
| 40 | 41.8 | 25.6 | 46.3 | 28.6 | 47.0 | 30.0 |

These results show that there are no apparent increase in amount of phosphate in the extractant as the extraction time and soil: extractant ratio increase in Taupo sandy silt, Ngaroma sandy loam, Kaingaros loamy sand. This may simply reflect the low amount of Al-bound phosphate in these soils. In Tirau silt loam on the other hand, there is an increase in the amount of phosphate extracted as extraction time and soil: extractant ratio are increased.

(e) The amount of iron-bound phosphate was obtained by subtracting the aluminium phosphate value from that obtained for aluminium- and iron-bound forms.

(f) Organically-bound phosphate was taken as by the difference between the combined 0.01 N HCl and 1N NaOH extraction values found for ignited and unignited samples.

Recently, Dormaar and Webster (1964) have provided evidence that the organic soil phosphorus may not be completely converted to inorganic forms even at temperatures as high as 650°C and that losses by volatilization may occur at temperature as low as 400°C. In view of the probable high proportion of organic phosphorus in yellow brown pumice soils it was considered interest to investigate whether there was any loss of phosphorus by way of volatilization. A further possibility, that an apparent loss of phosphate might arise through conversion of ortho-phosphate to meta-and pyro-phosphate was also borne in mind. (Fife, unpublished data). To test these points 1 ml of 50 ppm P solution was added to 0.25 g. of soil ( i.e. equivalent 20 mg/100 g. soil) and steam dried before ignition. It was ignited at 500-550°C for one hour and extracted with 0.01 N HCl and then following 1 N NaOH. The results obtained as shown below.

| | mg.P/100 g. soil | | | |
|---|---|---|---|---|
| | Ignition Method | | Perchloric acid digest | |
| | Untreated sample | P treated sample | Untreated sample | P treated sample |
| Taupo sandy silt | 52.7 | 72.7 | 55.2 | 73.5 |
| Ngaroma sandy loam | 65.1 | 85.1 | 66.7 | 85.8 |
| Kaingaroa loamy sand | 35.0 | 55.0 | 35.3 | 55.0 |
| Tirau silt loam | 157.1 | 177.9 | 156.4 | 177.3 |

* All samples are top-soil.

The results show that there is no loss of P by way of volatilization during ignition; nor is there any indication of incomplete combustion of the soil organic matter or of conversion of ortho-phosphate to meta- or pyro-phosphate.

### 4. Phosphate extraction procedure using an anion exchange resin.

0.5 g. of soil sample (80 mesh) was placed in a centrifuge tube and one gram of resin (½ mm. diameter) was added. 25 ml. of distilled water was introduced to the tube which was stoppered and shaken on the end-over-end shaker for 16 hours. The resin was then separated from the soil by washing through a fine nylon screen with 100 ml. of distilled water. The resin was quantitatively washed from the screen to a 50 ml. beaker with 25 ml. of 10% NaCl solution and the beaker was placed on a steam bath for one hour. The resin was then filtered and washed with warm 10% NaCl solution until 50 ml. of leachate was obtained. Phosphate was determined on an aliquot of the leachate.

The foregoing procedure which involves removal of phosphate from the resin by NaCl washing was adopted in preference to liberation of phosphate by ignition of the resin; it was found that the latter procedure resulted in substantial loss of phosphate.

### 5. Procedure for laboratory addition of phosphate.

One hundred grams of each soil was evenly spread over a 7½ in. watch glass and a $KH_2PO_4$ solution (100 ml. containing 20,000 ppm P) was added to the soil which was then well mixed and spread out again. The soils were then air-dried and mixed. Each soil was subdivided into 6 batches and bottled in 4 oz.

screw-cap jars. Ten ml. of distilled water were then added to the soil followed by few drops of ether-toluene mixture (Roger 1942, Kurtz et al 1946, Drobnik 1961) to limit microbial activity. The bottles were weighed and sealed. These bottles were occasionally weighed; if any loss of moisture was observed, distilled water was added to make up the loss.

Distilled water and ether-toluene mixture were added to samples of the untreated soils to provide controls. Phosphate-treated soils without toluene were also employed to see whether there was any changes due to microbial activity. In this case the bottles were not sealed from the air, but the amount of moisture was kept constant by keeping the bottles in a container at high humidity to prevent any excessive loss of moisture from the soil. These bottles were occasionally weighed. If any loss of moisture was observed distilled water was added to make up the loss.

## 6. Isotopic exchange kinetic procedure for exchangeable soil phosphate. (Furkert 1962, Shao 1963, Spedding priv. comm.)

### (a) Mathematical analysis of data.

The following mathematical justification is derived from Furkert (1962) (M.Sc. degree thesis. On file, Victoria University of Wellington.)

Experiments with isotopic exchange reactions are carried out in equilibrium systems. In an equilibrium system, if there are A grams of P in the liquid phase and B grams. of exchangeable P in the solid phase and the rate of absorption and desorption is equal to R. If the specific rate constant for the exchange is K, at equilibrium.

$$A \underset{K}{\overset{K}{\rightleftharpoons}} B \qquad \text{then } R = KB.$$

At zero time, a minute quantity of radio-active labelled $^{32}P$ is added to the liquid phase. The chemical equilibrium of the whole system is supposed to remain undisturbed, but due to radio-active inequilibrium, $^{32}P$ in the solution will exchange with exchangeable $^{31}P$ in the solid phase until the whole system has attained the same specific activity. That is, the ratio between $^{32}P$ and $^{31}P$ is the same in both phases. This is possible because the state of chemical equilibrium is dynamic and characterized by a continuous adsorption and dissolution of the same number of $^{31}P$ atoms in a given time.

Thus, if at zero time $T_o$ counts are introduced into the liquid phase, and at time t there are x counts in the solid phase, then there will be $(T_o - x)$ counts remaining in the liquid phase. If the count rate is measured continuously and plotted against time on a strip chart recorder a graph of $(T_o - x)$ versus time t will be obtained. This graph will be a curve and its slope will be equal to the rate of fall of the count rate in the solution phase, that is equal to $\frac{dT}{dt}$ where $T = (T_o - x)$ = count rate at time t.

This curve will gradually flatten out and eventually as the count falls to a steady value, the slope will ~~be~~come to zero.

Now $\frac{dT}{dt}$ = rate at which activity is leaving the solution phase + rate at which it is entering it. (Due to the adsorption and dissolution of the molecules).

i.e. $\frac{dT}{dt} = -\frac{R(T_o - x)}{A} + \frac{Rx}{B} = -\frac{RT_o}{A} + \frac{Rx}{A} + \frac{Rx}{B}$

(where A is the amount of P in the solution and B the amount of exchangeable P in the solid phase.)

Now $T = T_o - x$, therefore $x = T_o - T$

Therefore $\frac{dT}{dt} = -\frac{RT_o}{A} + \left(\frac{RT_o}{A} - \frac{RT}{A}\right) + \left(\frac{RT_o}{B} - \frac{RT}{B}\right)$

i.e. $\frac{dT}{dt} = \frac{RT_o}{B} - \left(\frac{R}{A} + \frac{R}{B}\right) T$ ..................(1)

In order to obtain T as a function of time, equation (1) is integrated. Thus we obtained.

$T = \frac{T_o A}{A+B} + Ce^{\frac{-R(A+B)\ t}{AB}}$ ....................... (2)

where C is a constant, e is the exponential

Now when $t=0$, $T=T_o$, equation (2) becomes

$T_o = \frac{T_o\ A}{A + B} + C$, therefore $C = T_o\left(1 - \frac{A}{A+B}\right) = \frac{T_o\ B}{A+B}$

$T = \frac{T_o\ A}{A+B} + \frac{T_o\ B}{A+B}\ e^{\frac{-R(A+B)t}{AB}}$

i.e. $\frac{T}{T_o} = \frac{A}{A+B} + \frac{B}{A+B}\ e^{-\frac{R(A+B)t}{AB}}$ .............(3)

Now when the count rate has fallen to a steady value, then this value will be the same as that for $t=\infty$, and if at $t=\infty$, $T=Z$ then from (3)

$\frac{Z}{T_o} = \frac{A}{A+B}$

If a graph is now prepared of $\log_e T$ versus, t, a curve levelling off to steady value will be obtained. This steady value may be subtracted from the rest of the curve, where the resultant graph will be a straight line. As this steady value is equal to $\frac{T_oA}{A+B}$, the straight line will be correspond to the exponential part of the equation (3) and will be related to the exchangeable $^{31}P$ 'B' on the soil. For if this line cuts the $t=0$ axis at x then Z (= $\frac{AT_o}{A+B}$) has been subtracted from the curve, x = $\frac{T_oB}{A+B}$

$$\text{i.e. } \frac{x}{T_o} = \frac{B}{A+B} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (4)$$

If there are two (or more) types of exchangeable $^{31}P$ in the solid phase, then a total of two (or more) sloping lines will be obtained with intercepts x,y,w, etc.

As was derived earlier, the rate is equal to the specific rate constant multiplied by the amount of exchangeable $^{31}P$ on the soil-solid phase.

$$\text{i.e. } R = K_bB \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (5)$$

The equation derived for the count rate T at any time t is

$$\frac{T}{T_o} = \frac{A}{A+B} + \frac{B}{A+B}\, e^{-\frac{R(A+B)t}{AB}} \quad \ldots\ldots\ldots (3)$$

and so the new value T' for the count rate after the steady value $\frac{AT_o}{A+B}$ has been removed is given by

$$\frac{T'}{T_o} = \frac{B}{A+B}\, e^{-\frac{R(A+B)t}{AB}}$$

which on substitution of the value for R from the equation (5) gives

$$\frac{T'}{T_o} = \frac{B}{A+B}\, e^{-\frac{K_b(A+B)t}{AB}}$$

which can be written as

$$\log_e\left(\frac{T'}{T_o} \times \frac{A+B}{B}\right) = -\frac{K_b\,(A+B)t}{A} \quad \ldots\ldots\ldots\ldots (6)$$

Now $t_{\frac{1}{2}}$ is the time that the count rate takes to decrease to one half of its original value, and thus equation (6) reduces to $\log_e(\frac{1}{2}) = \frac{-K_b(A+B)t_{\frac{1}{2}}}{A}$ .................... (7)

as $-\log_e \frac{1}{2} = \log_e 2 \doteqdot 0.693$ equation (7) can be written as

$$K_b = \frac{A \times 0.693}{(A+B)t_{\frac{1}{2}}} \quad .................... (8)$$

If there are two or more types of exchangeable $^{31}P$ (B,C,D, etc) on the soil-solid phase, then equation (8) will apply to 'B', where 'B' is the type of $^{31}P$ that exchanges fastest with $^{31}P$ in solution. To obtain a similar equation for 'C', the slower exchanging type of $^{31}P$ on the soil sample, it is considered that the rate of exchange of 'C' is so much slower than that of 'B' that the exchange of 'C' with 'B' and also with 'A' may be considered as indistinguishable. Thus the equation for the determination of the specific rate constant $K_c$ for the exchange of 'C' with the rest of the $^{31}P$ present will be obtained by replacing 'B' by 'C' and 'A' by (A+B) in equation (8) leading to

$$K_c = \frac{+(A+B) \times 0.693}{(A+B+C)t_{\frac{1}{2}}} \quad ,.............. (9)$$

where $t_{\frac{1}{2}}$ now refers to the half-time of exchange of the slower exchanging 'C' type $^{31}P$.

If there are more types of $^{31}P$ (D,E, etc.) on the soil sample their specific rate constant ($K_d$,$K_e$, etc.) will be given by corresponding equation (9) where 'C' is replaced by 'D' and (A+B) by (A+B+C) and so on.

If, after adding $^{32}P$ to the solution, and replotting the data obtained on semi-logarithmic graph paper, a curve is obtained that can be resolved into a steady value Z, and two straight lines with intercepts with axis t=0 of x and y, then the soil sample will have two types of exchangeable $^{31}P$ on it, namely 'B', 'C'.

When the count rate has fallen to a steady value, $^{32}$P will be distributed in equlibrium between solution and solid phase. If it is assumed that $^{32}$P distributed itself in the same ratio as $^{31}$P, then the ratio of the radio activity will be the same as the ratio of the bulk of $^{31}$P present. As the final count rate (steady value) is equal to the initial count rate minus the amount of $^{32}$P adsorbed onto the soil, the ratio:

$$\frac{\text{final count (steady value)}}{\text{initial count}} \text{ and } \frac{^{31}\text{P in solution}}{^{31}\text{P in solution + exchangeable } ^{31}\text{P in solid phase.}}$$

will be equal.

That is for two types of $^{31}$P on the soil, 'B' and 'C',

$$\frac{Z}{T_o} = \frac{A}{(A+B+C)} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(10)$$

When considering only one exchangeable type of $^{31}$P the relationship $\frac{x}{T_o} = \frac{B}{A+B}$ ................(4)

was obtained and in the case of two (or more) type of exchangeable $^{31}$P this equation will be still valid for the fastest exchanging type of $^{31}$P, as it is obtained from the exponential term for the fastest exchanging type of $^{31}$P (if there is more then one type) by putting t=0 in the equation obtained by removing the steady value and also the exponential terms for any slower exchanging type of $^{31}$P.

If the second line corresponding to the 'C' type of $^{31}$P, cuts the t=0 axis at y, then y will be related to the amount of activity and hence to the total amount of exchangeable 'C' type $^{31}$P. However, all the activity apart from that in 'C' is 'A' and 'B' (assuming that the rate of exchanging of

'C' with 'A' is much less than that of 'B' with 'A') and only the fraction of this activity in 'A' will be counted. Therefore to obtain the amount of 'C' type $^{31}P$, it will be necessary to multiply y by the ratio $\frac{A+B}{B}$. Then if B is replaced by C and A by (A+B) as in the derivation of equation (9), the equation

$$\frac{y}{T_o} \times \frac{A+B}{A} = \frac{C}{A+B+C} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (11)$$

is obtained and similar reasoning leads to the equation

$$\frac{w}{T_o} \times \frac{A+B+C}{A} = \frac{D}{A+B+C+D} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (12)$$

where w is the intercept of the line, corresponding to a third, even more slowly exchanging type of $^{31}P$, with the t=0 axis.

As 'A' may be obtained from the determination of $^{31}P$ concentration in solution colorimetrically. 'B' may be calculated from the equation (4). Once 'B' is known 'C' may be calculated from equation (11). If there are any other types of exchangeable $^{31}P$, the amount of each may be calculated in turn by the use of equation (12) etc.

(b) Experimental.

(i) Counting apparatus. (PLATE 1)

A liquid-immersion Geiger tube (20th.Century electronics type DM 6)

(A Sedeco printing unit.)

A Philips rate-meter No.P.W.4042.

A Philips electronic counter No.P.W.4032.

A Philips high voltage supply/amplifier No.P.W.4022

An electronic quench circuit.

(A strip chart recorder.)

Circulatory apparatus (as shown in plate II)

### (ii) Set-up of the experiment.

In compartment C(Plate II) a layer of glass-wool was plugged into the narrow end leading to compartment A, without being tight enough to hinder circulation of the solution between compartments. Distilled water was then added, precautions being taken to ensure that no air bubbles were trapped at the glass-wool-water junction.

A layer of acid-washed sand about $\frac{1}{4}$ in. thick was placed on top of the glass-wool and water was added up to a level above the arm connecting compartment C and B. The soil sample to be studied was introduced into the compartment C, a little at a time with the centrifugal pump rotating at a high speed. Due to the direction of current flow, the soil sample settled down quickly on top of the sand and became spread evenly over it.

The compartment B was fitted with the liquid-immersion Geiger counter and compartment A with a glass centrifugal pump, which was connected to an electric rotator at its upper end. This controlled the speed of rotation of the pump and in turn the rate of diffusion of the whole system. During equilibration, liquid in the compartment C was sucked continuously through the soil and the glass-wool into compartment A, thence into compartment B where actual counting took place, and thence pumped into compartment C, thus completing the circulation. The soil was equilibrated for 3 weeks before

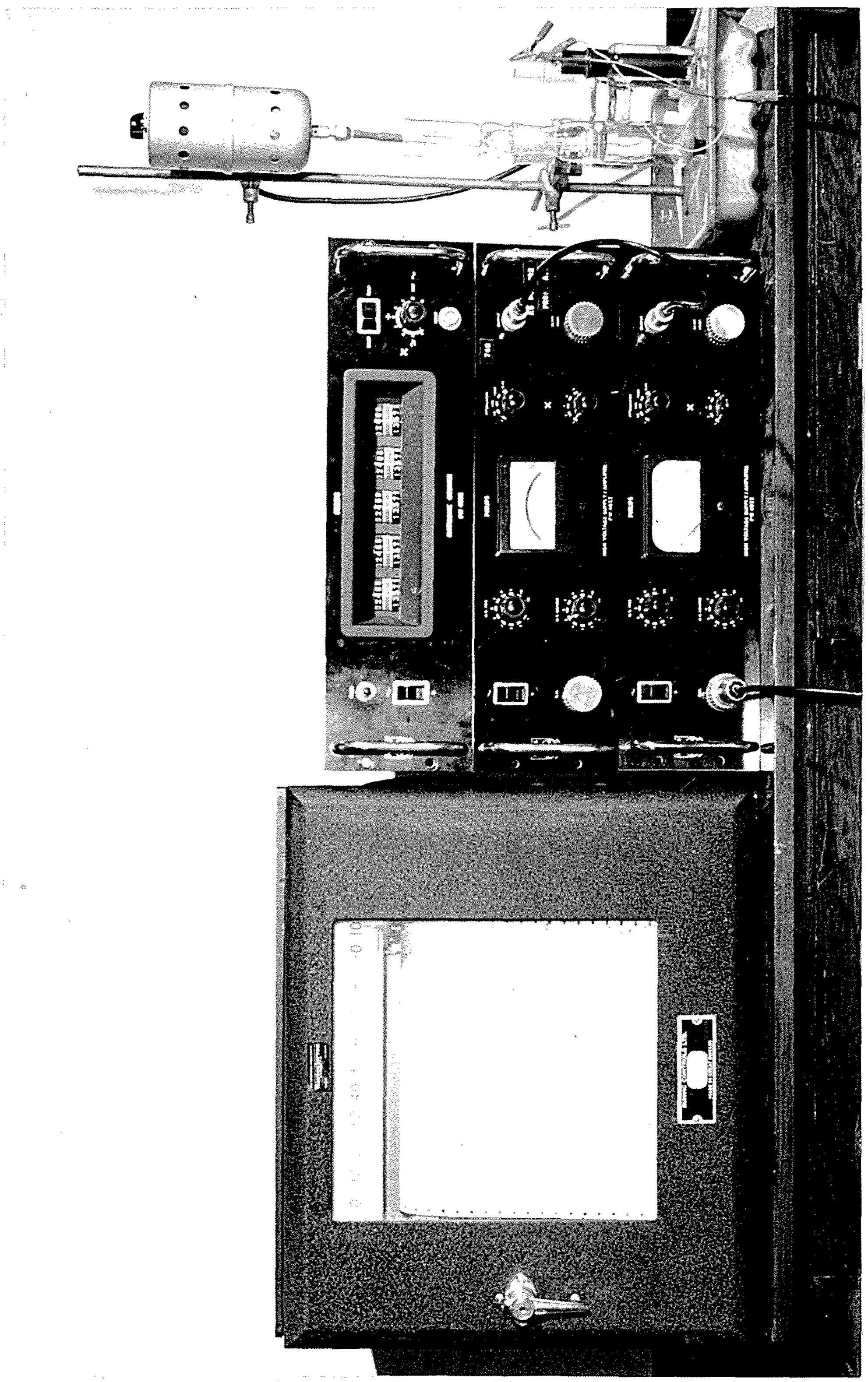


PLATE 1

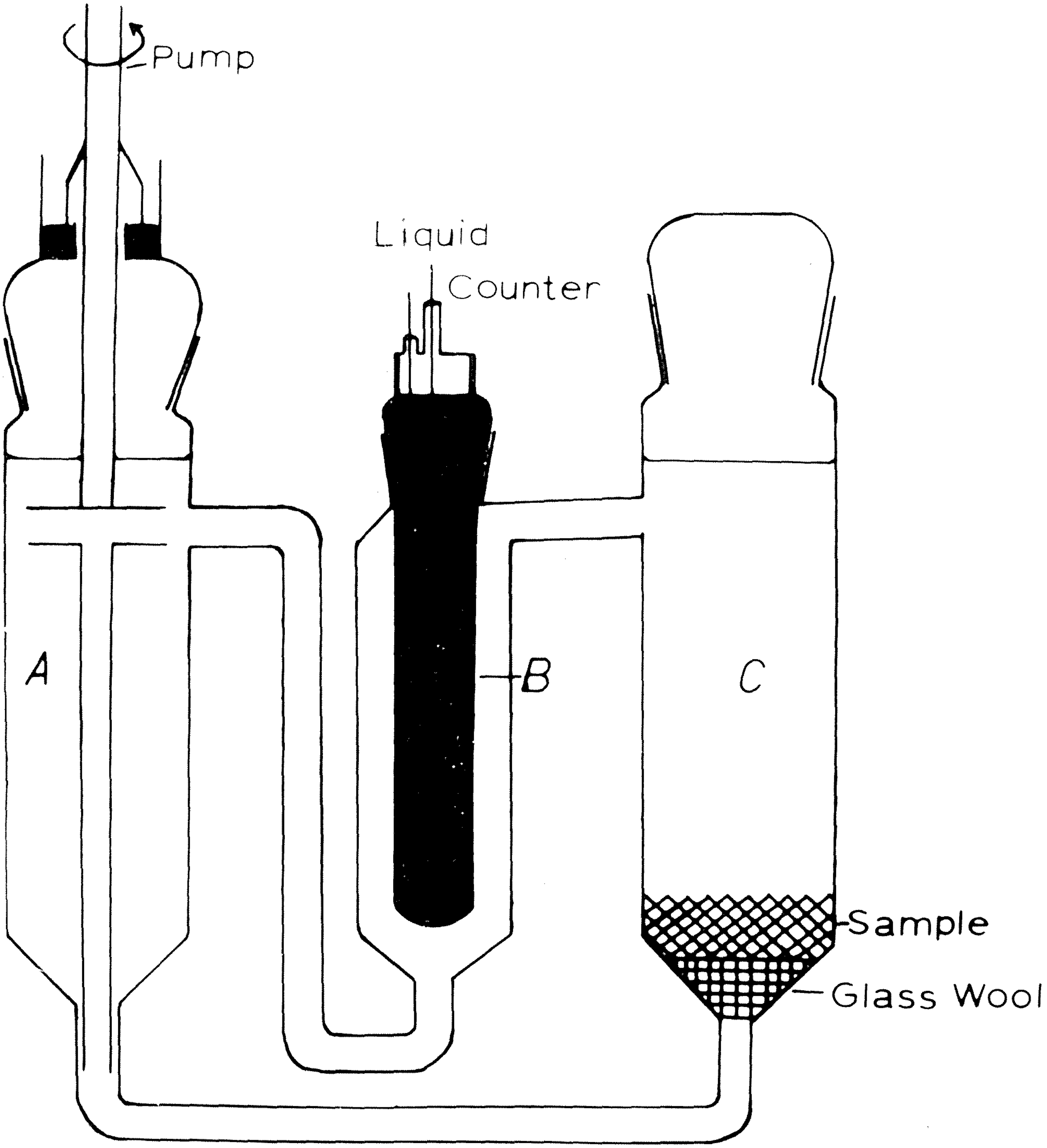


PLATE II

adding of $^{32}P$ (Wilson and Shao 1963)

(ii) Counting procedures.

Before introducing the $^{32}P$, the whole arrangement was set for background counting as well as checking that the counter was functioning its plateau voltage. It was critical for the counter to be operated in this region because otherwise any slight variation of the voltage supply would had a significant effect on the recorded counting rate. As the liquid counter was light sensitive the circulating apparatus was set up in darkened surroundings. The liquid counter was connected through a quench unit to the high voltage supply/ amplifier which in turn was connected to the electronic counter and printing machine which is a device by which every tenth (or hundredth etc.) counts registered on the electronic counter is recorded as one unit. After a suitable interval of time (say 10 minutes) the total number of these units was printed onto a strip of paper from which were read off when convenient. (alternatively a strip chart recorder may be used instead of a printing machine. In this case, the count rate versus time is tabulated in a graphical form. A rate-meter is needed permanently in this latter case.)

For counting $^{32}P$ activity, an additional rate-meter was introduced. It was mainly used for detecting the initial count rates. After the initial addition of $^{32}P$, most of initial counts were recorded directly from the rate-meter at suitable intervals so that more accurate counts could be obtained. The rest of counts were recorded in the printing unit, which had advantage of averaging out the count rates over a period of 10 minutes as opposed to a maximum period of time (100 seconds) with the rate-meter. This enabled a much accurate evaluation of the count rates to be obtained, than was possible with the rate-meter, provided that the rates were changing slowly or were stationary.

### (iii) Calculation of data.

At the completion of each experiment, the figures in the printing strip were tabulated on graph paper to obtain a graph of count rate versus time. This procedure enabled the statistical fluctuations to be smoothed out. Coincidence correction values and decay rates were added to the values obtained from the graph and background values were subtracted.

These values were then plotted on a semi-logarithmic graph paper such that a graph of $\log_e$ (count rate) versus time was obtained. It was found that in time the count rate fell to a steady value z.

The steady value z was subtracted from all the points and a new graph was obtained. It was usually found that a straight line could be drawn through the points at the lower end of this new graph. This line was extrapolated to zero time and intersected the zero-time axis at y. A third series of points was obtained by subtracting the values of the line through y from that of the points that lay above this line. It was usually found that a straight line could be drawn through all this series of points, cutting the zero time axis at x. Occasionally it was found necessary to repeat the procedure and so obtain a third straight line.

## 7. Assessment of microbial population.

The addition of phosphate to soils used in the work described previously may have affected their microbial populations. An increase in microbial activities may exert some influence on the results of phosphate analysis. To obviate any effect of added phosphate on numbers of micro-organisms in treated soils, an attempt was made to supress populations by application of a toluene-ehter mixture. Microbial populations in soils used in the series of experiments here reported were assessed by the total microbial count method.

### (a) Preparation of soil dilution series.

A pattern was prepared for plating of the soils in dilutions up to 100 millions. A soil sample weighing 10 g. was placed into a water blank containing glass beads, and shaked for 60 minutes in a horizontal position in a reciprocating shaker. The bottles were shaken vigorously by hand and immediately afterwards 10 ml. were transferred from the centre of the suspension to the next 90 ml. water blank with a sterile 10 ml. pipette. Each subsequent dilution was prepared in a similar manner.

### (b) Preparation of media.

Soil extract was prepared by mixing 1 kg. of garden soil with 1.5 litre tap water and heating the mixture in an autoclave (15 psi.) for 30 minutes. A small amount of calcium carbonate was added and the mixture was allowed to cool and settle partially. The warm soil suspension was filtered through a double filter paper in a Buchner funnel which was connected to a vacuum pump. The pH of the soil extract was adjusted to near neutrality by using dilute NaOH. Soil extract agar was made with: agar 20g. dipotassium phosphate 0.5 g.; sucrose 0.2 g.; and soil extract 1000 ml. and sterilized at 10 psi. for 20 minutes.

Csapek Dox agar (Oxoid preparation) contained: agar 18 g.; sodium nitrate 2 g.; potassium chloride 0.5 g.; magnesium glycerophosphate 0.5 g.; ferrous sulphate 0.01 g.; potassium sulphate 0.35 g.; and sucrose 30 g. and 1000 ml. distilled water. The pH was adjusted to 6.8-7.0.

### (c) Preparation of pour plates.

Petri dishes (10 cm. diameter.) were sterilized at 105°C for 48 hours. From the three highest dilution one ml. of freshly agitated suspension was withdrawn with a sterile pipette and transferred to each of 10 petri dishes. (5 replicates for each soil dilution were used for each medium.) Into each seeded petri dish was poured approximately 10-15 ml of agar media and the plates were rotated carefully 5 times in the clockwise direction and 5 times in the counter-clockwise direction to mix the agar with the inoculum. Petri dishes were left to stand upright until the agar has solidified after which they were inverted and transferred to incubators.

### (d) Incubation and counting of plates.

The Petri dishes were incubated at approximately 28°C. The first examination was carried out after 5 days and a further record was made after 10 days. Petri dishes showing more than 300 colonies and those showing large spreading colonies (over 2 cm.) were not recorded on either dates.

The total number of microbial colonies was recorded on plates from all 3 dilutions used and figures reported represent final counts. The recorded figures (to the nearest whole number) are given on the basis of oven dry-weight of soil samples.

## V. RESULTS AND DISCUSSION

### (a) Forms of phosphate in the untreated soils.

From the results obtained (Table 3) it is evident that in the untreated soils, the phosphate is mainly bound in organic forms; aluminium-, iron-and calcium-bound forms are present in small amounts only, with none of these fractions showing any preponderance among themselves with the exception that in Tirau silt loam the aluminium-bound phosphate is appreciably higher than both iron-and calcium-bound forms. The finding that a high proportion of the total phosphate is organically bound is in accord with the results reported by Jackman (1951, 1955) and Dixon (1954). Many workers have noted the rapid build up of humus in pumice soils under all type of vegetation. This is contrary to expection in view of the well aerated condition of these soils. A possible explanation may be abnormal biological activity, and the formation of clay-humus complexes which resist decomposition. Gieseking et al (1942) have shown that this property of clay to inhibit decomposition is most strongly exhibited by clays of high cation exchange capacity and possessing a capacity to bond basic proteinaceous groups. While experiments with allophane have not been reported, this mineral would certainly fall within the category of clays having high cation exchange capacity and on the basis of Gieseking's findings it could reasonably be expected to have a stabilizing influence on soil humus. Gieseking (1952) has shown that clay minerals

Table 3. Forms of phosphate in the untreated soils

( mg. P per 100 g. soil )

| Soil sample | Soil layer | Total P | Organic P | Al-P | Fe-P | Ca-P | Truog-P | Anion Excha Resin |
|---|---|---|---|---|---|---|---|---|
| Taupo sandy silt | Topsoil | 55.2 | 47.2 | 2.5 | 2.1 | 0.9 | 0.6 | 0.1 |
| | Subsoil | 44.3 | 37.1 | 3.8 | 1.6 | 0.7 | / | / |
| Ngaroma sandy loam | Topsoil | 66.7 | 58.3 | 2.7 | 3.0 | 2.7 | 0.1 | 0.2 |
| | Subsoil | 46.1 | 37.4 | 1.9 | 2.4 | 3.4 | / | / |
| Kaingaroa loamy sand | Topsoil | 35.3 | 28.1 | 3.9 | 1.7 | 1.6 | / | 0.1 |
| | Subsoil | 12.5 | 5.8 | 1.5 | 0.6 | 4.2 | / | / |
| Tirau silt loam | Topsoil | 156.4 | 94.8 | 41.8 | 9.9 | 10.6 | 1.1 | 0.1 |
| | Subsoil | 58.9 | 25.8 | 25.6 | 7.9 | 0.2 | / | / |

of high cation exchange capacity can adsorb phosphatase and this reduces their capacity to hydrolyze organic phosphorus compounds which are not themselves adsorbed. Dixon (1954) also postulated that (1) phosphorus occuring in the organic matter may be bound through protein groups to allophane, or (2) may be present in an unbound state but remains undecomposed through the phosphatase being inactivated by allophane. Fieldes (1962) also suggested that the stable linkage in mineral-organic colloids in yellow brown pumice soils may be between tetrahedral aluminium and organic phosphate groupings and that such a linkage may contribute to the characteristic slow decomposition of the humus in these soils.

### (b) The fate of the added phosphate.

As shown in Tables 4,5,6, and 7, a high proportion of the phosphorus added was recovered as aluminium-bound phosphate and even after prolonged contact between the added soluble phosphate and the soils, there was no indication of significant transfer of phosphate to other forms. This finding is contradictory to that of Chang and Chu (1961) who reported that soluble phosphate was fixed initially mainly as aluminium-bound phosphate, followed by iron-bound phosphate and calcium-bound phosphate in this order; as the time of contact was prolonged, the amount both of aluminium-and calcium phosphate decreased. They postulated that the first stage of fixation of added soluble phosphate by cations would occur at the surface of the solid phase and that the relative amounts and kinds of phosphate formed would depend of the specific area of the solid phase associated with aluminium, iron and calcium.

Table 4. Effect of time on the redistribution of added Soluble phosphate in Taupo sandy silt.
( mg. P / 100 g. soil)

| Phosphate fraction | Soil layer | P treated (with ether-toluene) | | | | | No. ether toluene | No P added withh ether-toluen |
|---|---|---|---|---|---|---|---|---|
| | | Time ( months ) | | | | | | |
| | | 2 | 4 | 6 | 8 | 10 | 10 | 10 |
| Organic P | Topsoil | 46.8 | 46.3 | 46.5 | 47.0 | 45.2 | 48.1 | 45.6 |
| | Subsoil | 39.1 | 39.9 | 39.8 | 41.4 | 37.6 | / | 37.1 |
| Al-P | Topsoil | 23.4 | 24.2 | 23.9 | 24.4 | 25.1 | 22.3 | 4.9 |
| | Subsoil | 22.9 | 22.9 | 24.4 | 24.4 | 23.6 | / | 5.0 |
| Fe-P | Topsoil | 2.0 | 1.8 | 3.1 | 2.2 | 2.4 | / | 1.5 |
| | Subsoil | 2.3 | 2.4 | 3.4 | 2.0 | 3.4 | / | 0.7 |
| Ca-P | Topsoil | 1.1 | 1.0 | -0.2 | -0.3 | 0.6 | 2.9 | 0.7 |
| | Subsoil | 0.4 | -0.5 | -0.9 | -1.1 | 0.1 | / | 0.4 |
| Truog available-P | Topsoil | 6.1 | 6.0 | 4.4 | 3.5 | 3.2 | 3.7 | 0.7 |
| | Subsoil | 4.0 | 3.9 | 3.6 | 2.8 | 2.8 | / | / |
| Anion exchange resin-P | Topsoil | 3.1 | 3.0 | 2.9 | 2.4 | 1.4 | 1.1 | 0.1 |
| | Subsoil | 1.8 | 1.3 | 1.1 | 0.7 | 0.6 | / | / |
| | | % of added phosphate recovered as | | | | | | |
| Organic P | Topsoil | 3 | 0.5 | 1.5 | 4 | -5 | 2 | |
| | Subsoil | 2.5 | 6.5 | 6.0 | 4 | -5 | / | |
| Al-P | Topsoil | 92.5 | 96.5 | 95.0 | 97.5 | 101 | 87.0 | |
| | Subsoil | 89.5 | 89.5 | 87.0 | 97.0 | 93 | / | |
| Fe-P | Topsoil | 2.5 | 1.5 | 8.0 | 3.5 | 4.5 | 0 | |
| | Subsoil | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | |
| [illegible] | Topsoil | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | |

Table 5. Effect of time on the redistribution of added soluble phosphate in Ngaroma sandy loam
( mg. P/ 100 g. soil)

| | | P treated | | | | | | No P added |
|---|---|---|---|---|---|---|---|---|
| | | ( with ether-toluene ) | | | | | No ether toluene | with ether toluene |
| Phosphate fraction | Soil layer | Time (months) | | | | | | |
| | | 2 | 4 | 6 | 8 | 10 | 10 | 10 |
| Organic P | Topsoil | 55.7 | 55.1 | 55.9 | 54.1 | 54.7 | 56.4 | 54.3 |
| | Subsoil | 38.7 | 38.7 | 38.0 | 38.4 | 37.7 | / | 36.1 |
| Al-P | Topsoil | 22.1 | 22.9 | 22.7 | 24.1 | 23.8 | 21.9 | 5.7 |
| | Subsoil | 21.2 | 22.5 | 22.1 | 22.6 | 22.1 | / | 3.1 |
| Fe-P | Topsoil | 4.7 | 4.1 | 3.9 | 3.2 | 3.6 | 3.4 | 1.9 |
| | Subsoil | 3.1 | 2.4 | 2.4 | 3.0 | 4.3 | / | 1.3 |
| Ca-P | Topsoil | 2.4 | 2.8 | 2.4 | 2.5 | 2.8 | 3.2 | 3.2 |
| | Subsoil | 3.7 | 4.5 | 3.6 | 2.1 | 2.0 | / | 4.6 |
| Truog available P | Topsoil | 5.3 | 5.1 | 5.1 | 2.8 | 2.6 | 3.5 | 1.0 |
| | Subsoil | 4.5 | 4.2 | 4.3 | 2.9 | 2.7 | / | 0.3 |
| Anion exchange resin-P | Topsoil | 2.4 | 2.2 | 2.3 | 1.4 | 1.6 | 1.5 | 0.1 |
| | Subsoil | 3.3 | 1.5 | 1.1 | 1.1 | 1.1 | / | / |
| | | % of added phosphate recovered as | | | | | | |
| Organic P | Topsoil | 8.0 | 5.0 | 9.0 | 5.0 | 3.0 | 11.5 | |
| | Subsoil | 5.0 | -2.0 | 4.5 | 6.5 | 3.0 | / | |
| Al-P | Topsoil | 82.0 | 86.0 | 85.0 | 92.0 | 90.5 | 81.0 | |
| | Subsoil | 90.0 | 97.0 | 95.0 | 97.5 | 95.0 | / | |
| Fe-P | Topsoil | 14.0 | 11.0 | 10.0 | 6.5 | 8.5 | 7.5 | |
| | Subsoil | [illegible] | [illegible] | [illegible] | [illegible] | 15.0 | / | |

Table 6. Effect of time on the redistribution of added Soluble phosphate in Kaingaroa loamy sand.

(mg. P / 100 g. soil.)

| | | P treated | | | | | | No P added |
|---|---|---|---|---|---|---|---|---|
| | | ( with ether-toluene) | | | | | No ether-toluene | with ether-tŏluene |
| Phosphate fraction | Soil layer | Time ( months ) 2 | 4 | 6 | 8 | 10 | 10 | 10 |
| Organic P | Topsoil | 28.7 | 28.1 | 27.7 | 27.6 | 26.6 | 29.5 | 25.9 |
| | Subsoil | 4.8 | 5.8 | 5.8 | 6.8 | 5.0 | / | 4.4 |
| Al-P | Topsoil | 23.1 | 25.0 | 24.5 | 26.9 | 25.8 | 22.3 | 5.4 |
| | Subsoil | 22.0 | 21.7 | 21.6 | 22.5 | 21.1 | / | 1.9 |
| Fe-P | Topsoil | 2.6 | 2.2 | 2.8 | 0.8 | 1.7 | 0.3 | 1.2 |
| | Subsoil | 0.5 | 0.4 | 0.4 | -0.4 | 1.8 | / | 0.3 |
| Ca-P | Topsoil | 1.1 | 0.1 | 2.4 | 0.1 | 1.3 | 3.3 | 2.3 |
| | Subsoil | 5.3 | 4.7 | 4.8 | 3.7 | 4.1 | / | 5.1 |
| Truog available P | Topsoil | 3.0 | 3.0 | 2.7 | 2.7 | 2.5 | 2.1 | 0.3 |
| | Subsoil | 4.5 | 3.9 | 3.7 | 3.7 | 3.4 | / | / |
| Anion exchange resin-P | Topsoil | 0.9 | 0.4 | 0.3 | 0.3 | 0.3 | 0.3 | 0.1 |
| | Subsoil | 0.7 | 0.4 | 0.3 | 0.3 | 0.2 | / | / |

% of added phosphate recovered as

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Organic P | Topsoil | 10.5 | 8.0 | 6.0 | 5.5 | -1.5 | 15.0 |
| | Subsoil | -2.5 | 0.5 | 2.5 | 7.5 | -1.5 | / |
| Al-P | Topsoil | 88.5 | 98.0 | 95.5 | 107.5 | 102.0 | 84.5 |
| | Subsoil | 100.5 | 99.0 | 98.5 | 103.0 | 96.0 | / |

Table 7. Effect of time on the redistribution of added soluble phosphate in Tirau silt loam.

( mg. P / 100 g. soil. )

| | | P treated | | | | | | No P added |
|---|---|---|---|---|---|---|---|---|
| | | ( with ether- toluene ) | | | | | No ether -toluene | with ether- toluene. |
| Phosphate fraction | Soil layer | Time (months) 2 | 4 | 6 | 8 | 10 | 10 | 10 |
| Organic P | Topsoil | 95.5 | 94.5 | 93.6 | 93.4 | 93.4 | 95.3 | 92.3 |
| | Subsoil | 24.2 | 25.5 | 25.6 | 25.8 | 24.2 | / | 25.1 |
| Al-P | Topsoil | 65.7 | 65.8 | 64.4 | 68.8 | 67.4 | 61.5 | 47.3 |
| | Subsoil | 45.8 | 45.4 | 44.6 | 45.1 | 45.0 | / | 26.6 |
| Fe-P | Topsoil | 8.2 | 8.8 | 10.9 | 7.0 | 9.5 | 11.4 | 7.4 |
| | Subsoil | 8.3 | 8.7 | 9.2 | 8.6 | 10.1 | / | 8.1 |
| Ca-P | Topsoil | 8.0 | 8.2 | 8.5 | 8.2 | 7.1 | 9.2 | 10.1 |
| | Subsoil | 1.3 | / | 0.2 | 0.1 | 0.3 | / | -0.3 |
| Truog available P | Topsoil | 3.6 | 3.7 | 3.3 | 2.6 | 2.1 | 2.3 | 1.4 |
| | Subsoil | 1.0 | 0.9 | 0.8 | 0.8 | 0.6 | / | / |
| Anion exchange resin-P | Topsoil | 0.9 | 0.7 | 0.7 | 0.6 | 0.6 | 0.2 | 0.1 |
| | Subsoil | 0.2 | 0.1 | 0.1 | 0.1 | 0.1 | / | / |

% of added phosphate recoverd as

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Organic P | Topsoil | 14.5 | 10.0 | 5.00 | 4.0 | 4.0 | 13.0 | |
| | Subsoil | -4.5 | 3.0 | 2.0 | 3.0 | -5.0 | / | |
| Al-P | Topsoil | 92.0 | 92.5 | 85.7 | 107.5 | 100.50 | 71.0 | |
| | Subsoil | 96.0 | 94.0 | 90.0 | 92.5 | 92.0 | / | |
| Fe-P | Topsoil | 4.0 | 7.0 | 17.5 | -2.0 | 10.5 | 20.0 | |
| | Subsoil | 1.0 | 3.0 | 5.5 | 2.5 | 2.5 | 10.0 | |

Table 8. Effect of ether-toluene on microbial population.
( No. of micro-organism (in millions)/g. of oven dry soil)

| Soil sample | Nutrient media | Ether-toluene treated | | No ether-tolue |
|---|---|---|---|---|
| | | dried at 37°C for 3 days | moist | dried at 37°C for 3 days. |
| Taupo sandy silt | Czapek Dox(rich) | 31 | 32 | 5 |
| | Soil extract(poor) | 9 | 8 | 5 |
| Ngaroma sandy loam | Czapek Dox(rich) | 62 | 48 | 300* |
| | Soil extract(poor) | 34 | 43 | 300* |
| Kaingaroa loamy sand | Czapek Dox(rich) | 89 | 95 | 37 |
| | Soil extract(poor) | 69 | 60 | 32 |
| Tirau silt loam | Czapek Dox(rich) | 61 | 53 | 36 |
| | Soil extract(poor) | 61 | 36 | 19 |

* Plates densely covered by bacterial colonies apparently of the same genus.

They indicated that the clay fraction is the main site of phosphate fixation. In the clay, the content of aluminium is much higher than that of either iron or calcium. Therefore, the added soluble phosphate is most likely to be fixed as aluminium-bound phosphate rather than as iron-bound phosphate or calcium-bound phosphate in the initial stage of the reaction. However as the solubility product of iron-bound phosphate is lower than that of either aluminium-and calcium-bound forms, they argued that as time elapsed, the aluminium- and calcium-bound forms of phosphate in soil should change to iron-bound forms.

The fact that in the present investigation no significant transfer of initially formed aluminium-bound phosphate is observed may have several explanations, but the three following appear to be of prime importance.

(i) The clay fraction of these soils contains a high proportion of amorphous aluminium hydroxide (Fieldes and Swindle 1954) of particle size about 100 Å. Thus it provides a high specific surface area for adsorption of the added phosphate. Amorphous aluminium hydroxide is known to be highly adsorptive for phosphate and reaction is rapid (Coleman 1944, 1945; Russell and Low 1954; Ellis and Truog 1955; Hsu and Rennie 1962a,b,). This component should thus be able to react rapidly with phosphate on contact.

(ii) As shown by the Tamm acid oxalate values in Table 2, the soils contain considerably greater amounts of active aluminium than active iron.

(iii) According to Fieldes' (1962) tetrahedral aluminium site theory, aluminium in allophane is held in tetrahedral co-ordination by linkage through oxygen to silicon. Fracture of $(-SiO)_4 \equiv Al^-$ linkages at the active surface leads to exposed $(-SiO)_3 \equiv Al$ sites which are electrostatically neutral but due to the lack of octet stability, the holes in the uncompleted aluminium tetrahedra will conveniently house an oxygen atom. The valence contributions $+\frac{3}{4}$ from aluminium and $+ 5/4$ from P balance the $-2$ from 0 resulting in structural stability. The phosphate in tetrahedral coordination with aluminium is thus most strongly retained as $(-SiO)_3 \equiv Al \overset{\frac{3}{4}}{—} O \overset{5/4}{—} P$.

As can be seen in Tables 4,5,6 and 7, no significant build up of organic phosphorus was found in the phosphate-treated soils and this was to be expected since there was no addition of fresh organic matter. The only possible increase in organic phosphate could occur as the result of microbial conversion of inorganic phosphate to the organic form. As shown in Table 8, there is a difference in microbial counts between the toluene-ether treated and the non-toluene-ether treated soils. This difference may be attributed either to (a) the effect of toluene-ether bringing about a reduction of certain groups of the microbial population and allowing other groups to survive and proliferate in the absence of antagonism and competition or (b) the toluene-ether providing a source of energy for surviving forms which would increase in numbers as a result of the presence of energy material of a special nature viz. the toluene-ether addition. In general ( as shown in Table 8) the richer medium gave increased numbers of micro-organisms. In the non-toluene-ether treated soils, except for Ngaroma sandy loam, the microbial numbers are much lower than in treated soils. The anomalous results obtained with the untreated Ngaroma sandy loam (where numbers of colonies were extremely large in both media and at all dilutions), indicate selective effects of the toluene-ether treatment. Colonies recorded in tests with this soil were obviously bacterial and appear to be of the same genus.

(c) <u>Truog-extractable phosphate and anion exchange resin extractable phosphate</u>. (Tables 4,5,6 and 7.)

For Taupo sandy silt and Tirau silt loam, the Truog-phosphate values are higher in the topsoil than in the subsoil. There are similar amount of Truog-phosphate values in topsoil and subsoil in Ngaroma sandy loam. In all these soils, as time of contact between added phosphate and soil was prolonged, the Truog-phosphate values decreased. This rate of decrease is greater in the topsoil than in the subsoil. However, the initial Truog-phosphate values are lower in the subsoil than in the topsoil, with the exception of Kaingaroa loamy sand where the Truog-phosphate value is higher in the subsoil. This may be due to the higher calcium-bound phosphate content of the subsoil as compared with the topsoil of the Kaingaroa loamy sand.

The amount of phosphate extracted by the anion exchange resin are generally lower than that extracted by Truog's reagent. As with the Truog-phosphate values, the amount of phosphate retained by the resin decreased as the time of contact between added phosphate and soil was extended.

### (d) Radio-isotope exchange kinetics on Tirau silt loam(Topsoil)

The results are shown in Table 9 and Figs.1,2,3 and 4. It is evident from Table 9, that the soil phosphate on the solid phase can be divided into 3 categoris, according to their rate of exchange, namely, rapidly exchangeable, slowly exchangeable and non-exchangeable phosphate. These findings are in accordance with those of several workers who have reported the isotopic exchange of orthophosphate ions between solution and soil, using $^{32}$P-phosphate as a tracer. Despite the variety of conditions used in such experiments, whenever the fractional isotopic exchange is reported in relation to the time factor, total isotopically exchangeable phosphate has been found to be made up, broadly speaking, of rapidly and slowly exchanging fractions (Barbier et al 1954; McAuliffe 1948; Wiklander 1950; Talibudeen 1957, 1958, 1960.)

In the present investigation, the technique employed enables the amount of rapidly and slowly exchangeable phosphate to be found. These two different forms of exchangeable phosphate could be due to two different forms of exchange sites present on the soil particles.

Table 9. Radio-isotope exchange kinetic on Tirau silt loam (Topsoil).

| | No P added | P treated | | | | |
|---|---|---|---|---|---|---|
| | | (with ether-toluene) | | | | No ether-toluene |
| | | Time (months) | | | | |
| | | 4 | 6 | 8 | 10 | 10 |
| | | (mg. P/g. soil) | | | | |
| * A | 0.017 | 0.0246 | 0.022 | 0.019 | 0.017 | 0.0175 |
| * B | 0.0092 | 0.0281 | 0.0224 | 0.0229 | 0.0118 | 0.0137 |
| * C | 0.0042 | 0.0441 | 0.0285 | 0.0125 | 0.0124 | 0.0131 |
| | | (hrs.) | | | | |
| * $t_{\frac{1}{2}B}$ | 1.5 | 2.5 | 1.5 | 2.5 | 1.5 | 1.5 |
| * $t_{\frac{1}{2}C}$ | 75.0 | 53.0 | 40.0 | 35.0 | 25.0 | 23.0 |
| | | $(hrs^{-1}) \times 10^{-3}$ | | | | |
| * $K_b$ | 300.0 | 129.0 | 220.0 | 126.0 | 273.0 | 259.0 |
| * $K_c$ | 8.0 | 7.0 | 11.0 | 15.0 | 19.0 | 21.0 |
| | | as % of total P | | | | |
| A | 1.08 | 1.39 | 1.24 | 1.07 | 0.96 | 0.98 |
| B | 0.59 | 1.58 | 1.26 | 1.29 | 0.66 | 0.77 |
| C | 0.27 | 2.49 | 1.61 | 0.71 | 0.70 | 0.74 |
| A+B+C | 1.94 | 5.56 | 4.11 | 3.07 | 2.32 | 2.49 |
| | | as % of added P | | | | |
| A | | 3.8 | 2.5 | 1.0 | 0.0 | 0.3 |
| B | | 9.5 | 6.6 | 6.9 | 1.3 | 2.3 |
| C | | 20.0 | 12.2 | 4.2 | 4.1 | 4.5 |
| Non-exchangeable P | | 66.7 | 78.7 | 87.9 | 94.6 | 92.9 |

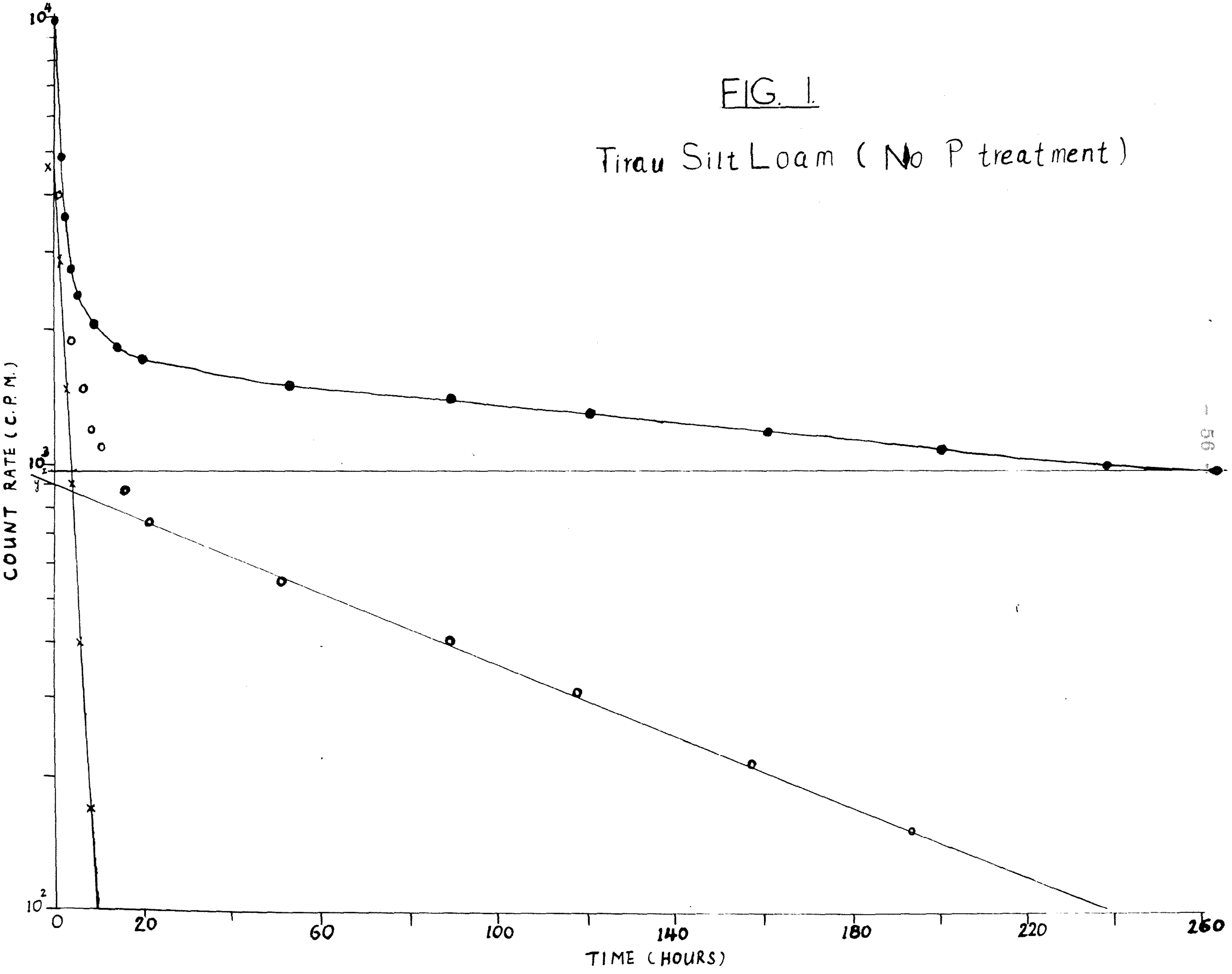
* A=P insolution; B= fast exchangeable P; C= slowly exchangeable P

*$t_{\frac{1}{2}B}$= half-life of B; $t_{\frac{1}{2}C}$= half-life of C

* $K_b$= specific rateconstant of B; $K_c$= specific rate constant of C

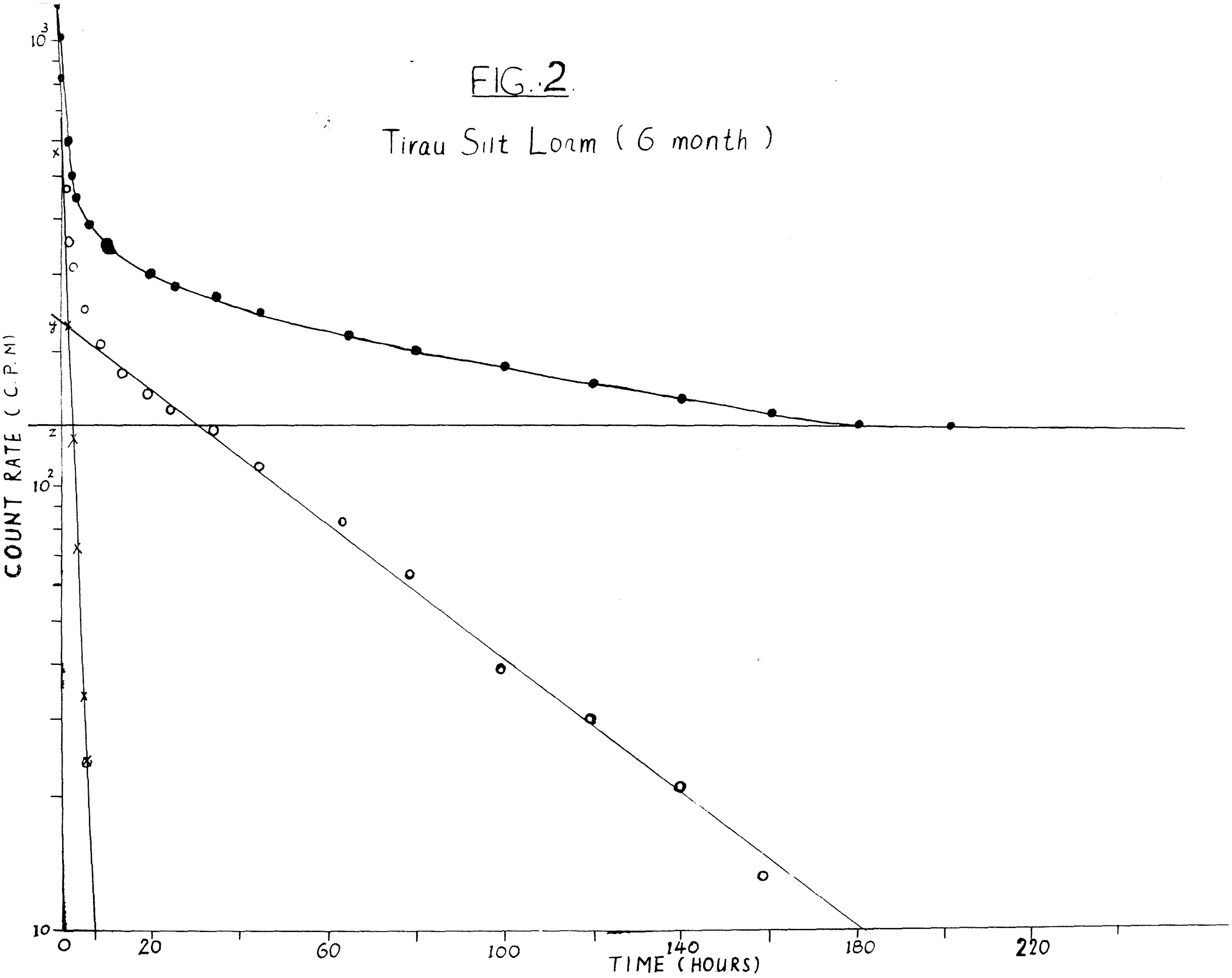
FIG. 1.

Tirau Silt Loam ( No P treatment )



# FIG. 2

Tirau Silt Loam (6 month)



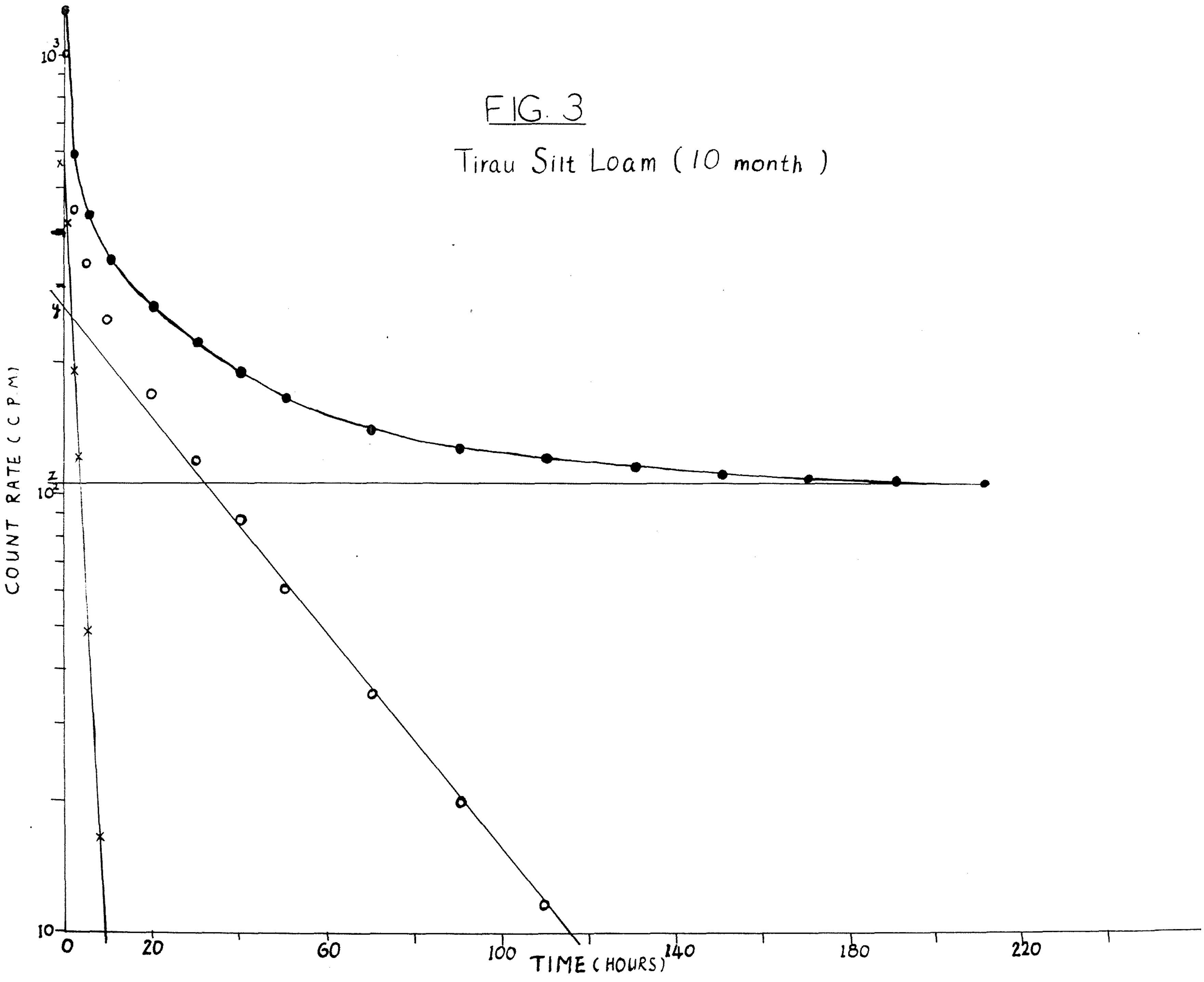


FIG. 3

Tirau Silt Loam (10 month )

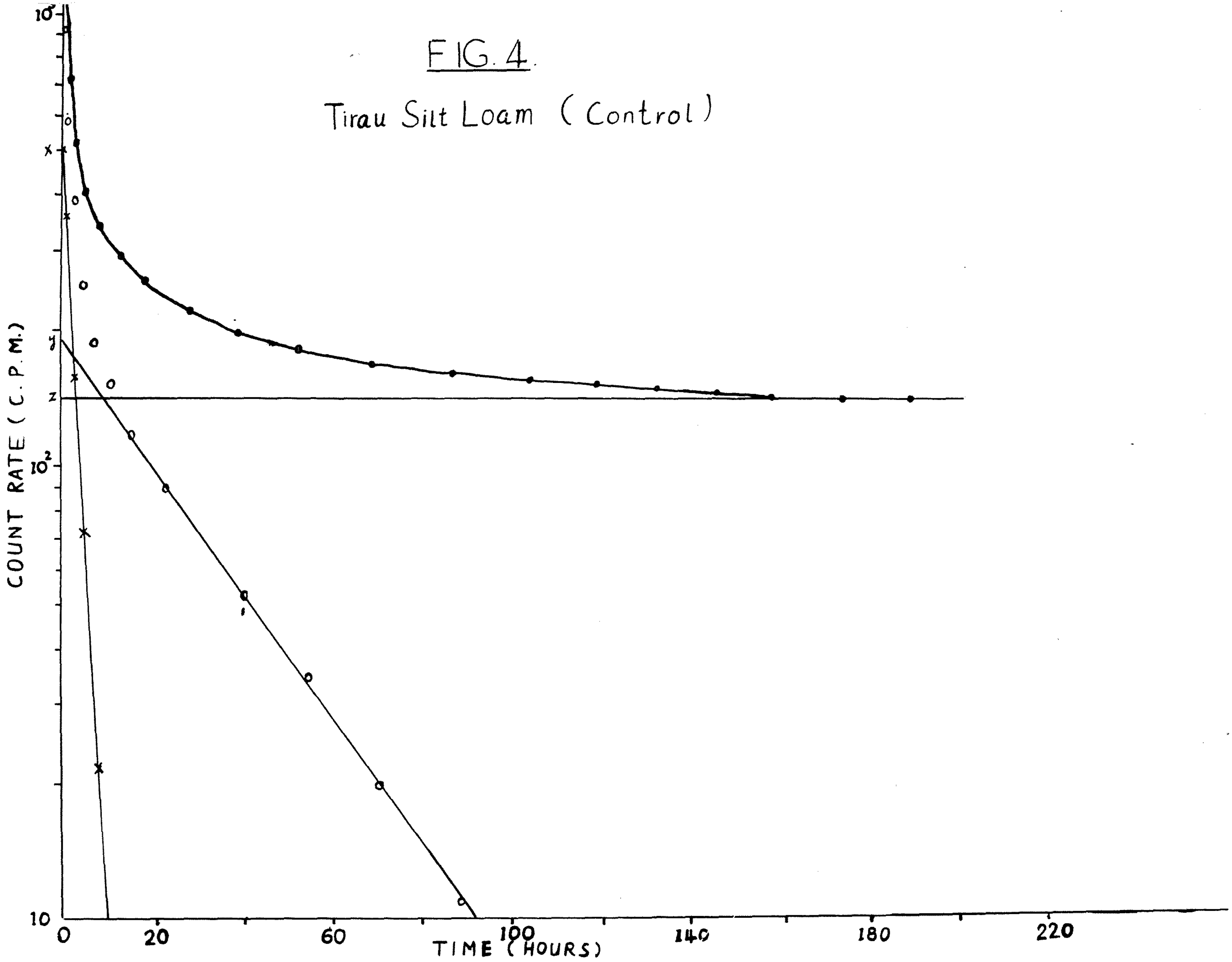


FIG. 4.

Tirau Silt Loam (Control)

However, it is hard to visualize, that there are only these two forms of exchange sites present. In the soil system, $H_2PO^-_{4\ \text{solution}} \Longleftrightarrow H_2PO_4$ -SOLID, is a dynamic equalibrium, which can be considered to result from a number of exchangeable phosphate compounds all of which are exchanging with the phosphate in the soil solution. Each individual reaction is represented by a given amount of phosphate as well as a specific rate constant. It has been suggested (Russell et al 1954; Seatz 1954) that different forms of inorganic phosphate in soil will undergo exchange at different rates. Organic phosphorus compound exchange only very slowly with orthophosphate. (Whal and Bonner 1951) Of the two categories of exchangeable phosphate delineated in the present study one has a specific rate constant ten times greater than the other. However, the particular rate constants separated may be averages of several constants, because there may be some other reactions which overlap each other.

These exchangeable phosphate categories, could probably belong to phosphate on adsorption sites of the soil surface. Talibudeen (1957) has however, divided the total soil phosphate into fractions of widely varying exchangeability as indicated schematically below.

## Soil phosphate fractions

$$\begin{tikzcd}
\text{Rapidly exchanging} & \text{Slowly exchanging} & \text{Very slowly exchanging} \\
\text{Physically sorbed phosphate, phosphate held on external surface of mineral and in macropores, labile organic phosphate.} \arrow[r, leftrightarrow] \arrow[dr, leftrightarrows, "PO_4"'] & \text{Chemi-sorbed phosphate, phosphate in internal surface of mineral and micropores, labile organic phosphate.} \arrow[r, leftrightarrow] \arrow[d, leftrightarrows, "PO_4"] & \text{Surface solid layer e.g apatite crystal, stable organic phosphate} \arrow[dl, leftrightarrows, "PO_4"] \\
& \text{Intermicellar phosphate} \arrow[d, leftrightarrows, "\text{very rapidly exchange of } PO_4"] & \\
& \text{Phosphate in soil solution.} &
\end{tikzcd}$$

The very slowly exchanging phosphate as presented above, probably is not being traced in the present study. This could perhaps be found if the rapidly and slowly exchanging phosphate were progressively stripped off the soil matrix, until only the very slowly exchanging solid phosphate remained. Such a situation could probably develop in the field where plants were grown for prolonged periods, without addition of phosphate fertilizer.

The two forms of exchangeable phosphate found in the present study are believed to be due differences in firmness of binding of adsorbed phosphate. The firmly adsorbed phosphate has a half-life of exchange ranging from 75 hours to 25 hours. The loosely adsorbed phosphate has a half-life of exchange of about 1.5-- 2.5 hours, ~~suggesting that there could be a con-~~

suggesting that there could be a considerable amount of exchange between adsorbed-$H_2PO_4$ and $H_2PO_4^-$ in solution over short periods of time. However, the nature of adsorption site is not understood. It is postulated that most of the exchangeable phosphate is adsorbed on the surface layer of inorganic soil particles or the organic colloids or gels. Some may be held in the lattice layer or macro- or micropores of soil particles. This adsorption may either be chemi-sorption or physical-sorption as postulated by Talibudeen (1957). The exchangeable phosphate that is physically sorbed and that which is held in macropores may contribute the rapidly exchangeable phosphate and the chemi-sorbed phosphate and the amorphous or crystalline forms may constitute the slowly exchangeable phosphate.

In a soil system, the $H_2PO_4^-$-solution and $H_2PO_4^-$-solid is always in a state of dynamic equilibrium which is characterized by a continuous desorption and adsorption, i.e., exchange of $H_2PO_4^-$ in solution and exchangeable-$H_2PO_4$ in solid phase. There is also probably an interchange between the rapidly exchangeable phosphate and slowly exchangeable phosphate. As shown in Table 9, as the time of contact between the added phosphate and soil was prolonged, the amount of exchangeable phosphate decreased, and the non-exchangeable forms increased, This could be due to several factors.

(i) The adsorbed phosphate on the surface layer of soil particles or the organic colloids or gels may move to the subsurface layer of the particles, through diffusion thus decreasing the amount of exchangeable phosphate.

(ii) Some of the $H_2PO_4^-$ may come into the solution and be precipitated by $Al^{3+}$ ions etc. in the solution; alternatively the amorphous precipitated phosphate may change to less soluble crystalline forms. Some of precipitated phosphate particles may act as seeding agents increasing the size with time, thus decreasing the surface area of exchange and causing a decrease the amount of exchangeable phosphate.

(iii) Some of the adsorbed phosphate could become tetrahedral-coordinated with aluminium and become strongly fixed and thus non-exchangeable as described by Fieldes' tetrahedral aluminium site theory.

Irrespective of the mechanism operating, it has been shown in the present case that the addition of soluble phosphate to Tirau silt loam results in 30% of the total added phosphate being in exchangeable form after four months. After ten months this has decreased to 5% of total added phosphate. Thus it would seen likely that small, frequent applications of phosphate would be more beneficial to the fertility of the soil than annual massive application. This, however, would probably not be an economic proposition but would certainly warrant further investigation particularly in actual field studies on the economics of the situation and on the effects on pasture of more frequent phosphate applications using different phosphate carriers.

It is of interest that the amount of phosphate in solution plus the exchangeable phosphate of the soil is higher than that of Truog-phosphate values or that of anion exchange resin extractable phosphate (Table 7 topsoil and Table 9). This shows that Truog's reagent and the anion exchange resin extracted only a certain proportion of the exchangeable phosphate, possibly the more readily exchangeable forms. Truog's reagent may extract other phosphate, but results show this to be unlikely. If this is the case, the behaviour of soil phosphate may be interpreted on the basis of the idea that there are at least two forms of phosphate present with different degree of availability, one is readily available, the other less so. This could well be regarded as a means of assessing the soil phosphate potential, by studying their rate of exchange and specific rate constants and the amount of phosphate in each. Thus one could use specific rate constants as an index of rate of phosphate release. The greater the specific rate constant, the faster the phosphate removed from the soil will be replenished from adsorbed phosphate and vice versa. If in a system, there are a large number of differing forms of phosphate with differing degrees of exchangeability, the system as a whole will appear in some degree analogous to that of soil water, as suggested by Schofield (1955). The phosphate potential will then show a steady change as the amount of phosphate in soil is altered. This could well be treated by $^{32}P$-phosphate as in the present investigation. Schofield (1955) also emphasized that it is not the amount of available $PO_4$ in the soil that primarily controls the uptake of phosphate by the plants, but the work needed to withdraw it from the pool. It is thus the energy levels with which different phosphate forms are adsorbed on the soil, together with the total amount of phosphate that will characterize the amount of plant-available phosphate during the growth period. Blanchet

## VI. CONCLUSION

In conclusion, it would appear on the basis of the evidence obtained in the present investigation, that aluminium is responsible for the fixation of a large preportion of the applied soluble phosphate in yellow brown pumice soils. This fixation process may involve the adsorption, coordination and preciptation of phosphate and possibly eventual crystallization as difficultly available aluminium phosphate. Conversion to more difficultly soluble forms is suggested by the finding that Truog-phosphate values and anion exchange resin extractable phosphate decrease with time and that isotopically exchangeable phosphate, ten months after the initial addition of phosphate, was only 5% of the total phosphate added. This behaviour could be due to diffusion of phosphate to subsurface layers and the development of definite crystalline phosphate as time proceeds; such conversion might be favoured by unusually high concentrations of phosphate such as have been employed in present study. Whether or not the results of these laboratory studies are paralleled in the field using normal rates of phosphate fertilizer application is not known.

# VII SUMMARY

A study was made over a period of ten months of the fate of phosphate added to four yellow brown pumice soils and their subsoils by means of a fractionation procedure developed by Fife (1959a,b; 1962,1963, priv. comm.). It was found that the main portion of the added phosphate was fixed as aluminium-bound phosphate and that there was no significant interchange of phosphate between aluminium-bound, iron-bound, calcium-bound and organically-bound phosphate throughout the period of investigation.

Truog's phosphate extraction procedure and an anion exchange resin method were employed to study the change of availability of phosphate over the period. It was found that Truog's reagent extracted a greater amount of phosphate than did the anion exchange resin method. However, both methods indicated that as time of contact between soil and added soluble phosphate was prolonged, the amount of extractable phosphate decreased.

The characteristics of the exchangeable phosphate fraction in one of the soils (Tirau silt loam) was investigated by application of simultaneous isotopic exchange kinetics. It was found that there were two types of exchangeable phosphate viz, rapidly exchangeable phosphate with a specific rate constant ten times greater than the slowly exchangeable form. The amount of exchangeable phosphate also decreased with time, dropping from 30% to 5% of the total added phosphorus, after six months contact.

# ACKNOWLEDGEMENTS

I wish to thank:

Dr. C.V.Fife for suggesting the topic of this thesis and for the valuable help given;

Dr. D.J. Spedding for many helpful discussions and guidance on the isotope work;

Dr. H. Jacks for assistance with the assessment of microbial populations;

Mr. A.C.Glenday of Grasslands Division, D.S.I.R., for his assistance with the statistical problems;

Miss M.G. Campbell and her staff for their help on the reference books.

## LIST OF REFERENCES

Amer.F., Bouldin,D.R. Black, C.A., and Duke, F.R. 1955 Characterization of soil phosphorus by anion exchange resin adsorption and $P^{32}$ equilibration. Plant and Soil 6: 391-.

Arambarri, P.,and Talibudeen,O.,1959a. Factors influencing the isotopically exchangeable phosphate is soils.
Part 1. The effect of low concentrations on organic anions. Plant and Soils 4: 343-
Part 2. The effect of base saturation with sodium and calcium on non-calcareous soils. Plant and Soils 4: 355-
Part 3. The effect of temperature in some calcareous soils. Plant and soils. 4: 364-

Barbier, G.,Lesaint, M., and Tyszkiewicz,E.,1954. Ann.Agron. 5: 923-.

Bailey, R.W.,1953. Composition of the soil-organic matter complex in pumice soils of the Taupo ash shower. N.Z.J.Sci.Tech.34A: 415-.

Baumgart, I.L., 1954. The pumice soils.(A summary). N.Z.So. Soil Sci. Pro. of the first conference. 17-.
1954. Some ash showers of the central north island. N.Z.J. of Sci. and Tech. 35B. 456-

Birrell, K.S. 1954. The effect of allophane on certain physical and chemical properties of volvanic soils. N.Z. So.Soil Sci.Pro. of the first conference. 27-.
1961. The adsorption of cation from solution by allophane in relation to effective size. J. of Soil Sci. 12: 307-.
1961. Ion fixation by allophane. N.Z.J. of Sci.4: 393-.

Birrell, K.S. and Fieldes, M.,1952. Allophane in volcanic ash soils. J.Soil Sci. 3: 153-.

Birrell, K.S., and Gradwell, M. 1956. Ion exchange phenomena in some soils containing amorphous mineral constituents. J.Soil Sci. 7: 130-.

Black, C.A., 1942. Phosphate fixation by kaolinite and other clays as affected by pH, phosphate concentration and time of contact. Soil Sci. Soc. Am. Pro. 7: 123-.

Blakemore, L.C., 1960. Chemistry of yellow brown pumice soils. N.Z.Soil News. 1: 15-.

Blanchet, R., 1958. Cited by Lamm, C.G. on A study of isotopic exchanges and chemical conversion between fertilizer-phosphorus and soil-phosphorus. Acta.Agri.Scan. 1960 11: 95-.

Bray, R.H. and Kurtz, L.T., 1945. Determination of total organic and available forms of phosphorus in soil. Soil Sci. 59: 39-.

Burd, J.S., 1948. Chemistry of phosphate ion in soil systems. Soil Sci. 65: 227-.

Chaminade, R.,1946. Ann. Agron. 16: 229-.

Chang, F.C., 1962. Determination of available phosphate in soil using isotope tracers. Soviet soil sci. No.9 937-.

Chang,S.C., and Chu, W.K., 1961. The fate of soluble phosphate applied to soils. J.Soil Sci. 12: 286-.

Chang,S.C., and Jackson, M.L.,1957. Soil phosphorus fraction. Soil Sci. 84: 133-.
1958. Soil phosphorus fractions in some representative soils. J.Soil Sci. 9: 109-.

Chang,S.C., and Juo, S.R., 1963. Available phosphorus in relation to forms of phosphate in soils. Soil Sci. 95: 91-.

Chandler, W.V., 1941. Phosphate adsorption by five Alabama soils as influenced by reaction, base saturation and free sesquioxides. J.Am. Soc.Agron. 33: 1-.

Coleman, R., 1942a. The adsorption of phosphate by kaolinitic and montmorillonitic clays. Soil Sci. Soc. Am. Pro. 7: 134-.

1942b. The mechanism of phoshpate fixation by montmorillonitic and kaolinitic clays. Soil Sci. Soc. Am. Pro. 9: 72-.

1944. Phosphorus fixation by the coarse and fine clay fractions of kaolinite and montmorillonite clays. Soil Sci. 58: 71-.

Cooke, I.J., and Hislop, J., 1963. Using anion exchange resin for the assessment of available soil phosphate. Soil Sci. 96: 308-.

Dean, L.A., 1938. An attempted fractionation of soil phosphorus. J. Agric. Sci. 28: 234-.

1949. Fixation of soil phosphorus. Adv. Agron.1: 1-.

1952. The evaluation of phosphorus fertility of soils through the medium of radiophosphorus. Trans. Int. Soc. Soil Sci. Comm. II and IV: 48-.

1956. Application of radioisotopes to the study of soils and fertilizers: A Review. Pro. Int. Conf. on the peaceful uses of atomic energy. 12: 89-.

Dickman, S.R., and Bray, R.H., 1940. Colorimetric determination of phosphate. Ind. Eng. Chem. Ana. edition. 12: 665-.

Dickman, S.R., and DeTurk, E.E.,1938. A method for the determination of organic phosphorus in soils. Soil Sci. 45: 29-.

Dixon, J.K., 1954. Some chemical aspects of pumice soils (A Summary.). N.Z. Soc. Soil Sci. Pro. first conf. 19-.

Dormaar, J.F., and Webster, G.R., 1964. Losses inherent in ignition procedures for determining total organic phosphorus. Canadian J. Soil Sci. 44: 1-.

Doughty, J.L., 1930. The fixation of phosphate by a peat soil. Soil Sci. 29: 23-.

Doughty, J.L., 1935. Phosphate fixation in soils, particularly as influenced by organic matter. Soil Sci. 40: 191-

Drobnik, J.,1961. The role of toluene in the measurement of the activity of soil enzyme. Plant and soil 14: 94-

Ellis, R.J., and Truog, E.,1955. phosphate fixation by montmorillaonite. Soil Sci. Soc. Am.Pro. 19: 451-

Fieldes, M.,1955. Clay mineralogy of New Zealand soils. Part II. Allophanee and related mineral colloids. N.Z.J.Sci.Tech. 37B: 336 -.

1962. The nature of the active fraction of soils. Int. Soil Sci. Conf. N.Z. 1962. 62-.

Fieldes, M.,and Schofield, R.K. 1960. Mechanism of ion adsorption by inorganic soil colloids. N.Z.J.Sci. 3: 563-.

Fieldes,M., and Swindale, L.D. 1954. Chemical weathering of silicates in soil formation. N.Z.J.Sci. Tech.36B: 140-.

Fieldes,M.,and Taylor, N.H.,1961. Clay mineralogy of N.Z. soil. Part V. Mineral colloids and genetic classification. N.Z.J.Sci. 4: 679-.

Fife, C.V.,1959. An evaluation of ammonium fluoride as a selective extractant for aluminium-bound phosphate I. Preliminary studies on non-soil systems. Soil Sci. 87: 13-.
II. Preliminary studies on soils. Soil Sci. 87: 83 -.
1962. III. Detailed studies on selected soils (1).

Soil Sci. 93: 113-.

1963. IV. Detailed studies on soils (2). Soil Sci. 96: 112-.

Fisher, R.A., and Thomas, R.P.,1935. The determination of forms of inorganic phosphorus in soils. J.AM. Soc. Agron. 27: 863-.

Fried, M., and Dean, L.A., 1952. A concept concerning the measurement of soil nutrient. Soil Sci. 73: 263-.

Furkert, R.J., 1962. Isotope exchange kinetics in clay-water systems. M.Sc. Thesis, Victoris University.

Gaarder, T., 1930. Medd. Vestland. forstl. Forsokssta *14*. (Chem. Abs. 24: 5408)

Ghani, M.O. 1943. (a) Fractionation of soil phosphorus: I. Method of extraction. *Ind. J. Agr. Sci. 13: 29-*.
(b) Studies on the distribution of different forms of phosphorus in soil II. Surface distribution. *Ind. J. Agri. Sci. 13: 283-*.

Gieseking, J. E., 1942. Resistance of clay-adsorbed proteins to proteolytic hydrolysis. *Soil Sci. 53: 205-*.
1952. The influence of clay minerals on the enzymatic hydrolysis of organic phosphorus compounds. *Proc. Soil Sci. Soc. Am. 16: 10-*.

Gleen, R.C., et. al. 1959. Flow sheet for soil phosphate fractionation. *Agronomy abs. 1959*.

Goring, C.H.I., and Bartholomew, W.V. 1952. Adsorption of mononucleotides, nucleic acids and nucleoproteins by clays. *Soil Sci. 74: 149-*.

Hemwall, J.B.,1957. The fixation of phosphorus by soil. *advance Agon. 9: 95-*.

Hsu, P.H. 1964 Adsorption of phosphate by aluminium and iron in soils. *Proc. Soil Sci. Soc. Am. 28: 474-*.

Hsu, P.H., and Rennie, D.A., 1962(a) Reactions of phosphate in aluminium systems. I. Adsorption of phosphate by X-ray amorphous aluminium hydroxide. *Can.J. Soil Sci. 42:197-*
II. Precipitation of phosphate by exchangeable aluminium on a cation exchange resin. *Ibid. 210-*.

Jackman, R.H., 1951. Phosphorus status of some pumice soils. *N.Z. glassland association proc. 13 conf. 176-*.
1955. Organic phosphorus in N.Z. soil under pasture. I. Conversion of applied phosphate to organic form. *Soil Sci. 79: 207-*
II. Relation between organic phosphorus content and some soil characteristics. *Ibid. 293-*.

1960. Organic matter stability and nutrient availability in Taupo pumice. N.Z.J. Agric. Res. 3: 6-.

Khin. A., and Leeper, G.W. 1960. Modification in Chang and Jackson's procedure for fractionating soil phosphorus. Agrochimica, 4: 247-.

Kittrick, J.A., and Jackson, M.L., 1955. (a) Rate of phosphate reaction with soil minerals and election microscope observation on the reaction mechanism. Proc. Soil Sci. Soc. Am. 19: 292-.
(b) Application of solubility product principles to the variscite-kaolinite system. Ibid 455-.
(c) Common ion effect on phosphate solubility. Soil Sci. 79: 415-.
1956. Electron microscope observation of the reaction of phosphate with minerals, leading to a unified theory of phosphate fixation in soil. J.Soil Sci. 7:81-.

Kurtz, L.T. 1942. Elimination of fluoride interference in the molybdenum blue reaction. Indus. Engin. Chem. Anal. Ed. 14: 855-.

Kurtz, L.T., DeTurk, E.E., and Bray, R.H., 1946. Phosphate adsorption by Illinois soil. Soil Sci. 61: 111-.

Lamm, C.G., 1961. A study of isotopic exchanges and chemical conversions between fertilizer-phosphorus and soil phosphorus. Acta Agric. Scand. 7: 95-.

Lamm, C.G., Hansen, E.H., and Jorgensen, J.A., 1963. Isotopic exchange in soil fertility studies. Soil Sci. 95: 16-.

Larsen, S.,1952. The use of $P^{32}$ in studies on the uptake of phosphorus by plants. Plant and Soil 4: 1-.

Lavety, S.C., and McLean, E.D. 1961. Factors affecting yields and uptake of phosphorus by different crops. II. Kinds of phosphate, native, applied and formed. Soil Sci. 91: 166-.

Lindsay, W.L., Frazier, A.W., and Stephenson, H.F., 1962. Identification of reaction products from phosphate fertilizers in soil. *Proc. Soil Sci. Soc. Am. 26: 446-.*

Mattingly, G.E.G., 1957. The use of the isotope $^{32}P$ in recent work on soil and fertilizer phosphorus. *Soil and fertilizers. 20: 59-.*

Mattson, S. 1931. The law of soil colloidal behaviour; IV. Isoelectric precipitates. *Soil Sci. 31: 57-.*

Mattson,S.,Koutler-Anderson, E.,Miller, R.B., and Vahtras, K. 1951. Phosphate relationships of soil and plant. VIII. Electrokinetics, amphoteric behaviour and solubility relationship of calcium. *Ann. Roy. Agric. Coll. Sweden. 20: 19-.*

McAuliffe, C.D., and Hall, N.S., et al. 1948. Exchange reactions between phosphates and soils: Hydroxylic surfaces of soil minerals. *Proc. Soil Sci. Soc. Am. 12: 119-.*

Midgley, A.R.,1940. Review of phosphate fixation. *Proc. Soil Sci. Soc. Am. 5: 84-.*

Miller, R.B. 1954. Phosphate relationship of soil and plant. XI. The amphoteric behavior and solubility relationship of some iron and aluminium phosphates. *Ann. Roy. Agric. Coll. Sweden. 21: 161-.*

Pierre, W.H., 1948. The phosphate cycle and soil fertility. *J. Am. Soc. Agron. 40: 1-.*

Rommine, D.S. and Metzger, W.H., 1939. Phosphate fixation by horizons of various soil types in relation to dilute acid extractable iron and aluminium. *J. Am. Soc. Agron. 31. 99-.*

Regers, H.T., 1942. Dephosphorylation of organic phoshporus compounds by soil catalysts. *Soil Sci. 54: 439-.*

Russell, R.S., Rickson, J.B. and Adam, S.N., 1954. Isotopic equilibrium between phosphates in soil and their significance in the assessment of fertility by tracer methods. *J.Soil Sci. 5: 85-*.

Russell, G.C. and Low, P.F., 1954. Reaction of phosphate with kaolinite in dilute solution. *Proc. Soil Sci. Am. 18: 22-*.

Saunders, D.H., and Metelerkamp, H.R. 1962. Use of an anion exchange resin for determination of available soil phosphorus. *International Soil Sci. Conf. 1962. 847-*.

Saunders, W.M.H., 1959. Effect ofphosphate topdressing on a soil from andestic volcanic ash. I. Forms of soil phosphorus and a method of their determination. *N.Z.J.Agric. Res. 2: 427-*.
II. Effect on distribution of phosphorus and on related chemical properties. *Ibid. 455-*
III. Phosphate retention and pH. *Ibid. 659-*.
1964. Extraction of soil phosphate by anion exchange membrane. *N.Z.J. Agric. Res. 7: 427-*.
1965. Phsophate retention by N.Z. soils and its relationship to free sesquioxides, organic matter and other soil properties. *N.Z.J. Agric. Res. 8: 3--*.

Schofield, R.K. 1955. Can a precise meaning be given to available soil phosphorus? *Soil and Fertilizer, 18: 373-*.

Seatz, L.F. 1954. Phosphate activity measurement in soils. *Soil Sci. 77. 43-*.

Shao, Y.T. 1963. Isotope exchange kinetics applied to soil problems. *M.Sc. Thesis. Victoria University*.

Sheard, R.W. and Caldwell, A.G. 1955. The use of anion exchange resin in phosphorus fertility studies. *Can. J. Agric. Sci. 35: 36-*.

Sherman, M.S. 1942. Colorimetric determination of phosphorus in soils. *Ind. Eng. Chem. Analyst. Ed. 14: 182-.*

Soil Bureau information series. 1962. *Data on soil profiles.*

Swenson, R.W., Cole, C.V., and Seiling, D.H. 1949. Fixation of phosphate by iron and aluminium and replacement by organic and inorganic ions. *Soil Sci. 67: 3-.*

Talibudeen, O., 1954. The determination of isotopically exchangeable phosphorus in some Rothamsted soils. *Proc. 2nd Conf. on radioisotopes. 1: 405-.*
1957. Isotopically exchangeable phosphorus in soils. II. Factors influencing the estimation of labile phosphate. *J.Soil. Sci. 8: 86-.*
1958. III. The fractionation of soil phosphorus. *J. Soil. Sci. 9: 120-.*
1960. Isotopic exchange of phosphate in soil. *Report of the Rothamsted experimental station for 1960. 246-.*

Taylor, N.H. 1933. Soil processes in volcanic ash beds. *N.Z.J.Sci. Tech. 14: 338-.*

Taylor, C.B. 1946. *Nature 158: 447-.*

Teakle, L.J.H., 1928. Phosphate in the soil solution as affected by reaction and cation concentration. *Soil Sci. 25: 143-.*

Toth, S.S. 1937. Anion adsorption by soil colloids in relation to changes in free iron oxides. *Soil Sci. 44: 299-.*

Truog, E. 1930. The determination of the readily available phosphorus of soils. *Am. Sco. Agric. 10: 874-.*

Turner, R.C. and Rice, H.M. 1952. Role of fluoride ion in release of phosphate adsorbed by aluminium and iron hydroxides. *Soil Sci. 74: 141-.*

Volk, V.V., and McLean, E.O. 1963. The fate of applied phosphate in four Ohio soils. *Proc. Soil Sci. Soc. Am. 27:53-.*

Wiklander, L. 1950. Kinetics of phosphate exchange in soils. Ann. Rov. Coll. Sweden. 17: 407-.

Wild, A. 1949. The retention of phosphate by soil. A Review. J. Soil. Sci. 1: 221-.

Williams, C.H. 1950. Studies on soil phosphorus. I. A method for the partial fractionation of soil phosphorus. J. Agric. Sci. 40: 233-.

III. Phosphorus fractionation as a fertility index in S. Australiam soi. Ibid. 257-.

Williams, R. 1937. The solubility of soil phosphorus and other phosphorus compounds in sodium hydroxide solution. J. Agric. Sci. 27: 260-.

Wilson, A.T., and Furkert, R.J. 1962. A new technique for study adsorption on solid surface. Intern. soil conf. N.Z. 1962. 98-.

Yuan, T.L., Robertson, W.K. and Veller, J.R. 1960. Forms of newly fixed phosphorus in three acid sandy soils. Proc. Soil Sci. Soc. Am. 24: 447-.

# APPENDIX II.

## Test of control mean (1 rep.) against treatment mean (5 rep.)

e.g. Tirau silt loam (topsoil). Al-P (%)

| | Treatment<br>(ther-toluene) | Control<br>(no ether-toluene) |
|---|---|---|
| | 92.5 | |
| | 92.0 | |
| | 85.0 | |
| | 107.5 | |
| | 100.5 | 71.0 |
| SUM = | 478.0 | 71.0 |
| MEAN = | 95.6 | 71.0 |

Total S.S.= 794.5

Between S.S. = 504.3

F test of significance of control versus treatment.

| Source of Var. | S.S. | d.f. | M.S. | F. ratio | F. ratio | Results |
|---|---|---|---|---|---|---|
| Between (treat. and control) | 504.3 | 1 | 504.3 | 6.95 | (5%)10.13<br>(1%)34.12 | NS |
| Residual | 290.2 | 4 | 72.5 | | | |
| Total | 794.5 | 5 | | | | |

S.E. of Mean (treatment) = ± 3.9

S.E. of e Mean (control) = ± 8