Part I

# AN EVALUATION OF AMMONIUM FLUORIDE AS A SELECTIVE EXTRACTANT FOR ALUMINIUM-BOUND SOIL PHOSPHATE.

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# EXTRACTION OF PHOSPHATE BY FLUORIDE: IV

# AN EVALUATION OF AMMONIUM FLUORIDE AS A SELECTIVE EXTRACTANT FOR ALUMINIUM-BOUND SOIL PHOSPHATE: IV DETAILED STUDIES ON SOILS (2)

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TABLE 1

Description of soils

| Soil Type | pH | Parent Material | Free iron oxides(%) | Predominant Clay Minerals (4)* |
|---|---|---|---|---|
| Stratford sandy loam† | 6.0 | Andesitic ash | 1.26 | Allophane A |
| Kariwari friable clay | 5.1 | Basalt | 9.41 | Gibbsite with some meta-halloysite |

The genetic classification of these soils is given in (6)

* Refers to literature cited.

† In (6) read Stratford sand for Stratford Sandy loam

TABLE 2

Effect of time of extraction and soil: extractant ratio on retention by Stratford sandy loam of added $P^{31}$ orthophosphate in the presence of 0.5M $NH_4F$ at pH 8.5

| Soil: Extractant Ratio | Equilibration Time | P in Soil Extract | | P Added | Proportion of P | |
|---|---|---|---|---|---|---|
| | | | In presence of added P | | Recovered in extract | Retained by Soil |
| | hours | ppm. | | ppm. | % | |
| 1:400 | 24 | 2.06 | 3.02 | 1.00 | 96 | 4 |
| | 64 | 2.07 | 3.03 | 1.00 | 96 | 4 |
| 1:800 | 24 | 1.04 | 2.02 | 1.00 | 98 | 2 |
| | 64 | 1.04 | 2.01 | 1.00 | 97 | 3 |

TABLE 3

Effect of soil: extractant ratio on retention by Stratford sandy loam of added $P^{32}$ orthophosphate in the presence of 0.5M $NH_4F$ at pH 8.5

| Soil: Extractant Ratio | Proportion of $P^{32}$ | |
|---|---|---|
| | Recovered in extract | Retained by soil |
| | % | |
| 1:50 | 88 | 12 |
| 1:200 | 94 | 6 |
| 1:800 | 96 | 4 |
| 1:3200 | 97 | 3 |
| 1:6400 | 98 | 2 |

Equilibration time: 64 hours

TABLE 4

Base status of Kerikeri friable clay and Alexandra sandy loam

| Soil | Cation Exchange Capacity | Total Exchangeable Bases | Ca | Mg | Base Saturation |
|---|---|---|---|---|---|
| | me.% | me.% | me.% | me.% | % |
| Kerikeri friable clay | 22.0 | 6.9 | 6.3 | 1.6 | 31 |
| Alexandra sandy loam | 21.7 | 18.7 | 14.3 | 3.2 | 81 |

New Zealand Soil Bureau data

TABLE 5

Effect of pretreatment of Kardiori friable clay with 0.5M $NH_4Cl$ on subsequent release of phosphate by 16 - hour extraction at 1:100 dilution with 0.5M $NH_4F$ at pH 8.5

| Nature of pretreatment with 0.5M $NH_4Cl$ | Phosphate extraction procedure | P released |
|---|---|---|
| | | mg/l |
| Nil | Direct extraction with 0.5M $NH_4F$ | 14.7 |
| Soil treated with solution at 1:100 ratio in centrifuge tube with periodic stirring for 1 hour and then centrifuged. Process repeated a further five times. | Extraction with 0.5M $NH_4F$ carried out after acetone drying of pretreated samples | 16.8 |
| Soil shaken with solution at 1:50 ratio for 30 hours but not centrifuged | 1M $NH_4F$ at pH 8.5 added to suspension of soil in 0.5M $NH_4Cl$ to provide 0.5M $NH_4F$ in the combined solution | 16.0 |
| Nil | Direct extraction with 0.5M $NH_4Cl$ and 1M $NH_4F$ mixed in equal volumes | 14.0 |

[a]No measurable amounts of P were dissolved by the 0.5M $NH_4Cl$ pretreatments

TABLE 6

Retention by Koriheri friable clay of added $P^{31}$ orthophosphate in the presence of 0.5M and 1M $NH_4F$ at pH 8.5 at the 1:200 soil:extractant ratio for several equilibration times

| Concentration of Reagent | Equilibration Time | P in Soil Extract | | P added | Proportion of P | |
|---|---|---|---|---|---|---|
| | | | In presence of added P | | Recovered in extract | Retained by soil |
| | hours | ppm. | | ppm. | % | |
| 0.5M | 24 | 0.86 | 1.57 | 1.00 | 71 | 29 |
| | 72 | 1.07 | 1.78 | 1.00 | 71 | 29 |
| | 600 | 1.85 | 2.54 | 1.00 | 69 | 31 |
| 1M | 24 | 1.16 | 1.93 | 1.00 | 77 | 23 |
| | 600 | 2.35 | 3.12 | 1.00 | 77 | 23 |

TABLE 7

Effect of soil: extractant ratio on retention by Kerikeri friable clay of added $P^{32}$ orthophosphate in the presence of 0.5% $NH_4F$ at pH 8.5

| Soil: Extractant Ratio | Proportion of $P^{32}$ | |
|---|---|---|
| | Recovered in extract | Retained by soil |
| | % | |
| 1:50 | 52 | 48 |
| 1:200 | 69 | 31 |
| 1:800 | 80 | 20 |
| 1:3200 | 88 | 12 |
| 1:6400 | 93 | 7 |
| 1:12800 | 97 | 3 |

Equilibration time: 72 hours

## POSITIONS

1. The author is indebted to R.G. William, Macaulay Institute, Aberdeen, for supplying the leucophosphite sample. The mineral was prepared and characterised by E.L. Ardidge at the Macaulay Institute.

2. This ability of alkaline 0.5M $NH_4F$ to effect complete liberation of aluminum - bound phosphate from an allophanic soil lends support to the contention that the rise in phosphate solubility in the alkaline extractant over the 24-72 hour range found for the soils of low free alumina content discussed in the previous paper (7) is due to hydrolysis of original iron-bound phosphate, rather than to continuing attack on a more resistant fraction of the aluminum-bound form.

3. From the satisfactory agreement found between $P^{31}$ and $P^{32}$ recovery values at comparable soil: extractant ratios it may be concluded that $P^{32}$ distribution between soil and extractant is uncomplicated by an isotopic exchange effect.

4. This feature of the curve is attributable to the decreasing stability of the fluoaluminate complex as the pH is raised.

5. One-hour neutral 0.5M $NH_4F$ extraction value corrected by subtraction of 10 per cent of the NaOH-soluble P in residue.

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(2) BIRRELL, K.S. 1961 Ion fixation by allophane. New Zealand J. Sci. 4:393 - 144.

(3) CHANG, S.C., and JACKSON, M.L. 1957 Fractionation of soil phosphorus. Soil Sci. 84:133 - 144.

(4) FIELDES, M., and TAYLOR, N.H. 1961 Clay mineralogy of New Zealand. Soils: 5. Mineral Colloids and genetic classification. New Zealand J. Sci. 4:679 - 706.

(5) FIFE, C.V. 1959 An evaluation of ammonium fluroide as a selective extractant for aluminum-bound soil phosphate: I. Soil Sci. 87:13 - 21

(6) FIFE, C.V. 1959 An evaluation of ammonium fluoride as a selective extractant for aluminum-bound soil phosphate: II. Soil Sci. 87:83 - 88.

(7) FIFE, C.V. 1962 An evaluation of ammonium fluoride as a selective extractant for aluminum-bound soil phosphate: III. Soil Sci. 93:113 - 125

## LEGENDS FOR FIGURES

Fig. 1 Effect of extraction time and soil: extractant ratio on the release of phosphate from Stratford sandy loam by 0.5M $NH_4F$ at pH 8.5.

Fig. 2 Relationship between pH and phosphate release in 0.5M $NH_4F$ for Stratford sandy loam at a soil: extractant-ratio of 1:100. (Extraction time 24 hours).

Fig. 3 Relationship between pH and phosphate release in 0.5M $NH_4F$ for Stratford sandy loam and Kerikeri friable clay at a soil: extractant ratio of 1:800. (Extraction time 90 hours. Kerikeri samples preleached with 0.5M $NH_4Cl$).

Fig. 4 Relationship between pH and phosphate release in 0.5M $NH_4F$ for strengite and leucophosphite (Mineral: extractant ratio 1:500. Extraction time 16 hours).

Fig. 5 Effect of pretreatment of Kerikeri friable clay with 0.5M $NH_4Cl$ on subsequent release of phosphate by 16 - hour extraction with 0.5M $NH_4F$ for a range of pH values.

Fig. 6 Effect of extraction time and soil: extractant ratio on the release of phosphate from Kerikeri friable clay by 0.5M $NH_4F$ and 1M $NH_4F$ at pH8.5.

Fig. 7 Release of phosphate from Kerikeri friable clay by prolonged extraction with 0.5M $NH_4F$ and 1M $NH_4F$ at pH 8.5.

Fig 1

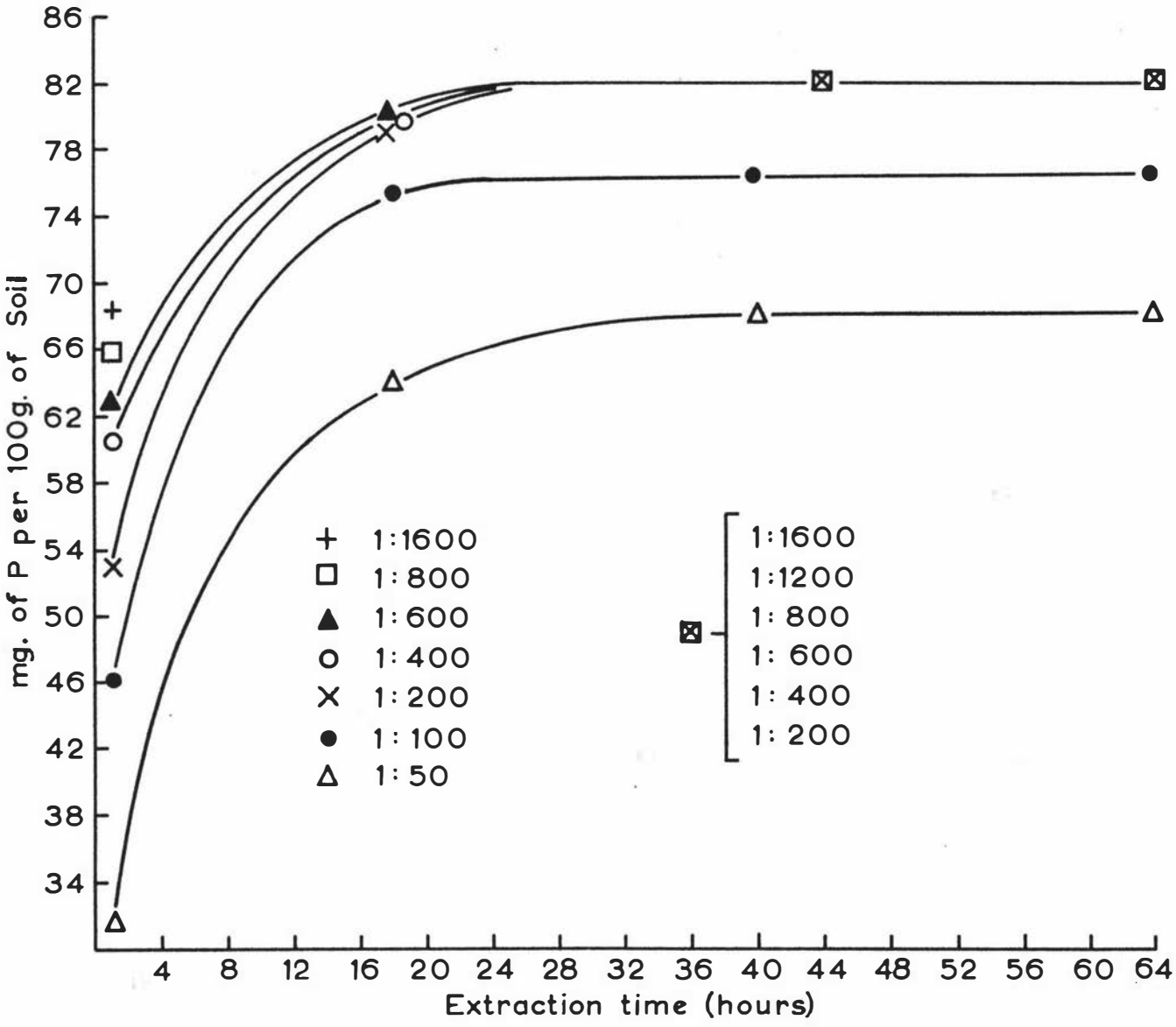

mg. of P per 100g. of Soil
86
82
78
74
70
66
62
58
54
50
46
42
38
34
4
8
12
16
20
24
28
32
36
40
44
48
52
56
60
64
Extraction time (hours)
+ 1:1600
□ 1:800
▲ 1:600
o 1:400
× 1:200
● 1:100
△ 1:50
⊠ 1:1600
1:1200
1:800
1:600
1:400
1:200

Fig 2

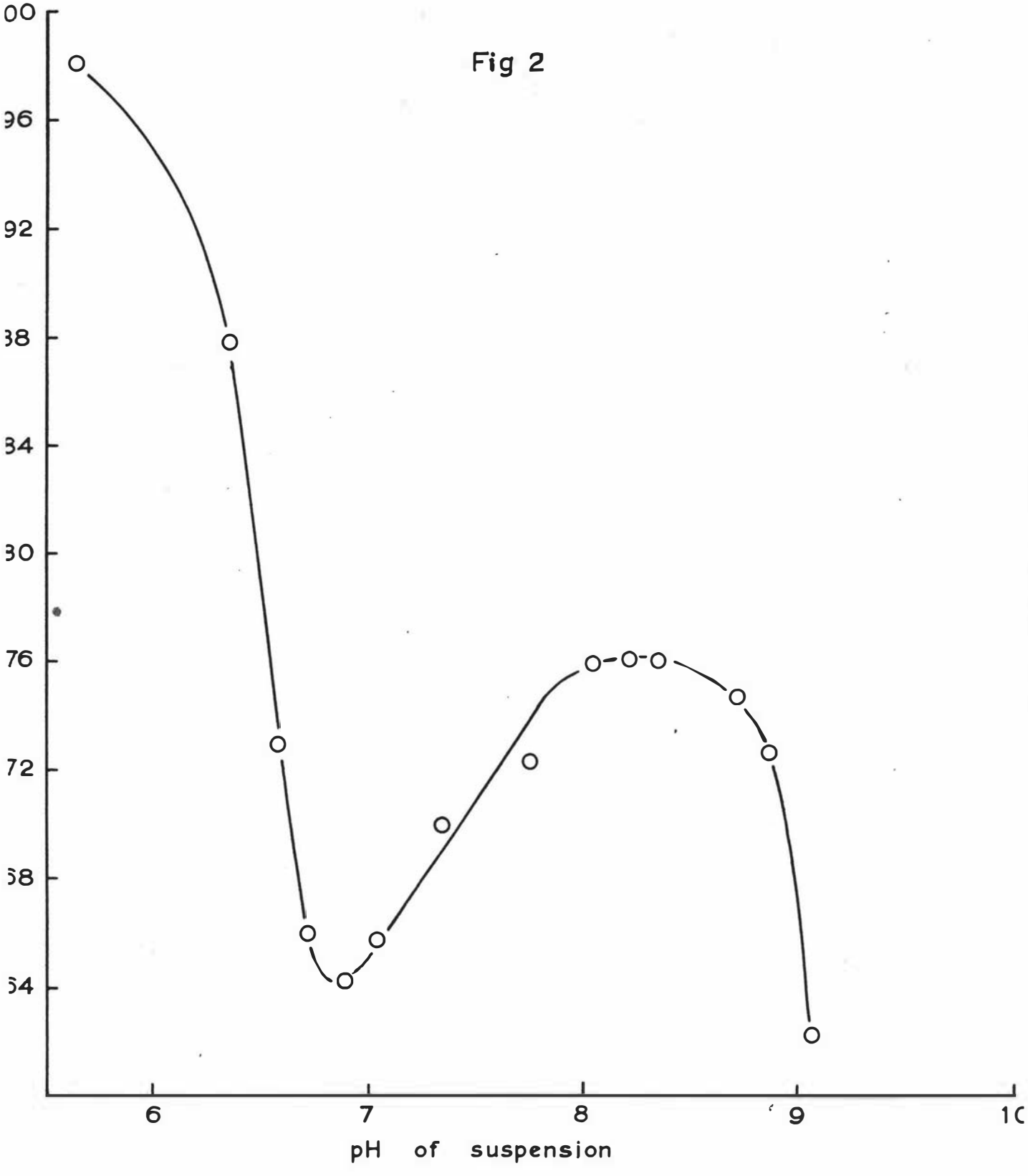
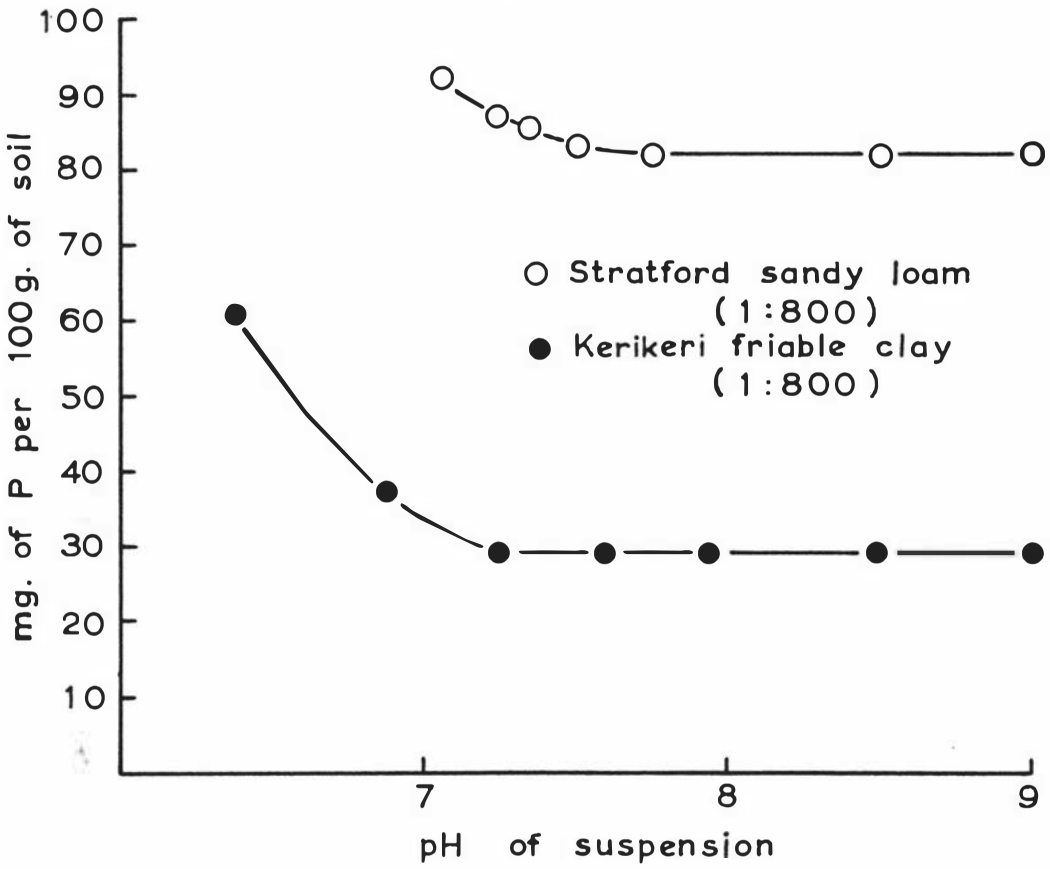


Fig 3


100
90
80
70
60
50
40
30
20
10
mg. of P per 100g. of soil
7
8
9
pH of suspension
○ Stratford sandy loam (1:800)
● Kerikeri friable clay (1:800)

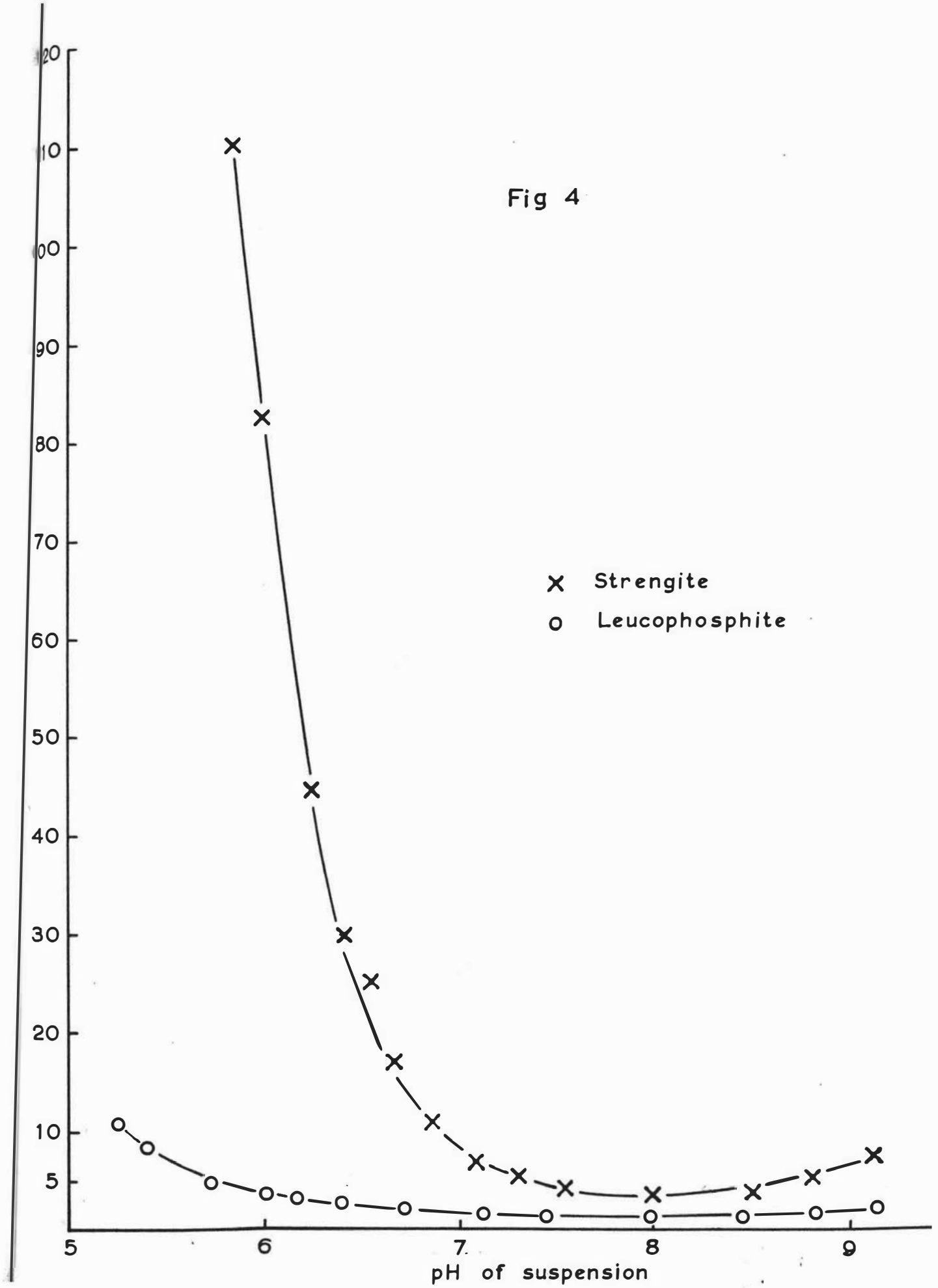
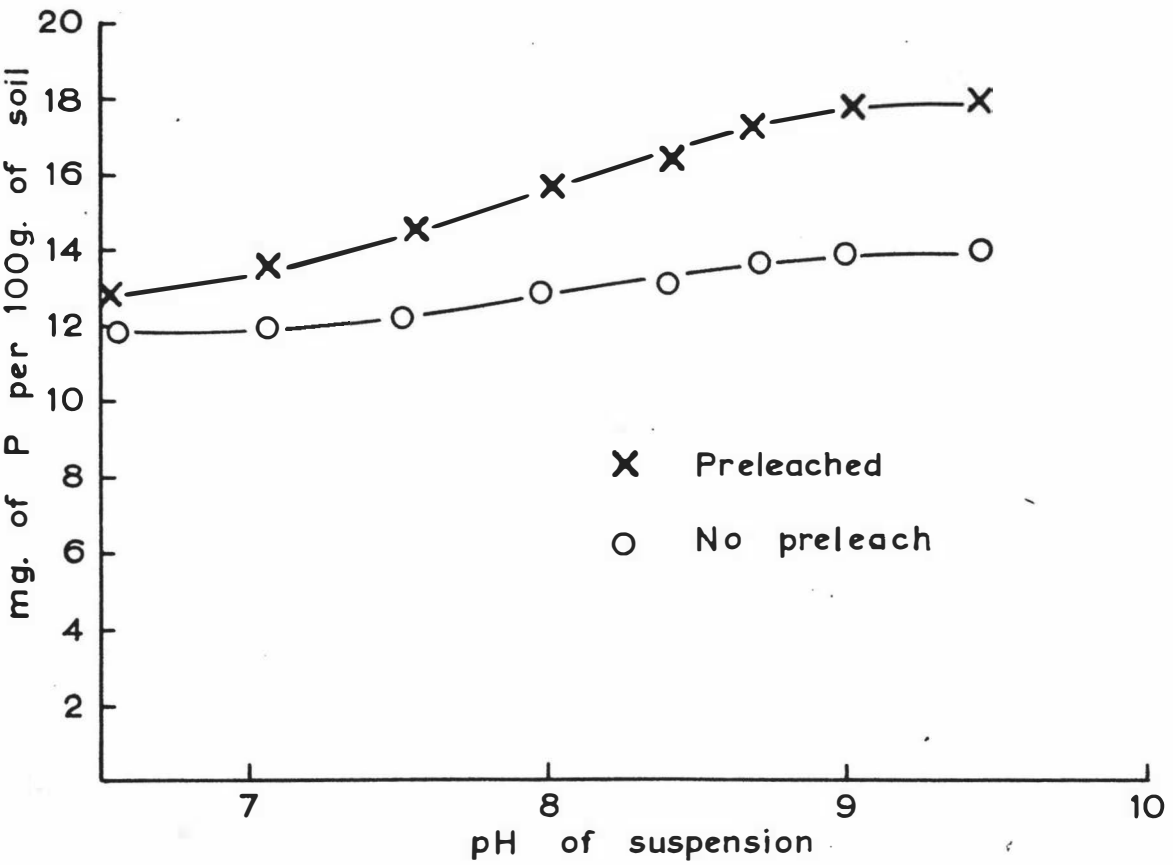


Fig 4
120
110
100
90
80
70
60
50
40
30
20
10
5
× Strengite
o Leucophosphite
5
6
7
8
9
pH of suspension

Fig 5


20
18
16
14
12
10
8
6
4
2
mg. of P per 100g. of soil
7
8
9
10
pH of suspension
X Preleached
O No preleach

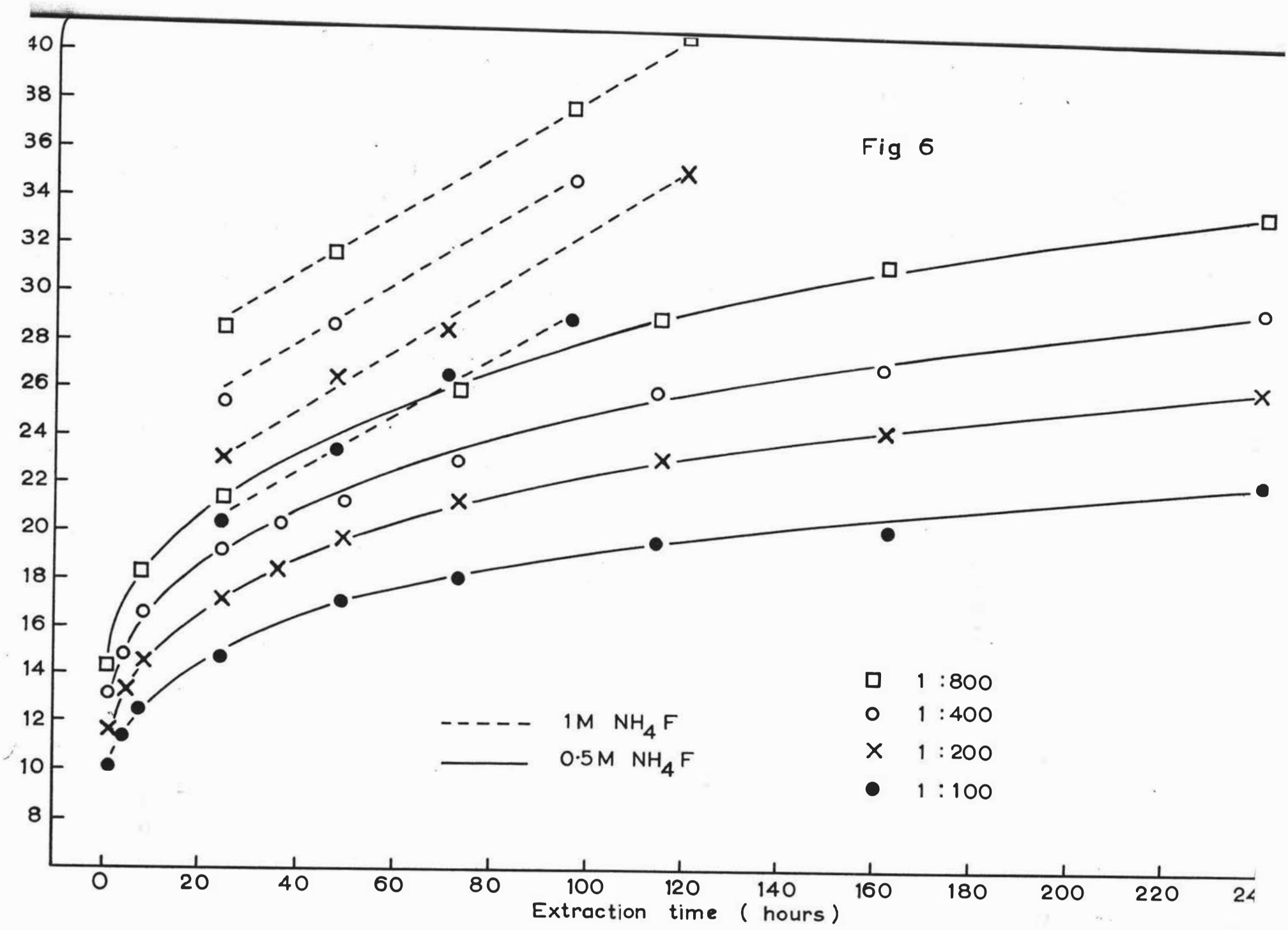
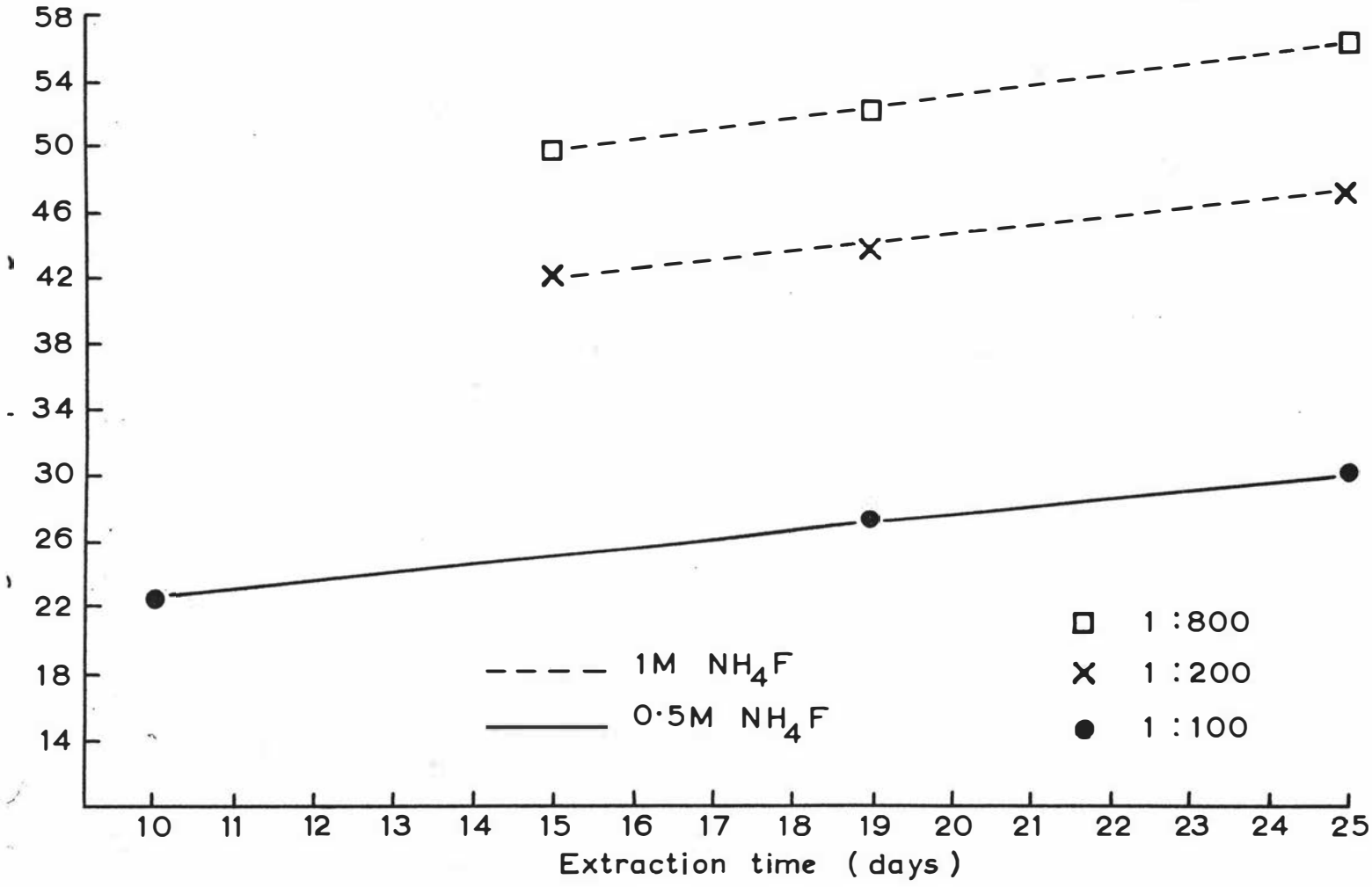


Fig 6
40
38
36
34
32
30
28
26
24
22
20
18
16
14
12
10
8
0
20
40
60
80
100
120
140
160
180
200
220
Extraction time ( hours )
1M NH4F
0·5M NH4F
1 : 800
1 : 400
1 : 200
1 : 100

Fig 7


58
54
50
46
42
38
34
30
26
22
18
14
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
Extraction time ( days )
1M $NH_4F$
0·5M $NH_4F$
1 : 800
1 : 200
1 : 100

In the previous paper of this series (7) the conditions under which a satisfactory quantitative evaluation of the aluminum-bound phosphate fraction in soils is likely to be attained by alkaline fluoride extraction were defined on the basis of studies carried out on three New Zealand soils. This paper reports results obtained for two additional soils, which because of their high phosphate fixing capacity and type of clay mineral assemblage, were considered as possibly presenting special problems in respect of the aluminum-bound phosphate determination.

## MATERIALS

### Soils

The soils used are described in table 1. Samples ground to pass an 80-mesh sieve were used for analysis.

### Minerals

Synthetic strengite (previously described (7) ) and synthetic leucophosphite[1] were the minerals used. The x-ray data for the leucophosphite were in very close agreement with those given by Axelrod et al (1) for the naturally occurring mineral. The chemical composition ($P_2O_5$, 37.3 per cent; $Fe_2O_3$, 38.5 per cent, $K_2O$, 10.9 per cent; and $H_2O$, 12.4 per cent) is in good agreement with the empirical formula $K_2O \cdot 2Fe_2O_3 \cdot 2P_2O_5 \cdot 5H_2O$. The sample used was ground to pass a 100-mesh sieve.

RESULTS FOR STRATFORD SANDY LOAM

Figure 1 shows the effect of extraction time and soil: extractant ratio on the release of phosphate from unpreleached samples of Stratford sandy loam by 0.5% $NH_4F$ initially at pH 8.5. Preliminary experiment had indicated that fluoride-extractable phosphate values for this soil were unaffected by prior removal of divalent exchangeable cations.

It is evident from figure 1, that in the 24-64 hour range, the pattern of phosphate release differs from that shown by the soils previously studied (7). Thus not only is the amount of phosphate liberated at any particular dilution independent of time, but also, within the limits of experimental accuracy, independent of soil: extractant ratio at dilutions greater than about 1:200. The former characteristic must imply that there is no continuing release of original soil phosphate, for, as indicated by the results in table 2, retention of phosphate by the soil remains constant in this time range and is therefore without effect on the form of the release curve. It may be concluded that solution of original aluminum-bound phosphate is complete in 24 hours[2] and that original iron-bound phosphate in this soil does not undergo the slow progressive hydrolysis indicated for this component in the soils previously reported on (7). The independence of phosphate release on soil: extractant ratio at dilutions above about 1:200 suggests low retention of phosphate by free iron oxides and this is confirmed by the high percentage recovery of added known amounts of phosphate found at these dilutions (tables 2 and 3.) This finding was not anticipated as the phosphate solubility behaviour shown by the soil at the 1:100 dilution over a range of pH in 0.5% $NH_4F$ (Fig. 2) closely coincides with that found for the $Fe(OH)_3$-phosphate system in the initial study (5), apart from the marked decline in solubility indicated at high pH values[4]. Evidently, although active in retaining phosphate at near neutral pH values, the free iron oxide component of the soil has little capacity for retaining it at pH 8.5. It is possible that the

greater apparent sensitivity of iron-binding of phosphate to pH change above the neutral point found for this soil as compared with that found for the soils previously studied (7), may be associated with the wider range of initial pH values required to produce a given range of pH in the equilibrium suspensions. Thus acidification of the 0.5% $NH_4F$ to pH 4.5 was necessary to provide a neutral suspension after 16-hour equilibration at the 1:100 dilution. Figure 3 shows that the effect of pH in regulating adsorption of phosphate by the free iron oxide component of the Stratford soil in the alkaline range becomes subdued at high dilution. The pattern of phosphate solubility obtained under these conditions approximates to that shown for strengite and leucophosphite (Figure 4) and found for rockbridgeite (5) except that no rise in phosphate solubility comparable with that found for the minerals in the more strongly alkaline solutions occurs in the soil system. Figure 3 shows also that a similar situation holds for Kerikeri friable clay; it was previously reported (6) that at the 1:100 dilution this soil exhibits a similar but less pronounced solubility trend in alkaline 0.5% $NH_4F$ to that shown for Stratford sandy loam in Figure 2.

The Stratford soil produced a pH shift even in the alkaline reagent initially at pH 8.5. At the 1:100 soil: extractant ratio pH 8.75 was attained in the suspension after 24-hour equilibration while pH 8.85 was reached when a 1:50 ratio was employed; prolonging the extraction time to 64 hours resulted in little further pH rise at either ratio. These shifts in pH consequent upon the presence of allophane as the predominant clay mineral, are of sufficient magnitude to lower phosphate retention by free iron oxides and may contribute to the low percentage retention of added phosphate found at the 1:50 dilution (table 3) as compared with that previously reported for soils producing no comparable pH rise in the alkaline extractant (7).

It is evident from Figure 2 that the efficiency of phosphate extraction decreases when equilibrium values above pH 8.5 are attained in the 1:100

suspensions. The decrease in the phosphate release values found as the soil: extractant ratio was narrowed from 1:200 to 1:50 (Figure 1) may therefore reflect incomplete solution of original aluminum-bound soil phosphate in addition to increasing retention by free iron oxide of phosphate liberated from the aluminum-bound condition. This is borne out by the somewhat lower aluminum-bound phosphate value (78 mg. of P per cent) obtained by correction to an absorption-free basis (by means of the $P^{32}$ retention value in table 3) of the phosphate release value obtained at the 1:50 ratio, than that obtained (86 mg. of P per cent) by similar correction of the limiting phosphate release value shown in Figure 1 for the 1:200 and higher dilutions. It is of interest to compare this latter value with that obtained (36 mg. of P per cent) for unoccluded aluminum phosphate by the method of Chang and Jackson (3)[3].

## RESULTS FOR KERIKERI FRIABLE CLAY

Preliminary study showed that pretreatment with 0.5% $NH_4Cl$ was not without effect on the amount of phosphate released from the Kerikeri soil by the alkaline fluoride reagent. This finding was unexpected, for as indicated in table 4, this soil is less well supplied with divalent exchangeable cations than is Alexandra sandy loam, one of the soils for which release of phosphate by 0.5% $NH_4F$ at pH 8.5 was shown previously (7) to be uninfluenced by 0.5% $NH_4Cl$ pretreatment. Table 5 shows the magnitude of the effect at the 1:100 dilution and illustrates also that the enhanced phosphate release by fluoride following pretreatment is not contingent upon removal of divalent cations from the system. Precipitation of alkaline earth phosphates cannot therefore be the cause of the lower phosphate release values obtained by direct fluoride extraction. Table 5 further shows that an extractant 0.5% with respect to fluoride and 0.25% with respect to chloride is no more efficient in releasing phosphate than is 0.5% $NH_4F$ alone. It seems likely therefore that the effect of the pretreatment is to render a fraction of the original aluminum-bound soil phosphate more readily soluble in 0.5% $NH_4F$ possibly as a result of the slightly acidic condition ruling in the preleach stage. The effect would

thus be confined to soils from which complete solution of aluminum-bound phosphate is not effected by fluoride extraction, a situation which will be shown to apply with the Kerikeri soil. Figure 5 shows that the magnitude of the pretreatment effect decreased as the pH of the fluoride extractant was lowered and that it was largely suppressed when pH 6.5 (requiring an initial acidification of the extractant to pH 3.7) was attained in the equilibrium suspension. In this experiment the soil samples were preleached on 7 cm. filter papers and were left to dry at room temperature without acetone washing. The effect of this preleach procedure on the subsequent release of phosphate by 0.5% $NH_4F$ at pH 8.5 is seen to be more marked than that found in the experiments reported in table 5.

The detailed investigation of the effect of time and dilution on phosphate release from the Kerikeri soil by fluoride was restricted to unpreleached samples; the results obtained are presented in figures 6 and 7. It is evident that in contrast to the solubility behaviour shown by Stratford sandy loam, there is no suggestion of an approach to a limiting phosphate release value as the soil: extractant ratio is widened. Further, it is evident that when the strength of the reagent was increased to 1% substantially greater amounts of phosphate were extracted. In contrast with this finding, the near limiting values obtained for Stratford sandy loam and for the soils previously studied (7) were not affected by substitution of 1% $NH_4F$ for the 0.5% reagent. Figures 6 and 7 indicate also that the effect of time of extraction on phosphate release differs from that found for the Stratford soil. It differs also from that found for the three soils previously reported on (7) which for extraction periods beyond about 3 days released no additional amounts of phosphate to the alkaline 0.5% reagent.

The distribution of added known amounts of $P^{31}$ orthophosphate and of $P^{32}$ orthophosphate between soil and extractant[3] as a result of equilibration under a range of experimental conditions is shown in table 6 and 7. In

keeping with the results obtained with all soils previously examined, the fractional retention of added phosphate against 0.5% $NH_4F$ extraction at pH8.5 was unaffected by extraction time in the range over which retention values were investigated (table 6) and a similar situation obtained in the 1% reagent although a lower proportion of the added phosphate was retained by the soil in the presence of the stronger reagent. It has previously been shown (5) that 0.5% $NH_4F$ in alkaline solution possesses some specific ability unconnected with soluble fluoferrate ion formation to limit adsorption of phosphate by ferric hydroxide, and it is probable that the lowered phosphate retention observed in the 1% reagent is an intensification of this effect.

The reduced capacity of the free iron oxide component of the soil to adsorb phosphate in the presence of 1% $NH_4F$ accounts only in part for the higher phosphate release values found in this reagent. Thus conversion of the 25-day extraction values (table 6) to an adsorption free basis produces an aluminum-bound phosphate value of 61.0 mg. P per cent for 1% $NH_4F$ extraction as compared with 53 mg. P per cent for 0.5% $NH_4F$ extraction. It is evident, therefore, that the more efficient extraction of aluminum-bound phosphate by the 1% reagent shown by the relative slopes of the phosphate release curves found for the two reagents during the earlier stages of extraction (figure 6) is maintained throughout the whole range of extraction time investigated.

The three soils discussed in the preceding paper of this series (7) showed a small progressive release of phosphate as the extraction time was increased in the 24-72 hour range, and this effect was attributed to slow hydrolysis of original iron-bound phosphate. In view of the previously reported (6) extremely low phosphate concentrations supported by the Kerikeri soil in alkaline 0.5% $NH_4Cl$ it is likely that, as found for Stratford sandy loam which exhibits similar solubility characteristics in this reagent, original iron-bound phosphate would contribute only negligible amounts of phosphate to the fluoride extracts. On this assumption, the rise in phosphate solubility

observed in 1% and 0.5% $NH_4F$ throughout the whole time range investigated for the Kerikeri soil would be attributable entirely to continuing dissolution of aluminum-bound phosphate, and correction to an adsorption-free basis of the phosphate-release value for any given extraction period would provide a measure of aluminum-bound phosphate dissolved in this time. As indicated in figures 6 and 7, however, no limiting phosphate solubility was attained within the extended extraction period investigated. Although such a limit might possibly be reached by further prolongation of extraction time it may be concluded that, for all practical purposes, neither the 0.5% or 1% reagent is capable of yielding a satisfactory evaluation of the aluminum-bound phosphate content of this soil

The method of Chang and Jackson (3) for the determination of aluminum phosphate[5] yielded a value of 7 mg. of P per cent for this soil. This may be compared with the 61 mg. of P per cent found by conversion to an adsorption-free basis of the 25-day extraction value obtained using 1% $NH_4F$ at pH 8.5 as the extractant.

## DISCUSSION

From the results obtained with Stratford sandy loam it is evident that, the alkaline $NH_4F$ extraction procedure is likely to afford a satisfactory means of determining aluminum-bound phosphate in soils containing considerable amounts of allophane or amorphous alumina. Stratford sandy loam itself may be taken as probably typifying the least difficult case liable to be encountered in applying the method to soils in general, because the phosphate release values obtained by alkaline 0.5% $NH_4F$ extraction at the higher dilutions provide, for all practical purposes, a direct measure of aluminum-bound phosphate.

The failure to obtain complete extraction of the aluminum-bound form of phosphate from Kerikeri friable clay is almost certainly connected with the

presence of important amounts of gibbsite in the clay fraction of this soil. Birrell (2) has reported that this mineral, in contrast to the behaviour shown by allophane is attacked only slowly by fluoride even under acid conditions. It is probable that an environment favouring the formation of crystalline alumina has also favoured formation of crystalline aluminum phosphates in intimate association with the gibbsite and that the release of this phosphate is limited by the resistance of the gibbsite lattice to fluoride attack.

The degree of crystallinity attained by the hydrated oxides in the clay fraction of the Kaikeri soil is less than that occurring at the mature stage of red and brown loam development in New Zealand and considerably less than in certain mature tropical soils derived from basalt (4). It seems therefore that there exists a substantial body of soils for which a satisfactory evaluation of aluminum-bound phosphate content will not be readily achieved by alkaline $NH_4F$ extraction.

## SUMMARY

The effect of extraction time and soil: extractant ratio on the release of soil phosphate by $NH_4F$ at pH 8.5 was examined for two additional New Zealand soils.

With Stratford sandy loam, the efficiency of phosphate extraction by 0.5% $NH_4F$ increased as the soil: extractant ratio was widened from 1:50 to 1:200, but any further increase in the efficiency of extraction at greater dilution up to the limit at which it was practicable to work was not distinguishable from experimental error in the 24-64 hour range of extraction time. High recovery of added known amounts of $P^{31}$ or $P^{32}$ orthophosphate in the alkaline fluoride extracts following equilibration at the wider soil: extractant ratios indicated low phosphate retention by the free iron oxide component of the soil under these conditions. Extension of extraction time within the 24-64 hour range was without effect on this retention and resulted

in no further liberation of phosphate from the soil, signifying that dissolution of aluminum-bound phosphate was complete within 24 hours and that original iron-bound phosphate was not undergoing progressive hydrolysis. No correction for the contribution of iron-bound phosphate to the extracts was therefore necessary, and in view of the low retention of phosphate by free iron oxides, the phosphate release value obtained by 24-hour extraction at the wider soil: extractant ratios was for all practical purposes considered a satisfactory measure of the aluminum-bound phosphate content of this soil. Substantial rises in pH occurred in the reagent when the soil was extracted at narrow ratios. Under these conditions the efficiency of phosphate extraction was apparently reduced as corrections of the release values to an adsorption-free basis did not produce an aluminum-bound phosphate value as high as that obtained at wider ratios.

With Kerikeri friable clay, treatment with 0.5% $NH_4Cl$ had some effect on the amount of phosphate subsequently extracted by 0.5% $NH_4F$ at pH 8.5. This effect was shown to be unconnected with the removal of divalent exchangeable cations. No upper limiting value for phosphate release was obtained for this soil either by extension of extraction time to 25 days or by increasing the concentration of the alkaline reagent to 1%. This behaviour was attributed to slowness of attack by fluoride on the gibbsite component of this soil and consequent slow release of associated aluminum-bound phosphate. In the light of the unsatisfactory results obtained with the Kerikeri soil attention was drawn to the limitations of the alkaline $NH_4F$ extraction procedure as a general method for the determination of aluminum-bound phosphate.