"THE RELATIVE SIGNIFICANCE OF IRON - BINDING AND ALUMINIUM - BINDING OF PHOSPHATE IN SOILS REPRESENTATIVE OF THE MAIN NEW ZEALAND GENETIC GROUPINGS AS REVEALED BY FRACTIONATION METHODS AND BY PHOSPHATE FIXATION STUDIES IN THE LABORATORY."

by

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TABLE OF CONTENTS

TABLE OF CONTENTS (Cont'd)

ACKNOWLEDGEMENTS

BIBLIOGRAPHY

APPENDIX

LIST OF TABLES AND FIGURES

PRESENTED IN THE TEXT.

Page

A. TABLES.

B. FIGURES.

I.

A. INTRODUCTION

Although a great body of evidence points to the presence of iron - and aluminium - bound phosphate in soils as products of the phosphate fixation process, until recently no satisfactory procedures have been available for the quantitative assessment of the amounts of these forms in soils.

Chang and Jackson (1957) were the first workers to propose a scheme of phosphate fractionation, which included the separate determination of iron - and aluminium - bound phosphates. The limitations of their procedure have been discussed by Fife (1959a, 1959b and 1962), who has proposed (1962) a modified method for the determination of the aluminium - bound soil phosphate fraction. Fife (unpublished results) has subsequently incorporated this procedure into a general scheme of soil phosphate fractionation, which includes the selective determination of iron - bound and calcium - bound phosphates.

The iron - and aluminium - bound forms of phosphate in soils are of secondary origin derived in the case of virgin soils from original apatite and in the case of fertilized soils by fixation of applied phosphate. Their proportionate incidence in any given soil is a reflection of the relative tendency for iron and aluminium compounds to fix phosphate derived by weathering of apatite or from added phosphate fertilizers. It was considered of interest to investigate whether the ratio of iron - bound to aluminium - bound phosphate in a range of New Zealand soils followed any pattern which could be linked with the established genetic classification of these soils. It was further considered of interest to investigate whether a relationship existed between the ratio of these forms found in field soils and that found by laboratory fixation studies.

Any laboratory study of the relative contribution of iron and aluminium compounds to the phosphate fixation process demands a procedure for the removal of one of these compounds so that the phosphate retaining properties of the other may be investigated. Ideally the fixing capacity should be studied

(a) after dealumination,

(b) after deferration,

and the summation of these quantities compared with the phosphate fixing capacity of the whole soil, steps being taken in all cases to ensure that alkaline earth cations, which may fix phosphate by precipitation reactions, are first removed from the systems. Unfortunately there appears to be no procedure whereby iron oxides can be removed from soils without simultaneous removal of aluminium. Fife (unpublished data) has, however, concluded that prolonged treatment of soils with 0.5 M NH_4F at pH 8.5 should completely eliminate aluminium - binding of phosphate by virtue of the ability of this reagent to form complex ions with aluminium but not with iron at this pH value. Soils dealuminated in this way should therefore serve for studies on phosphate retention by free iron oxides. Strongly alkaline solutions such as 1 M NaOH may also be expected to achieve dealumination through the formation of soluble aluminates. Both these methods were investigated in the present study.

B. REVIEW OF LITERATURE.

1. The Fractionation of Soil Phosphorus

Fisher and Thomas (1935) employed a method consisting of two extractants for use with acid and calcareous soils.

(a) 0.002 N H_2SO_4 and 0.3% K_2SO_4 at pH 2.0

(b) a solution of acetic acid and sodium acetate buffered at pH 4.98 to 5.02

Their phosphate fractions were grouped as

(a) Calcium, magnesium and manganese phosphates,

(b) Aluminium and iron phosphates,

(c) Adsorbed phosphorus and apatite.

Williams (1937) drew attention to the solubility of soil phosphorus in solutions on the alkaline side of neutrality, and employed sodium hydroxide as an extractant. His soil phosphorus fractions consisted of three main groups;

(a) Alkali - soluble phosphorus
    Phosphorus in combination sesquioxide
    Organic Phosphorus
    Exchangeable phosphorus of clay complex,
    Phosphorus in hydrolysable combination with calcium
    Phosphorus in water - soluble form.

(b) Alkali - insoluble phosphorus
    Phosphorus in compounds of apatite class.

(c) Doubtful Group
    Phosphorus in interior of clay lattice.
    Phosphorus in combination with titanium.

Dean (1938) attempted the combination of an acid and an alkaline extraction. The soil was digested at 95°C with 0.25 N NaOH and the residue was further treated for one hour with 0.5 N H_2SO_4. He divided the soil phosphorus into three broad fractions;

(a) Organic compounds soluble in NaOH.

(b) Inorganic compounds soluble in NaOH and H_2SO_4.

(c) Insoluble compounds.

Ghani (1943a) repeated much of Dean's work and observed that the alkali - soluble phosphorus was increased if the soil was pre-treated with dilute acids prior to alkali treatment. This effect was attributed to the removal of exchangeable divalent cations, which precipitate phosphate in alkaline solution. He thus modified Dean's procedure by making a pre-treatment of the soil with 0.5 N acetic acid for the removal of exchangeable metal ions. The soil was then treated repeatedly with 0.25 N NaOH and finally with 2 N H_2SO_4. His phosphorus fractions consisted of five groups;

(a) Acetic acid - soluble phosphates representing mono - , di - , and tri - calcium phosphates,

(b) Alkali - soluble inorganic phosphates representing iron and aluminium phosphates,

(c) Alkali - soluble organic phosphates,

(d) Sulphuric acid soluble phosphates of apatite type,

(e) Insoluble phosphates.

A disadvantage of Ghani's procedure was that some of the phosphate brought into solution by the acetic acid was re-adsorbed by the soil and was then extracted in the alkali extraction. To overcome this objection, Ghani (1943c) suggested the use of 8 - hydroxyquinone as a means of blocking re-adsorption or precipitation of phosphate by active iron and aluminium during the acetic acid extraction.

This suggestion was further explored by Williams (1950a, 1950b). His fractionation consisted of successive extractions with 2.5% acetic acid - 1% 8 - hydroxyquinoline and finally 0.1 N NaOH. The use of cupferron was found to be less effective than 8 - hydroxyquinoline.

Although higher acetic acid - soluble phosphate values were obtained by these workers by the use of these blocking reagents, it cannot be concluded that the phosphate found in solution was a true measure of the more readily soluble calcium phosphates because any reagent capable of preventing resorption of phosphate must also have an enhanced capacity for dissolving original soil phosphate. It is probable therefore that part of the increased amounts of acetic acid - soluble phosphate liberated was derived from the original iron - and aluminium - bound soil phosphate.

An approach from a somewhat different angle was adopted by Bray and Kurtz (1945). These workers considered that the forms of soil phosphate of greater significance to plant growth were the acid - soluble (mainly calcium - bound) and adsorbed (or exchangeable) phosphate and their fractionation procedure was designed to delineate these categories. The adsorbed phosphate was extracted with 0.5 N NH_4F. A solution of 0.1 N HCl and 0.5 N NH_4F was used as a combined extractant and the acid - soluble form was found by difference of the combination and adsorbed forms.

This difference procedure for determining acid - soluble phosphate fraction assumes that the release of phosphate by NH_4F is independent of the pH at which extraction is carried out. Fife (1959a, 1959b) has shown that this is not the case and it is clear from his work that the difference procedure of Bray and Kurtz (1945) for phosphate fractionation must give a grossly exaggerated value for calcium - bound phosphate. It is also evident that the so - called adsorbed or exchangeable form included considerable amounts of phosphate derived from the iron - and aluminium - bound forms, which would certainly not fall within the category of "exchangeable" phosphate as now defined by the "isotopic" exchange techniques (Talibudeen 1954, 1957, 1958, Arambarri and Talibudeen 1959a, 1959b, 1959c).

Bauwin and Tyner (1954) also adopted this procedure of Bray and Kurtz in their studies non - extractable phosphorus distribution in some Grey - Brown Podzolic, Prairie, and Planosol soil profiles.

Chang and Jackson (1957) adopted the use of neutral ammonium fluoride as a selective extractant of unoccluded aluminium phosphate in their comprehensive scheme of soil fractionation. They divided soil phosphorus into discrete chemical forms; calcium phosphate, aluminium phosphate, iron phosphate, reductant - soluble (iron oxide coated) iron phosphate, occluded aluminium - iron phosphate and organic phosphorus. Their procedure is summarised below.

Phosphorus Fractionation. (Chang & Jackson.)

Phosphorus Fraction	Extractant	Forms of Phosphate Extractable	Method Adapted From.
(a) Al-phosphate	Neutral 0.5 N NH_4F	Al-phosphate completely Fe-phosphate too (Fife)	Bray and Kurtz (1945)
(b) Fe-phosphate	0.1 N NaOH	Al-phosphate Fe-phosphate Organic phosphorus	Williams (1950)
(c) Ca-phosphate	0.5 N H_2SO_4	Ca-phosphate completely Al- and Fe- phosphate considerably	Dean (1938)
(d) Reductant soluble Fe-phosphate (iron oxide occluded)	$Na_2S_2O_4$ - citrate	Fe-phosphate completely Al-phosphate negligibly	Aguilera and Jackson (1953)
(e) Occluded Al-phosphate	Neutral 0.5 N NH_4F	Al-phosphate completely Fe-phosphate too (Fife)	-
(f) Occluded Al-Fe-phosphate	0.1 N NaOH	(Alternative or addition to (e) Al- and Fe-phosphate completely	-
(g) Organic phosphorus	2.0 N H_2SO_4	Organic phosphorus	Bray and Kurtz (1945)

The main objections to the phosphate fractionation procedure of Chang and Jackson (1957) is that the assumptions are made that

(a) the dissolution of unoccluded aluminium phosphate is achieved by one hour extraction in neutral 0.5 N NH_4F.

(b) the resorption of phosphate liberated by fluoride from aluminium - bound forms does not occur in the presence of fluoride.

Chang and Jackson adopted the use of neutral ammonium fluoride as a selective extractant for unoccluded aluminium phosphate following the work of Turner and Rice (1952), who showed that the role of aluminium in liberating phosphate was one of formation of complexes of fluorine ions with iron and aluminium ions. The relative attack on these two ions varied with pH of the extractant.

Fife (1959a, 1959b) carried out critical studies of the stability of fluoferrate and fluoaluminate ions in NH_4F solution at different pH values both in artificial and in soil systems. It is evident from his results that the neutral ammonium fluoride as employed by Chang and Jackson extract considerable amounts of iron - bound soil phosphate as well as aluminium - bound soil phosphate. Fife thus proposed the use of 0.5 M NH_4F at pH 8.5 instead of at lower pH.

The resorption of phosphate liberated from the aluminium - bound forms during fluoride extraction by the free iron oxides of the soil may be of significance in some soils; especially those with high iron activity. This could be minimised, as suggested by Fife (1962), by extrapolating the 24 - 72 hour phosphate release curve for each soil to zero time. The value thus obtained after correction to an adsorption free basis is taken as a measure of the content of the aluminium - bound soil phosphate.

A fractionation procedure of soil inorganic phosphate proposed by Fife (unpublished data) divides soil inorganic phosphorus into;

Calcium - bound phosphate,
Iron - bound phosphate,
Aluminium - bound phosphate.

This procedure is summarised below but only the abbreviated method for determination of aluminium - bound soil phosphate is shown.

Extractant	Forms of Phosphate Extracted
0.1 N HCl	Calcium - bound phosphate + unknown proportions of iron - bound and aluminium - bound phosphate.
1 M NaOH on soil residue from foregoing extraction	Remaining iron - and aluminium - bound phosphates.
Neutral 1 M NaCl preleach on separate sample	Minor amounts of easily soluble phosphate which are added to the iron - and aluminium - bound forms extracted by 1 M NaOH.
1 M NaOH on soil residue from foregoing extraction	Iron - and aluminium - bound phosphate.
0.5 M NH_4F at pH 8.5 for 24 hours at the highest practicable dilution.	Aluminium - bound phosphate.

2. The Retention of Phosphate by Iron and Aluminium Compounds of Soils.

The earliest evidence of the reactions of phosphate ions with hydrated oxides of iron and aluminium came from Voelcker (1863) and Warington (1866) working on phosphate retention by iron and aluminium oxides.

Reactions of phosphate ions with artificial gels of silica, alumina, and iron were studied by Gordon and Starkey (1922), Starkey and Gordon (1922), Lichtenwalner et al. (1923), Miller (1928), Ghosh and Bhattacharyya (1930), McGeorge and Breazeale (1932) and Murphy (1939). This had also been demonstrated with ferric hydroxide (Kelley and Midgley (1943), with soluble iron and aluminium (Teakle 1928, Gaarder 1930, Mattson 1930, Pugh 1934, Murphy 1939 and Swenson et al. 1949). Ford (1933) showed by X-ray patterns that goethite and bauxite but not hematite retained phosphate.

The evidence in support of the retention of phosphate by iron and aluminium compounds of soils can be divided into four main groups.

(a) Correlations have been established between phosphate sorption and the amounts of iron and aluminium in soils.

Mattson (1927, 1931), Scarseth et al. (1934) and Toth (1937) observed that the phosphate sorption of soil colloids varied inversely as the $SiO_2/(Fe_2O_3 + Al_2O_3)$ ratio. Gile (1933) found in pot experiment that the efficiency of superphosphate decreased as the $SiO_2/(Fe_2O_3 + Al_2O_3)$ ratio of the soil colloids decreased. Gaarder and Grahl - Nielsen (1935) showed that the phosphate sorption capacity of forty - three soils increased with the ratio of basoids to acidoids.

The amounts of acid - soluble iron and aluminium and the amount of phosphate sorption of soils have been correlated by a number of workers (Fraps 1922, Antipou - Karateav et al. 1933, and Raychaudhur et al. (1941).

Vries De and Hetterschij (1938) and Coleman (1944) had established a correlation between the amounts of iron and aluminium and phosphate dissolved by dilute acids.

Metzger (1941), using forty-two soil samples found a significant correlation between total Al_2O_3, Fe_2O_3, $(Al_2O_3 + Fe_2O_3)$, and phosphate sorption. He established a correlation between the percentage total Fe_2O_3 that dissolved in 0.002 N H_2SO_4.

(b) Iron and aluminium have been removed from soils and soil colloids and the effect on phosphate sorption has been studied.

Toth (1937, 1939) and Kelley and Midgley (1943) used the hydrogen sulphide method of Drosdoff and Truog (1935) to show that the removal of iron and aluminium oxides from soil colloids reduced phosphate sorption. This effect varied with the colloid under investigation. Using the method of Truog et al. (1936) for removing iron and aluminium, a similar result had been reached by other workers (Metzger 1940, Chandler 1941, Black 1942 and Coleman 1942a, 1944).

(c) Iron and aluminium compounds have been added to soils and soil colloids and the effect on phosphate sorption has been studied.

Wolkoff (1924) added ferric chloride to a soil treated with rock phosphate and found a reduction in the amount of phosphate soluble in 0.2 N nitric acid. Aluminium chloride had no effect. Doughty (1930) saturated a peat soil with iron and aluminium ions by leaching with solutions of ferric chloride and aluminium chloride and recorded an increase in phosphate sorption. The maximum sorption was at pH 2.5 for ferric chloride treatment and pH 4.0 for aluminium chloride treatment. Scarseth (1935) found that a low - iron bentonite sorbed much more phosphate in the pH range 3.7 - 7.0 after being treated with a ferric chloride solution.

Davis (1943a, 1943b) reported that ferric chloride and aluminium chloride that had been added to soil - $Ca(OH)_2$ - H_2O - air system increased phosphate sorption especially at low pH values. He concluded that only at pH values lower than 4.5 were appreciable amounts of iron and aluminium formed that were insoluble in 0.002 N sulphuric acid.

(d) Compounds formed during phosphate sorption have been identified by comparing the effect of pH on phosphate sorption with the effect of pH on the solubility of iron and aluminium phosphates.

Teakle (1928) studied the effect of pH on the precipitation of iron and aluminium phosphates. With iron precipitation of phosphate was greatest at pH 3.0 and with aluminium at pH 6.8.

With equivalent amounts of Fe^{+++} and PO_4^{---}, Doughty (1930) found that the greatest precipitation was at pH 3.5 - 4.5 and Gaarder (1930) at pH 2.0 - 3.0. Both workers reported that precipitation occurred up to at least pH 8 in the presence of a considerable excess of iron. With equivalent amounts of Al^{+++} and PO_4^{---}, Doughty found greatest phosphate precipitation at pH 6.8 and Gaarder at pH 3.6 - 4.0, but with an excess of aluminium Doughty found the pH range of greatest precipitation became 6.5 - 8.5 and Gaarder 4.5 - 6.5. Rathje (1942) found that the greatest precipitation of phosphate by excess iron was at pH 3 and with excess aluminium at pH 4.

Similar results had been obtained by Murphy (1939) with ferric chloride and iron hydrosol, and by Perkins and King (1944) with limonite and hematite. McGeorge and Breazeale (1932) and Stelly and Pierre (1942) reported results on the effect of pH on the solubility of iron and aluminium phosphate minerals. The latter found that the lowest solubility of aluminium phosphate minerals, variscite and wavellite, was in the pH range 4.5 and 7.0, and of the iron phosphate minerals vivianite and dufrenite was in the pH ranges 6.0 - 7.0 and

and 3.0 - 6.0 respectively.

Rosman (1927) reported the first experiment that accurately related phosphate sorption of soil to the pH value. He found that the greatest sorption with the electrodialysed clay fraction of Putnam silt loam was at pH 3.0 - 4.0 and little sorption at pH 10.

Doughty (1930) studied the retention of phosphate by a peat soil over the pH range 3.0 - 10.0 and attributed the retention at low pH values to iron and aluminium. Scarseth (1934) found that the greatest retention of phosphate by an electrodialysed betonite titrated with sodium hydroxide was at pH 6 - 7, which he thought was due to a reaction of the phosphate with the aluminium of the clay mineral. Allison (1943) found a similar maximum at pH 6.0 with three soils titrated with sodium hydroxide. He found another peak in the phosphate sorption - pH curve at pH 3.0 - 3.5, which he attributed to the presence of iron and aluminium hydrous oxides, especially the former.

Black (1942) working with a Cecil Clay, found a maximum in the phosphate - sorption curve at pH 3 - 4, which he thought was due to hydrous iron oxide. He concluded that the maximum in the phosphate - sorption curve at pH 6 - 7, which he found with a sample of kaolinite, was due to adsorption of free aluminium hydroxide.

Coleman (1942a, 1944) using montmorillonite and kaolinitic clays showed that most sorption of phosphate occurred at pH 3.0, but after removal of free iron oxides the sorption was reduced so as to be about the same at pH 3.0, 7.0, and 9.5.

From the results of the various workers reviewed above, it may thus be concluded that there are some differences in the exact pH ranges of maximum phosphate retention or minimum phosphate solubility of iron and aluminium. However, two generalisations may be made concerning the relationship between pH and phosphate retention in solution containing iron and aluminium.

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

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

Mattson et al. (1953) showed that in artificial systems and in soil systems where iron and aluminium were present it was possible to obtain two separate phosphate solubility minima.

Saunders (1959c) employed the pH - phosphate retention curves to show the parts played by iron and aluminium in retaining phosphate in New Plymouth black loam. pH phosphate retention curves were drawn for New Plymouth black loam at low, moderate and high phosphorus status. He concluded from these curves that the large capacity of this soil to retain added phosphate was due to a high content of active aluminium.

II. MATERIALS.

Description of Soils.

The soils used are shown with their genetic grouping and type of parent material in Table 1. In Table 2 they are re-listed with relevant chemical and mineralogical data, the latter being derived from the published data of Fieldes (1955,1957), Fieldes et al (1954, 1955, 1957) and Birrell and Fieldes (1952).

Soil Bureau laboratory numbers are included for samples derived from this source. These represent unfertilized sites and as far as it has been possible to confirm the remaining soils with the exception of Manawatu silt loam (serial No. 24) have received little or no fertilizer. The Manawatu silt loam sample is representative of an area which has received annual applications of phosphate over a period of years.

Table 1.

Description of Soils.

Serial No. (S.B. Lab. No.)	Soil Type	Parent Material	Genetic No.	Genetic Classification
(1) (2079)	Tekapo silt loam	loess from greywacke	1b	Brown-grey earths moderately leached
(2)	Tokomaru silt loam	alluvium from greywacke	2b	Yellow-grey earths weakly leached
(3) (4995)	Ruapuna silt loam	alluvium from greywacke	3a	Transitional yellow-grey to yellow-brown earths moderately leached
(4) (1603)	Katrina fine sandy loam	loess from greywacke	4	Yellow-brown earths weakly weathered
(5) (631)	Mangaomeko hill soil	mudstone	5a	Yellow-brown earths moderately weathered
(6) (1499)	Waiwera clay loam	Claystone	6a	Yellow-brown earths strongly weathered
(7)	Te Kopuru sand	sandstone	7a	Yellow-brown earths moderately weathered podzolized
(8)	Ngaio silt loam	greywacke	7a	Yellow-brown earths moderately weathered podzolized
(9)	Wharekohe	silicified	7b	Yellow-brown earths

Table 1 (Cont'd)

Description of Soils.

Serial No. (S.B. Lab. No.)	Soil Type	Parent Material	Genetic No.	Genetic Classification
	silt loam	claystone	7b	Yellow-brown earths strongly weathered podzolized
(10) (5771)	Oparawa gritty silt loam	alluvium from greywacke and tertiary sediments	8	Gley podzol
(11) (1438)	Arapohue clay	limestone	11	Rendzinas
(12) (5474)	Tarakohe silt loam	tertiary limestone (hard)	11	Rendzinas
(13) (1306)	Ngakonui sandy silt	rhyolitic ash	13a	Yellow-brown pumice soils
(14) (3563)	Levin silt loam	alluvium [illegible] greywacke and volcanic ash	14a	Yellow-brown loams
(15)	Te Kowhai	rhyolite alluvium	14a	Yellow-brown loams

Table 1 (Cont'd)

Description of Soils

Serial No. (S.B. Lab. No.	Soil Type	Parent Material	Genetic No.	Genetic Classification
	silt loam	with admixed andesitic ash		
(16)	New Plymouth black loam	andesitic ash	14b	Yellow-brown loams
(17)	New Plymouth brown loam	andesitic ash	14b	Yellow-brown loams
(18)	Patua sandy loam	andesitic ash	14b	Yellow-brown loams
(19)	Hamilton clay loam	andesitic ash	15	Brown granular clay
(20) (1680)	Middlehurst silt loam	basaltic rocks	16a	Red-brown loams
(21) (1377)	Maunu loam	basalt	16a	Red-brown loams
(22) (1871)	Mangakahia clay loam	alluvium from dolerite	17	Gley soils

Table 1 (Cont'd)

Description of Soils.

Serial No. (S.B. Lab. No.)	Soil Type	Parent Material	Genetic No.	Genetic Classification
(23)	Hastings clay loam	alluvium from greywacke	17	Gley soils
(24)	Manawatu silt loam	alluvium from greywacke	20a	Recent soils from alluvium

Table 2.

Chemical and Mineralogical Data.

Serial No.	Genetic Horizon	Genetic No.	Soil Type	pH	Free iron oxide (Fe_2O_3)	Predominant clay minerals.
					%	
(1)	C	1b	Tekapo silt loam	5.8	0.86	weakly hydrated mica, illite, vermiculite, amorphous hydrous iron and aluminium oxides.
(2)	A	2b	Tokomaru silt loam	4.8	0.46	illite, vermiculite, montmorillonite, (interlayer) hydrous mica intermediates, and amorphous hydrous iron and aluminium oxides.
(3)	B	3a	Ruapuna silt loam	5.0	1.43	clay minerals same as 2b above.
(4)	A	4	Katrina fine sandy loam	5.0	1.67	same as 3a but amorphous hydrous alumina absent and crystalline iron oxides appear e.g. goethite.
(5)	A	5a	[illegible] hill soil	[illegible]	[illegible]	same as 4 but also include metahalloysite and secondary silica.
(6)	B	6a	Waiwera clay	5.8	2.19	more metahalloysite and secondary silica than 5 above.

Table 2 (Cont'd)

Chemical and Mineralogical Data.

Serial No.	Genetic Horizon	Genetic No.	Soil Type	pH	Free iron oxide (Fe_2O_3) %	Predominant clay minerals.
(7)	A	7a	Te Kopuru sand	4.9	0.11	same as 5 above.
(8)	A	7a	Ngaio silt loam	5.8	1.41	same as 5 above.
(9)	A	7b	Wharekohe silt loam	4.5	0.29	same as 6a above.
(10)	B	8	Oparawa gritty silt loam	4.8	2.15	same as 6a above.
(11)	B	11	Arapohue clay	7.0	1.10	clay vermiculite, montmorillonite, amorphous hydrous iron and aluminium oxides.
(12)	B	11	Tarakohe silt loam	5.9	2.70	same as 11 above.
(13)	C	13a	Ngakonui sandy silt	6.2	1.76	amorphous hydrous silica, allophane A, A B, and B.

Table 2 (Cont'd)

Chemical and Mineralogical Data

Serial No.	Genetic Horizon	Genetic No.	Soil Type	pH	Free iron oxide (Fe_2O_3) %	Predominant clay minerals.
(14)	A	14a	Levin silt loam	6.1	2.11	amorphous hydrous silica, iron and aluminium oxides and allophane.
(15)	A	14a	Te Kowhai silt loam	5.8	1.10	same as 14a above.
(16)	A	14a	New Plymouth black loam	6.3	2.42	same as 14a above.
(17)	A	14a	New Plymouth brown loam	6.1	1.84	same as 14a above.
(18)	A	14a	Patua sandy loam	5.5	1.10	same as 14a above.
(19)	A	15a	Hamilton clay loam	5.8	1.53	montmorillonite, metahalloysite, and allophane.
(20)	B	16a	Middle-hurst silt	6.1	2.51	amorphous hydrous Fe, Al and Ti oxides, crystalline

Table 2 (Cont'd)

Chemical and Mineralogical Data.

Serial No.	Genetic Horizon	Genetic No.	Soil Type	pH	Free iron oxide (Fe_2O_3)	Predominant clay minerals.
					%	
			loam			gibbsite, anatase, boehmite and goethite.
(21)	B	16a	Mamu loam	6.1	1.45	same as 16a above.
(22)	B	17	Mangakahia clay loam	6.2	0.80	probably montmorillonite and other micaceous materials.
(23)	A	17	Hastings clay loam	6.0	0.78	same as 17 above.
(24)	A	20a	Manawatu silt loam	5.6	0.76	not known.

III. EXPERIMENTAL

1. Preparation of Soil Samples.

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

2. Determination of pH.

A Cambridge pH meter fitted with a Beckman glass electrode was employed for pH measurement.

3. Determination of Free Iron Oxides.

The dithionite - citrate - bicarbonate method of Jackson, (Jackson 1958, pg. 168 -), was employed.

4. Determination of Phosphate.

This was carried out by the method of Dickman and Bray (1940). Colour measurement was made on a Beckman spectrophotometer at 815 mu. When ammonium fluoride extractant was used the boric acid procedure of Kurtz (1942) was employed to eliminate interference in colour development by fluoride.

5. Fractionation Procedures.

(a) The Determination of Alkali - Soluble Soil Phosphate.

The following procedure recommended by Fife (priv. comm.) was adopted.

(i) Reagents.

0.5 M NaCl: 29.23 gm. per litre.

1.0 N NaOH: 40.0 gm. per litre.

Approximately 1.0 N HCl: diluted 10 N HCl 100 ml. to 1 litre.

(ii) Procedure.

The soil sample (0.125 gm.) was placed on a moistened 7 cm. filter, and leached with successive portions of 0.5 M NaCl of total volume about 50 ml. The amounts of phosphate removed by this preleach were very small and were neglected in view of the fractionation procedure as used in the present work.

The soil residue on the filter was washed twice with acetone, placed on a rack and put aside to air-dry overnight. The dried soil and filter paper were placed in a 50 ml. centrifuge tube, 25 ml. of 1.0 N NaOH was added and after stoppering the tube was shaken vigorously by hand to reduce the paper to a pulp. The tube was placed in an end-over-end shaker (40 r.p.m.) and shaken for 40 hours. After centrifugation an aliquot of double the volume required for the subsequent phosphate determination was shaken with an equal volume of dilute HCl of just sufficient strength to slightly over neutralise the NaOH; shaken and centrifugedto precipitate organic matter. One half of the supernatant solution was taken for the phosphate determination. With most of the soils, the organic matter blank was negligible at 815 mu.

(b) The Determination of Aluminium-bound Soil Phosphate.

The simplified procedure of Fife (1962) was employed.

(i) Reagents.

0.5 M ammonium fluoride: 18.5 gm. per litre. Adjusted to pH 8.5 with ammonia.

(ii) Procedure.

0.25 gm. sample of soil was placed in a 50 ml. centrifuge tube with 25 ml. of 0.5 M NH_4F at pH 8.5 and shaken for 24 hours, centrifuged to clear the extract and phosphate was determined on a suitable aliquot.

A preliminary experiment was carried out to determine the highest dilution at which it was practicable to work. Fife (1962) has recommended this practice in routine determination of aluminium - bound soil phosphate in order to avoid correction for resorption of phosphate by the free iron oxides. The soil extractant ratios selected are shown in Table 3.

(c) The Determination of Iron - bound Soil Phosphate.

This was found by difference of the results obtained for method 5 (a) and 5 (b).

6. The Determination of Phosphate Retention by NH_4F - treated Soils in 0.5 M NH_4Cl at Different pH Levels.

a. Reagents.

0.5 M ammonium chloride: 26.8 gm. per litre.

Standard P solution containing 50 ug. per ml: 0.2194 gm. KH_2PO_4 per litre.

b. Procedure.

(i) Dealumination of Soils.

This was carried out by extracting 0.25 gm. sample with 20 ml. 0.5 M NH_4F at pH 8.5 for 12 hours. After centrifugations the supernatant liquid was discarded and this process was repeated a further six times. The soil residue was then washed with 20 ml. of 0.5 M NH_4Cl using five centrifugations and finally twice with 10 ml. acetone and left to air-dry overnight in the centrifuge tube.

(ii) Preparation of NH_4Cl - Phosphate Mixtures.

A bulk solution of 0.5 M NH_4Cl was prepared and successive portions of this were adjusted by addition of either hydrochloric acid or ammonia solution to provide a series of twelve solutions covering a range of pH from about 2.5 to 9.0. These solutions were enriched by an addition of standard phosphate containing 50 ug. per ml. to produce a final phosphate concentration of 10 ug. per ml. Four additional solutions in the same pH range were prepared without the addition of phosphate. The pH levels adopted are shown below:

Solution No.	pH	Solution No.	pH
1	2.69	2	3.18
3	3.77	4	4.57
5	4.99	6	6.57
7	7.44	8	7.80
9	8.10	10	8.51
11	8.70	12	9.01
13 (NP)	3.31	14 (NP)	4.82
15 (NP)	7.41	16 (NP)	9.00

NP : no added phosphate

A salt solution containing phosphate was used in preference to water to ensure the system remained flocculated during equilibration and to provide reasonably well - buffered conditions in alkaline solutions. The decision to employ a concentration of 10 ug. per ml. of phosphate in the enriched solutions was made on the basis of a preliminary trial using the soils containing the highest and lowest amount of free iron oxide. It was shown in this trial that a conveniently measurable concentration of phosphate remained in the equilibrium extract of these soils over the whole range of pH investigated when this concentration was employed.

(iii) Equilibration Procedure.

To each of sixteen dealuminated samples of each soil were added 25 ml. of the range of phosphate enriched NH_4Cl and unphosphated NH_4Cl solutions described above. The centrifuge tubes were stoppered and put in the end-over-end shaker for 24 hours. At the end of this period, the suspension was centrifuged and a suitable aliquot of the extract was taken for colorimetric determination of phosphate. The residual soil and extract in the centrifuge tube were used to obtain the final pH.

7. The Determination of Phosphate Retention by "untreated" Soils at Alkaline pH levels.

a. Reagents.

All reagents except 0.5 M NH_4F given under paragraph 6 a were used.

b. Procedure.

(i) Pre-leaching of Soils.

This was done by placing 0.25 gm. sample on a moistened 7 cm. filter and leached with successive portions of 0.5 M NaCl of total volume about 50 ml. to remove exchangeable bases. The leachate was discarded and the soil residue was washed twice with acetone and left to air-dry overnight.

(ii) Preparation of NH_4Cl - Phosphate Mixtures.

These were prepared by the same method given under paragraph 6 b (ii) except in this case only the alkaline range was investigated. For Tekapo silt loam where phosphate retention patterns at acid range were also determined, the NH_4Cl - phosphate enriched solutions at acid pH range prepared in 6 b (ii) were used.

(iii) Equilibration Procedure.

The pre-leached soil residue and the filter paper were put in centrifuge tube and it was then treated with the same equilibration procedure as those given under paragraph 6 b (iii). The term "untreated" used here referred to the fact that the soil was not subjected to dealumination prior to equilibration procedure.

8. The Determination of Phosphate Retention by NaOH - treated Soils at Alkaline pH levels.

a. Reagents.

1 N NaOH: 40.0 gm. per litre.

All reagents except 0.5 M NH_4F given under paragraph 6 a were used.

b. Procedure.

(i) Dealumination of Soils.

0.25 gm. of soil was pre-leached with about 50 ml. of 0.5 M NaCl as in paragraph 7 b (i). It was then washed with acetone and left to air-dry overnight. After that drying the soil residue and the filter paper were put in a centrifuge tube, 20 ml. of 1 N NaOH was added and the tube put in the shaker for 12 hours. After centrifugation the supernatant liquid was discarded and the process was repeated a further three times. The soil residue was then washed with 20 ml. of 0.5 M NH_4Cl using five centrifugations and finally twice with 10 ml. acetone and left to air-dry overnight in the centrifuge tube.

A preliminary experiment was carried out using soil extract ratio of 1:50. Owing to difficulties of removing organic matter, the soil extractant ratio for subsequent work was reduced to 1:100.

(ii) Preparation of NH_4Cl - Phosphate Mixtures.

These were prepared by the same method given under paragraph 6 b (ii) except in this case only the alkaline range was investigated.

(iii) Equilibration Procedure.

IV. RESULTS AND DISCUSSION

1. Free Iron Oxide Contents of the Soils.

The results are shown in Table 2. The free iron oxide contents of the zonal soils show considerable variations. Te Kopuru sand contains the least quantity, while relatively high amounts occur in the B horizons of Waiwera clay loam and Oparawa gritty silt loam.

The intrazonal soils, except the gley soils, possess relatively high amounts of free iron oxide with the B horizon of Tarakohe silt loam showing the highest content. Levin silt loam, New Plymouth black loam and the B horizon of Middlehurst silt loam also have relatively high amounts. Mangakahia clay loam, and Hastings clay loam, the two gley soils studied have relatively low contents of iron oxide. A low content of free iron oxide is also apparent in Manawatu silt loam, the only azonal soil studied.

These observations appear to be explained from a consideration of the known properties of the soils and the nature of their soil - forming processes. The parent materials of the zonal soils have predominant primary minerals consisting normally of quartz, feldspar, and micas with minor amounts of the more basic minerals which weather directly to oxides. Thus chemical weathering in the moderately leached brown - grey earths and the weakly leached yellow - grey earths is slow, while in the moderately and strongly weathered yellow - brown earths, it is rapid, resulting in soils with relatively higher amounts of free iron oxides.

Fife (1945) has shown that increased weathering in the moderately to strongly gleyed sub-group of the yellow - grey earths caused a substantial downward movement of iron in the profile, leaving the topsoil with low free iron oxide contents. Probably a similar movement occurs in those yellow - brown earths which are not complicated by podzolization, as indicated by the decrease in free iron oxide content with increased leaching in Mangaomeko hill soil as compared with Katrina fine sandy loam and also by the relatively high iron oxide content of the B horizon of Waiwera clay loam.

Podzolization of the moderately and strongly weathered yellow - brown earths depletes the topsoil of its free iron oxide content. Te Kopuru sand and Wharekohe silt loam show this effect.

Swindale (1959) has observed that in gley podzols, where gleying is caused by a perched water table, there is a band of intact iron oxide accumulation in the B horizon. This is very likely to have occurred in Oparawa gritty silt loam. By contrast, a low free iron oxide content in the A horizon of this soil has been indicated by Fife (1959b).

The rendzina soils studied have relatively high free iron oxide contents. Pohlen (1956) has stated that this high content of free iron oxides in certain brown rendzina soils is inherited from the limestone. This may probably be the case in Tarakohe silt loam.

The yellow - brown pumice soils and the yellow - brown loams are derived from volcanic parent materials, containing considerable amounts of mixed amorphous hydrous oxides of iron, aluminium, and silica. The yellow - brown loams, which are soils of intermediate weathering, formed from andesitic ash, contain up to sixty per cent of clay consisting of allophane and amorphous hydrous oxides of iron, aluminium and silica (Fieldes and Swindale, 1954). This probably explains the relatively high content of free iron oxides in these soils as found in the present study.

Fieldes and Swindale (1954) have indicated that the basic volcanic glass of the yellow - brown loams weathers more readily than the acidic volcanic glass of the red - brown loams to form amorphous hydrous iron and aluminium oxides. Thus a higher free iron oxide content of the yellow - brown loams would be expected. However, Middlehurst silt loam and Maunu loam have iron oxide contents very similar to those of the yellow - brown loams. This is almost certainly due to the immaturity of these red - brown loams.

The process of gleying depletes the soil of its free iron oxides. This is indicated by the comparatively low iron oxide content of Mangakahia clay loam and Hastings clay loam. In the only azonal soil studied, the iron oxide content is comparatively low, in keeping with the unweathered state of the constituent minerals.

2. Soil Phosphate Fractions.

The amounts of iron - and aluminium - bound phosphate fractions together with the ratios of iron - to aluminium - bound phosphates are shown in Table 3.

Aluminium - bound phosphate appears to be in relatively greater amounts in soils, which are rich in amorphous alumina. The majority of the intrazonal soils derived from volcanic parent materials show this effect. Ngakonui sandy silt, Levin silt loam, New Plymouth brown loam, Middlehurst silt loam and Maunu loam contain relatively higher amounts of aluminium - bound phosphate. Ngakonui sandy silt, Levin silt loam, New Plymouth black loam and New Plymouth brown loam contain considerable amounts of allophane and amorphous hydrous oxides of iron, aluminium and silica as their clay fraction (Birrell and Fieldes, 1952; Fieldes, 1955, 1956; Fieldes and Swindale, 1954; Fieldes and Williamson, 1955; and Fieldes et al. 1957). Fieldes and Williamson (1955) have shown that Middlehurst silt loam contains high amounts of amorphous materials including alumina.

Iron - bound phosphate is present in relatively higher amounts in a much wider range of soils than aluminium - bound phosphate. Levin silt loam, Middlehurst silt loam and New Plymouth black loam contain relatively larger amounts. Appreciable amounts also occur in Ngakonui sandy silt, Patua sandy loam, Hamilton clay loam, Mangakahia clay loam, Hastings clay loam, Ruapuna silt loam, Tarakohe silt loam and Manawatu silt loam.

A reasonably good relationship exists between the free iron oxide contents and the amounts of iron - bound phosphate in Te Kopuru sand and Wharekohe silt loam, where low iron oxide contents are associated with low iron - bound phosphate. No such relationship exists in the other soils. Ruapuna silt loam and Maunu loam have very similar iron oxide contents but differ quantitatively in their iron - bound phosphate. The same is also true of Arapohue clay, Te Kowhai silt loam, and Patua sandy loam. Mangakahia clay loam, Hastings clay loam and Manawatu silt loam have relatively low amounts of free iron oxides but contain appreciable amounts of iron - bound phosphate. Waiwera clay loam and Oparawa gritty silt loam have high iron oxide contents but contain low amounts of iron - bound phosphate. This appears to suggest that it is the form, rather than the actual amount of iron oxide, which determines phosphate retention.

The ratios of iron - to aluminium - bound phosphates indicate that most of the soils studied have a higher relative incidence of iron - to aluminium - bound phosphates. However, Te Kopuru sand, Ngakonui sandy silt, New Plymouth brown loam and Maunu loam have higher aluminium - bound phosphate contents. This is likely to suggest that aluminium present in these soils is comparatively more active than iron in retaining phosphate as found by Saunders (1959c) for New Plymouth black loam.

Table 3

Soil Phosphate Fractions.

(Results expressed as mg. P per 100 gm. soil.)

Serial No.	Amount of Alkali - soluble P	Soil: Extractant Ratio in Aluminium P Determination	Amount of Aluminium-bound P	Amount of Iron - bound P	Ratio of Iron Pto Aluminium P
	mg. P/ 100 gm. soil		mg. P/ 100 gm. soil	mg. P/ 100 gm. soil	
(1)	8.45	1:100	0.98	7.47	1:0.1
(2)	19.50	1:400	5.53	13.97	1:0.4
(3)	58.50	1:800	18.85	39.65	1:0.5
(4)	23.30	1:400	4.39	18.91	1:0.2
(5)	14.30	1:200	2.28	12.02	1:0.2
(6)	6.50	1:100	0.69	6.81	1:0.1
(7)	6.50	1:400	6.18	0.22	1:28
(8)	9.75	1:200	1.76	7.99	1:0.3
(9)	3.90	1:100	0.93	2.97	1:0.3
(10)	8.45	1:50	0.20	8.25	1:0.0
(11)	10.40	1:200	2.28	8.12	1:0.3
(12)	24.05	1:200	2.52	21.53	1:0.1
(13)	66.30	1:1200	40.96	25.34	1:1.6
(14)	162.90	1:1200	74.09	88.81	1:0.8
(15)	13.00	1:200	1.63	11.37	1:0.1
(16)	107.90	1:800	47.77	60.13	1:0.8
(17)	46.79	1:800	26.98	19.81	1:1.4
(18)	37.64	1:800	13.98	23.66	1:0.6
(19)	51.35	1:400	6.18	45.17	1:0.1
(20)	109.10	1:800	24.96	84.14	1:0.3

Table 3 (Cont'd)

Soil Phosphate Fractions.

(Results expressed as mg. P per 100 gm. soil.)

Serial No.	Amount of Alkali - soluble P	Soil: Extractant Ratio in Aluminium P Determination	Amount of Aluminium-bound P	Amount of Iron - bound P	Ratio of Iron Pto Aluminium P
	mg. P/ 100 gm. soil		mg. P/ 100 gm. soil	mg. P/ 100 gm. soil	
(21)	55.25	1:800	48.75	6.50	1:7.5
(22)	30.55	1:200	2.68	27.87	1:0.1
(23)	50.70	1:400	8.29	42.41	1:0.2
(24)	52.00	1:800	15.92	36.08	1:0.4

3. Phosphate Retention Shown by the Soils at Different pH values in 0.5 M NH_4Cl following "de-alumination" by 0.5 M NH_4F.

The relationship between pH and phosphate retention by the "de-aluminated" soils is shown in figures 1, 2, 3, 4 and 5. The data from which these curves were constructed are presented in Appendix I.

The trend of phosphate retention shown by the soils over the range of pH investigated tends to follow a general pattern, namely, high retention at the more alkaline and more acid pH levels and low retention between them. An exception is Arapohue clay (figure 3) which shows decreasing retention with falling pH values up to about pH 5.0 which was the limit of acidity obtained in the equilibrium extract of this soil. The majority of the soils show a decrease in phosphate retention with decreasing pH from about pH 7.0 and 8.0 and a gradual increase from about pH 4.0 and 5.0. Reasonably sharp falls in phosphate retention with decreasing pH occur in Ngakonui sandy silt (figure 4), Middlehurst silt loam and Mangakahia clay loam (figure 5).

The phosphate retention pattern of Arapohue clay closely resembles that of calcium clays studied by Gilligan (1938), Heck (1934), Scarseth and Tidmore (1934), Chandler (1941), Pratt and Thorne (1948), and Ravikovitch (1934). These workers found that even at pH levels below neutrality, where calcium precipitation would not be expected, calcium clays retain more phosphate than do sodium, ammonium, or potassium clays. Whether this additional retention is a precipitation of calcium phosphate at the colloid surface (Kurtz, 1953) or a linking of phosphate to the colloid through a calcium ion on the exchange complex (Scarseth, 1935) is not clear.

Teakle (1928), Gaarder (1930), Stelly and Pierre (1942), Mattson et al. (1951), and Miller (1954) have come to the general conclusion that in soil - phosphate systems, the upper limits of maximum phosphate retention vary with the ratio of phosphate concentration to iron, aluminium and calcium, but the lower limits are more definite, namely pH 2.0 - 2.5 for iron, 3.5 - 4.0 for aluminium and pH 6.0 - 6.5 for calcium. Fife (priv. comm.) has shown that treatment of soils with 0.5 M NH_4F at pH 8.5 for three days completely eliminates retention of phosphate by aluminium. In the fluoride treated soil where iron - binding of phosphate is the only mechanism operating in phosphate fixation it is expected to show a gradual increase in phosphate retention with increasing pH from alkaline pH to acid pH levels. This, however, is not shown by the soils in the present study. This is possibly due to the fact that the soils contain residual fluoride, which interferes with phosphate retention at acid pH levels. Turner and Rice (1952) have observed that insoluble fluoaluminate complex formed on the surface of the alumina gels which they studied. These insoluble fluoaluminate complex presumably is left in the soils following treatment with 0.5 M NH_4F at pH 8.5 for three days. With the lowering of pH in 0.5 M NH_4Cl, the residual fluoride becomes more soluble, thus attacking the iron - bound phosphate forming fluoferrate ions, releasing phosphate to the system and causes a fall in phosphate retention from about pH 7.0 and 8.0 as observed in the present study.

From figure 1, 2 and 3, Tokomaru silt loam, Te Kopuru sand and Wharekohe silt loam which contain low iron oxide contents, show a reasonably good relationship between the phosphate retention and the iron oxide contents. This, however, does not occur in the other soils. Arapohue clay (figure 3), Te Kowhai silt loam and Patua sandy loam (figure 4), containing the same amounts of iron oxides, show widely different phosphate retention values at all pH levels.

Tarakohe silt loam (figure 3), Middlehurst silt loam (figure 5), and New Plymouth black loam (figure 4) containing relatively higher iron oxide contents do not exhibit higher retention patterns. This observation further supports the view that it is the form or activity of the free iron oxide components in the soils rather than the actual amount, which determines phosphate retention by soils.

In terms of equal amounts of free iron oxides, it is evident that Arapohue clay (figure 3) has a greater iron oxide activity in retaining phosphate than Patua sandy loam (figure 4) which in turn has a greater activity in retaining phosphate than Te Kowhai silt loam (figure 4). Similarly, the iron oxides in Oparawa gritty silt loam (figure 3) are considerably more active in retaining phosphate than that in Levin silt loam (figure 4). This may thus provide a means of evaluating the activity of the free iron oxide components of soils in binding phosphate for soils possessing very similar iron oxide contents.

4. Phosphate Retention Shown by "untreated" Soils at Alkaline pH values in 0.5 M NH_4Cl.

The relationship between pH and phosphate retention by "untreated" soils is shown in figures 1, 2, 3, 4 and 5. The data from which these curves are constructed are shown in Appendix II.

The object of finding phosphate retention by "untreated" soils is to gather information on the relative retentive capacity of iron and aluminium in soils by comparing it with that of fluoride treated ones. As it becomes evident that in fluoride treated soils some interference of residual fluoride on phosphate retention occurred at pH values from about 7.0 and 8.0 to the more acid pH levels, a comparison of fluoride treated and "untreated" soils is possible only at the alkaline pH levels. For this reason, only the relationship between pH and phosphate retention at alkaline pH levels is determined for all the "untreated" soils except in Tekapo silt loam where phosphate retention over the more acid range is also determined.

The trend of phosphate retention appears to follow a general pattern, namely, a decrease in phosphate retention with increasing pH over the alkaline range. Tekapo silt loam (figure 1) shows a maximum phosphate retention between about pH 6.0 and 7.0. This is the behavior of a soil system where iron - and aluminium - binding mechanisms are operating in phosphate fixation thus showing maximum phosphate retention between about pH 7.0 and 2.0 (Teakle 1928, Gaarder 1930, Doughty 1930, Stelly and Pierre 1942, Mattson et al. 1951, and Miller 1954). Saunders (1959c) has found maximum phosphate retention for New Plymouth black loam between pH 4.0 and 5.0 to be due to iron and aluminium.

At alkaline pH range, as the pH increases the capacity of iron and aluminium to retain phosphate decreases as observed in all soils. A similar decrease in phosphate retention occurs over the more acid pH range as the pH decreases, owing to the gradual dissolution of iron - and aluminium - bound phosphate thus bringing more phosphate into solution. This effect is shown by Tekapo silt loam, the only soil where the relationship between pH and phosphate retention is extended over acid pH range.

In terms of the percentage of phosphate retention, it is evident that the amount of retention by soils depends on their properties and nature of soil - forming processes. Thus the weakly weathered Katrina fine sandy loam (figure 1) has a higher phosphate retention over the pH range investigated than the moderately weathered Mangaomeko hill soil or the moderately weathered and podzolized Te Kopuru sand (figure 2). The intrazonal soils as a whole have high phosphate retention values owing to their high contents of amorphous oxides of iron and aluminium. New Plymouth brown loam, Ngakonui sandy silt, New Plymouth black loam (figure 4), Maunu loam (figure 5) and Levin silt loam (figure 4) have relatively high phosphate retention values. These observations of the relative retentive capacity of the "untreated" soils can be accounted for by the same explanation as that given to account for the relative amounts of iron oxide in the soils studied.

5. Phosphate Retention shown by the Soils at Alkaline pH values in 0.5 M NH_4Cl after treatment with 1.0 N NaOH.

The relationship between pH and phosphate retention in the alkaline range by the NaOH - treated soils are shown in figures 1, 2, 3 and 5. These curves were constructed from data presented in Appendix III. Figures 1, 2 and 3 also show the retention of phosphate exhibited by some of the NaOH - treated soils over both acid and alkaline range in 0.5 M NH_4Cl, when a 1:50 soil extractant ratio was employed; these curves were constructed from data presented in Appendix IV.

At the alkaline range of the pH investigated all the soils follow a general pattern of phosphate retention, namely a decrease in phosphate retention with increasing pH. It is evident from figures 1, 2, 3 and 5 that the trends of phosphate retention in all cases follow that of the "untreated" soils.

Waiwera clay loam (figure 2), Oparawa gritty silt loam and Arapohue clay show higher retention patterns following NaOH treatment than their corresponding "untreated" samples. In the NaOH - treated soil iron - binding of phosphate is the only mechanism operating it would therefore be expected that lower retention would be exhibited by the Na-OH - treated soils than by the "untreated" soils. The above observation appears to suggest that NaOH treatment has resulted in an increasing phosphate fixing capacity of the iron oxide component of these soils. A possible explanation of this increased activity is that some component of the organic matter occupying phosphate adsorption sites in the "untreated" soils was removed by the NaOH treatment. Alternatively in the "untreated" soils the phosphate fixing capacity of the free iron oxide may be limited by the presence of aluminium oxide surface films.

For soils, where the relationship between pH and phosphate retention are extended over acid pH range, the general trend is an increase in phosphate retention with decreasing pH from alkaline pH to acid pH levels (figures 1, 2 and 3). This is in accordance with the behaviour of a soil - phosphate system where only iron - binding of phosphate is the mechanism operating (Teakle 1928, Gaarder 1930, Doughty 1930, Stelly and Pierre 1942, Mattson et al. 1951 and Miller 1954). More phosphate is retained by the iron component of the soils as pH decreases in this acid range. In comparison with the fluoride treated soils (figures 1, 2 and 3), these phosphate retention patterns of the NaOH - treated soils show no interference of fluoride in phosphate retention over the acid pH levels investigated as there is nodecrease of phosphate retention over this acid pH range in the NaOH - treated soils, while in the fluoride treated soils a decrease in phosphate retention is shown by all soils. Taking phosphate retention at alkaline pH levels, the effect of decreasing soil extractant ratios from 1:50 to 1:100 (III - method 8) more than double the amounts of phosphate retained by soils in most of the soils (figures 1 and 2). This suggests that greater retention of phosphate occurs in soils with higher soil extractant ratios.

An important feature of NaOH treatment of Arapohue clay is that conversion of the original calcium clay of this rendzina soil to sodium clay by NaOH treatment removes the somewhat higher retention of phosphate with increasing pH as exhibited by this soil following fluoride treatment (figure 3). This sharp rise of phosphate retention exhibited by Arapohue clay following fluoride treatment (figure 3) is due to the effect of exchangeable calcium on phosphate retention (Heck 1934, Scarseth and Tidmore 1934, Ravikovitch 1934, Gilligan 1938, Chandler 1941, and Pratt and Thorne 1948). Thus presumably Arapohue clay after fluoride treatment still contains relatively high content of exchangeable calcium, as the limit of soil acidity of the equilibrium extract of this soil does not fall below about pH 5.0 as shown in figure 3.

Figure 1.

The relationship between pH and phosphate retention shown by four zonal soils after NH_4F treatment, NaOH treatment and no treatment.

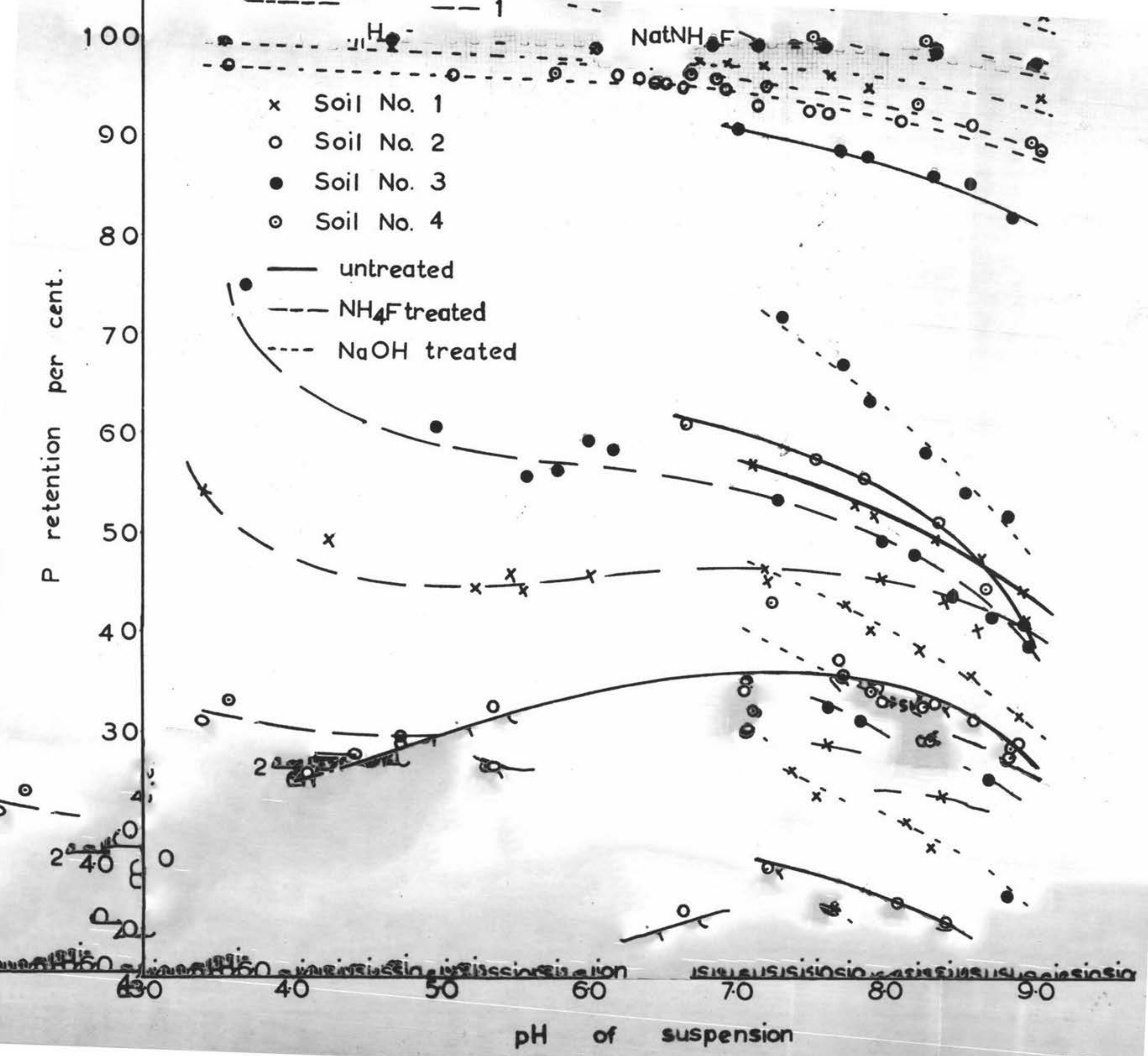

H
Na+NH4F
× Soil No. 1
○ Soil No. 2
● Soil No. 3
⊙ Soil No. 4
untreated
NH4F treated
NaOH treated
100
90
80
70
60
50
40
30
P retention per cent.
3.0
4.0
5.0
6.0
7.0
8.0
9.0
pH of suspension

Figure 2.

The relationship between pH and phosphate retention shown by four zonal soils after NH_4F treatment, NaOH treatment, and no treatment.

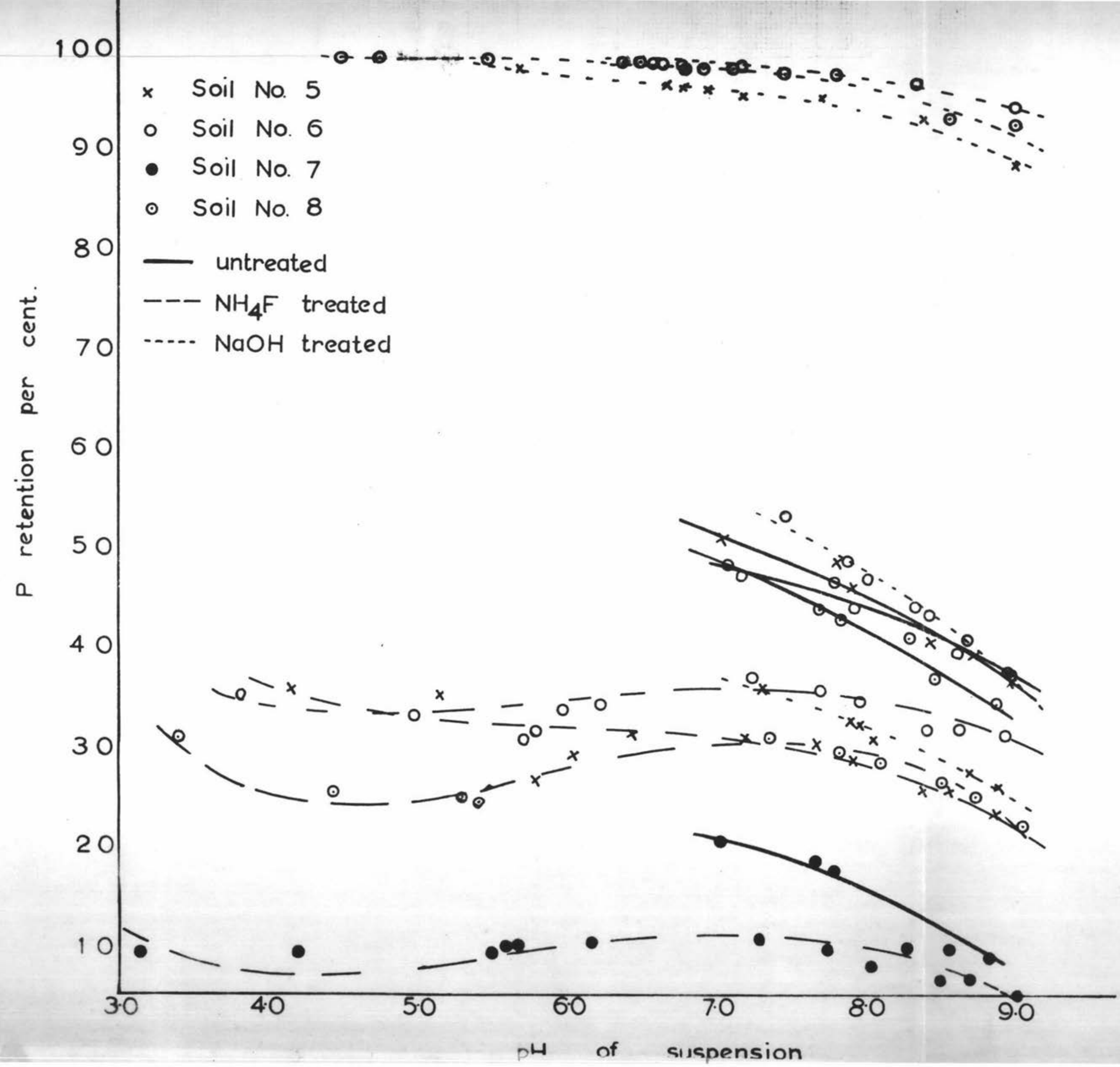

100
90
80
70
60
50
40
30
20
10
P retention per cent.
× Soil No. 5
○ Soil No. 6
● Soil No. 7
⊙ Soil No. 8
untreated
NH$_4$F treated
NaOH treated
3·0
4·0
5·0
6·0
7·0
8·0
9·0
pH of suspension

Figure 3.

The relationship between pH and phosphate retention shown by two zonal and two intrazonal soils after NH_4F treatment, NaOH treatment and no treatment.

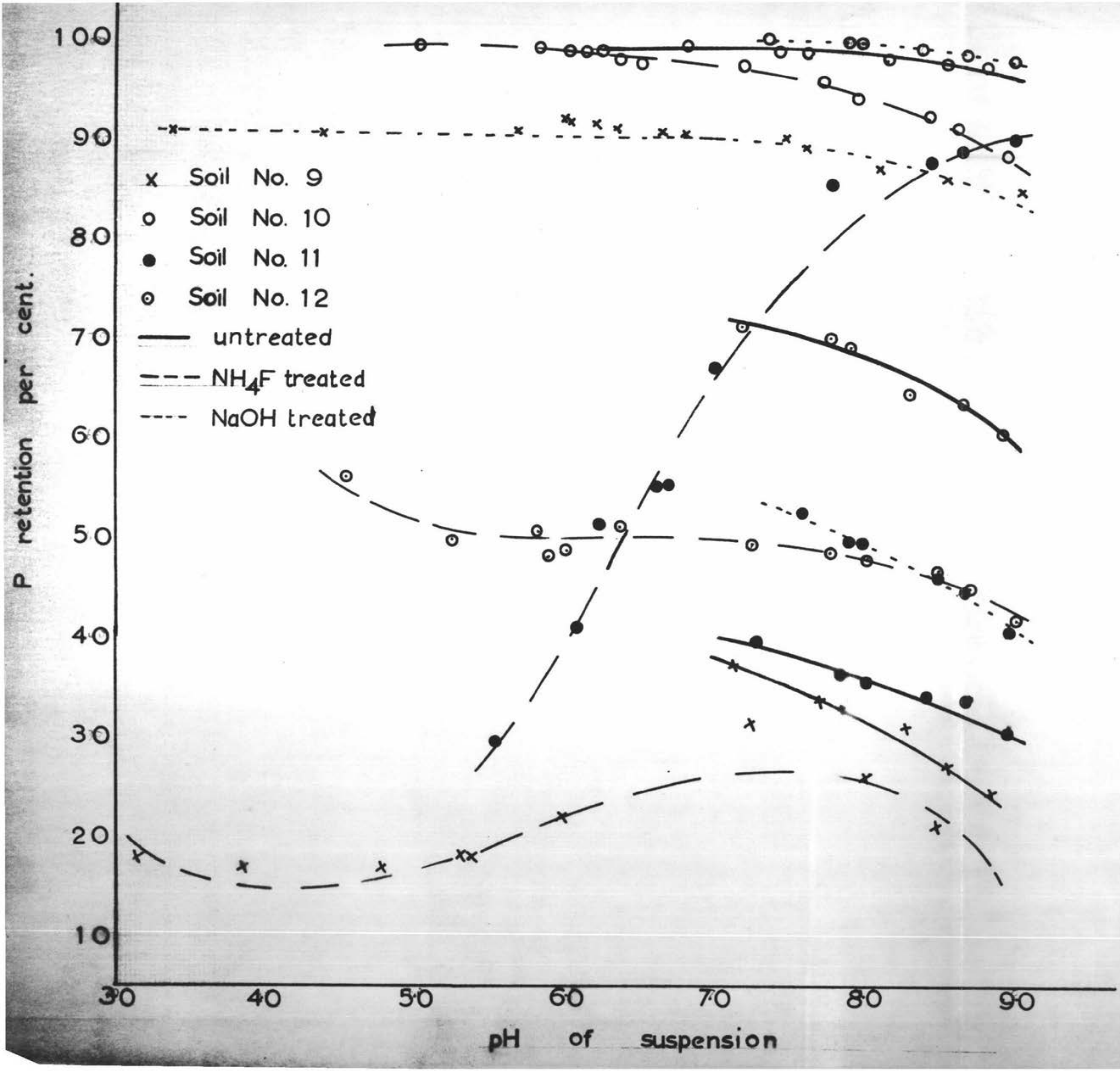
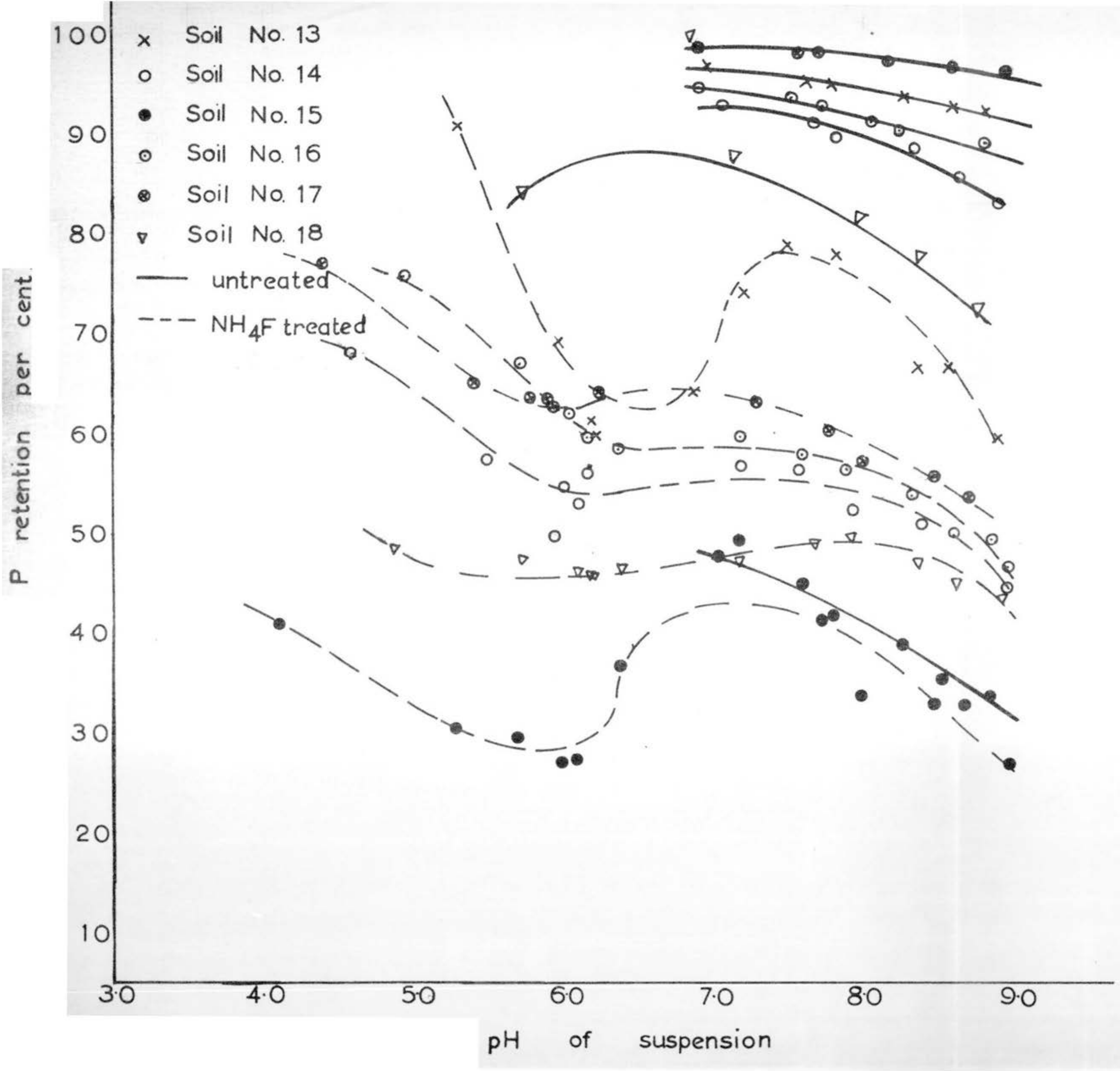

100
90
80
70
60
50
40
30
20
10
P retention per cent.
3·0
4·0
5·0
6·0
7·0
8·0
9·0
pH of suspension
x Soil No. 9
○ Soil No. 10
● Soil No. 11
⊙ Soil No. 12
untreated
NH$_4$F treated
NaOH treated

Figure 4.

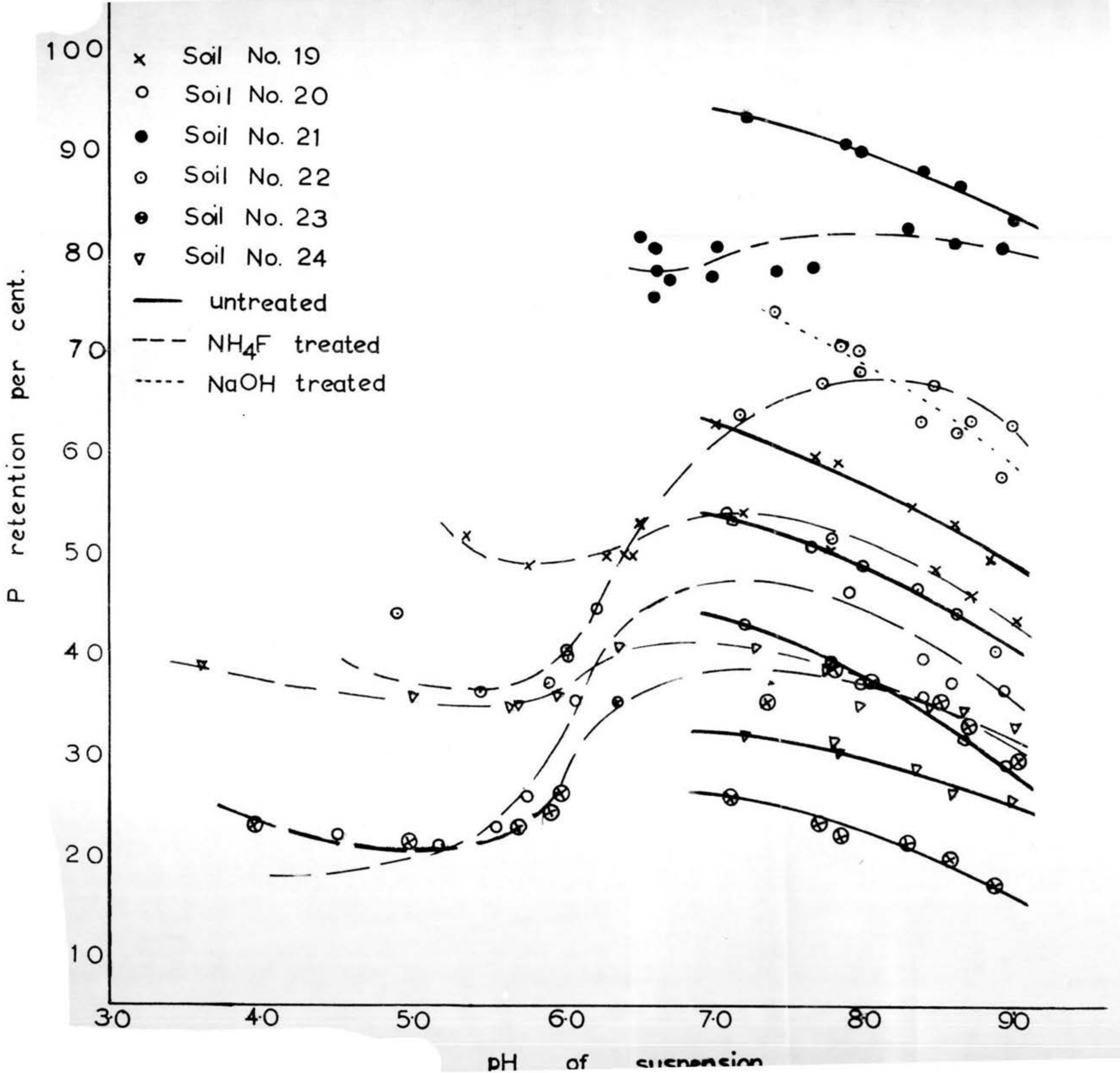
The relationship between pH and phosphate retention shown by six intrazonal soils after NH_4F treatment, and no treatment.



× Soil No. 13
○ Soil No. 14
● Soil No. 15
⊙ Soil No. 16
⊗ Soil No. 17
▽ Soil No. 18
untreated
NH$_4$F treated
P retention per cent
100
90
80
70
60
50
40
30
20
10
3·0
4·0
5·0
6·0
7·0
8·0
9·0
pH of suspension

Figure 5.

The relationship between pH and phosphate retention shown by five intrazonal and one azonal soils after NH_4F treatment, NaOH treatment and no treatment.


× Soil No. 19
○ Soil No. 20
● Soil No. 21
⊙ Soil No. 22
⊕ Soil No. 23
▽ Soil No. 24
—— untreated
- - - NH$_4$F treated
····· NaOH treated
P retention per cent.
100
90
80
70
60
50
40
30
20
10
3·0
4·0
5·0
6·0
7·0
8·0
9·0
pH of suspension

6. Comparisons of the Phosphate Retention shown by fluoride treated and "untreated" Soils at Four Selected pH levels in the Alkaline Range.

Four uniformly spaced pH values were selected in the alkaline pH range and the per cent phosphate retention shown by fluoride treated and "untreated" soils were read off from their respective curves (figures 1, 2, 3, 4 and 5). These data were presented in Table 4, which also shows the ratio of phosphate retention by fluoride treated soils to that of "untreated" soils. As phosphate retention in "dealuminated" soils following fluoride treatment was due entirely to iron - binding of phosphate, the retention of phosphate by soil components other than iron was calculated, wherever possible, * from the difference in phosphate retention between "untreated" and fluoride treated soils. The ratios of phosphate retention values of fluoride treated soils to these calculated values were also presented in Table 4.

The ratios of phosphate retention of fluoride treated soils to that of "untreated" soils indicate that for most of the soils studied except Arapohue clay, Middlehurst silt loam, Maunu loam, Mangakahia clay loam, Hastings clay loam, and Manawatu silt loam, lower phosphate retention shown by fluoride treated than by "untreated" soils. This is the expected situation because of the elimination of aluminium - binding of phosphate from the fluoride treated soils.

The phosphate retention values shown by the "untreated" soils represents the sum of the aluminium - and iron - binding reactions. If

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* In cases where fluoride treated soils have higher phosphate retention values than those of "untreated" soils, this calculation by difference is meaningless.

retention by the fluoride treated soils is taken as a measure of the iron - bound phosphate component then the difference in these values must represent the retention of phosphate due to fixation by aluminium. It is evident, however, from the iron - bound / aluminium - bound phosphate ratios shown in Table 4 that in the majority of the soils the laboratory assessment of the relative contribution of iron and aluminium to the phosphate fixation process are of little or no value in predicting the proportions of these forms which develop in the soils in the field. The fact that good prediction is shown for Tekapo silt loam, Oparawa gritty silt loam, Te Kowhai silt loam, Patua sandy loam, and Hamilton clay loam may be coincidental.

The ratios obtained by the laboratory procedure are, however, not strictly comparable with those which have developed naturally because the comparison is being made at different pH levels. In general the ratio of iron - bound / aluminium - bound phosphate is lower in the field soils than that shown in the laboratory. It is unlikely that a closer relationship between field and laboratory findings would have been revealed had it been possible to carry out the laboratory assessment at pH values close to those of the field soils; if anything a change in the opposite direction might be anticipated due to an increased phosphate retention by iron oxides. There is little doubt therefore that the removal of aluminium - binding of phosphate is accompanied by an activation of the iron - binding mechanism. This is likely to be due to the removal of organic matter and Al_2O_3 by fluoride treatment thus possibly exposing some otherwise protected iron oxide surfaces to phosphate adsorption.

Table 4

Comparisons of the Phosphate Retention shown by fluoride treated and "untreated" Soils at Four Selected pH values in the Alkaline Range.

Serial No.	pH	(a) Retention of "untreated" soils	(b) Retention of NH_4F-treated soils	Ratio of retention of NH_4F - treated to "untreated" soils	(c) Retention by soil components other than iron (a) - (b)	Ratio of iron - bound to aluminium - bound phosphate (b)/(c)
		%	%		%	
(1)	7.5	55.4	46.0	1:1.2	9.4	1:0.2
	8.0	52.5	45.3	1:1.2	7.2	1:0.2
	8.4	49.5	44.0	1:1.1	5.5	1:0.1
	8.8	46.0	41.7	1:1.1	4.3	1:0.1
(2)	7.5	35.9	29.0	1:1.2	6.9	1:0.2
	8.0	34.9	27.6	1:1.3	7.3	1:0.3
	8.4	33.0	26.0	1:1.3	7.0	1:0.3
	8.8	30.0	23.9	1:1.3	6.1	1:0.3
(3)	7.5	89.5	83.0	1:1.1	6.5	1:0.1
	8.0	87.4	50.0	1:1.7	37.4	1:0.7
	8.4	85.5	46.5	1:1.8	39.0	1:0.8
	8.8	83.0	40.5	1:2.1	42.5	1:1.1
(4)	7.5	57.9	30.5	1:1.9	27.4	1:0.9
	8.0	54.9	29.5	1:1.9	25.4	1:0.9
	8.4	50.5	28.5	1:1.8	22.0	1:0.8
	8.8	44.5	26.5	1:1.7	18.0	1:0.7
(5)	7.5	48.5	30.0	1:1.6	18.5	1:0.6
	8.0	45.0	28.5	1:1.6	16.5	1:0.6
	8.4	41.5	26.7	1:1.6	14.8	1:0.6
	8.8	38.5	24.0	1:1.6	14.5	1:0.6
(6)	7.5	46.5	35.5	1:1.3	11.0	1:0.3
	8.0	44.0	34.8	1:1.3	9.2	1:0.3
	8.4	41.5	33.5	1:1.2	8.0	1:0.2
	8.8	38.5	31.5	1:1.2	7.0	1:0.2

Table 4 (Cont'd)

Comparisons of the Phosphate Retention shown by fluoride treated and "untreated" Soils at Four Selected pH values in the Alkaline Range.

Serial No.	pH	(a) Retention of "untreated" soils	(b) Retention of NH_4F-treated soils	Ratio of retention of NH_4F - treated to "untreated" soils	(c) Retention by soil components other than iron (a) - (b)	Ratio of iron - bound to aluminium - bound phosphate (b)/(c)
		%	%		%	
(7)	7.5	18.5	10.7	1:1.7	7.8	1:0.7
	8.0	15.6	9.7	1:1.6	5.9	1:0.6
	8.4	12.8	8.5	1:1.5	4.3	1:0.5
	8.8	9.3	4.4	1:2.1	4.9	1:1.1
(8)	7.5	45.5	30.0	1:1.5	15.5	1:0.5
	8.0	42.0	29.0	1:1.5	13.0	1:0.4
	8.4	38.5	22.4	1:1.7	15.9	1:0.7
	8.8	35.0	24.5	1:1.4	10.5	1:0.4
(9)	7.5	35.0	27.5	1:1.3	8.5	1:0.3
	8.0	31.6	25.5	1:1.2	14.1	1:0.6
	8.4	28.4	23.2	1:1.2	5.2	1:0.2
	8.8	24.9	18.5	1:1.3	6.4	1:0.3
(10)	7.5	99.0	96.4	1:1.0	2.6	1:0.0
	8.0	98.4	94.5	1:1.0	6.1	1:0.1
	8.4	97.5	93.9	1:1.0	3.6	1:0.0
	8.8	96.5	91.0	1:1.1	5.5	1:0.1
(11)	7.5	38.4	75.5	1:0.5		
	8.0	35.9	82.5	1:0.4		
	8.4	33.5	85.6	1:0.4		
	8.8	31.0	88.6	1:0.4		
(12)	7.5	70.4	49.5	1:1.4	20.9	1:0.4
	8.0	68.0	48.0	1:1.4	20.0	1:0.4
	8.4	65.3	46.5	1:1.4	18.8	1:0.4
	8.8	61.5	44.1	1:1.4	17.4	1:0.4

Table 4 (Cont'd)

Comparisons of the Phosphate Retention shown by fluoride treated and "untreated" Soils at Four Selected pH values in the Alkaline Range.

Serial No.	pH	(a) Retention of "untreated" soils	(b) Retention of NH_4F-treated soils	Ratio of retention of NH_4F - treated to "untreated" soils	(c) Retention by soil components other than iron (a) - (b)	Ratio of iron - bound to aluminium - bound phosphate $^{(b)}/_{(c)}$
		%	%		%	
(13)	7.5	95.5	78.0	1:1.2	17.5	1:0.2
	8.0	94.4	75.0	1:1.3	19.4	1:0.3
	8.4	93.0	70.0	1:1.3	23.0	1:0.3
	8.8	91.9	61.6	1:1.5	30.3	1:0.5
(14)	7.5	91.6	55.3	1:1.7	36.3	1:0.7
	8.0	89.4	54.0	1:1.7	35.4	1:0.7
	8.4	87.0	51.8	1:1.7	35.2	1:0.7
	8.8	84.0	49.4	1:1.7	34.6	1:0.7
(15)	7.5	44.9	42.3	1:1.2	2.6	1:0.1
	8.0	41.0	39.0	1:1.1	2.0	1:0.1
	8.4	37.5	34.0	1:1.1	3.5	1:0.1
	8.8	33.5	28.6	1:1.2	4.9	1:0.2
(16)	7.5	93.1	58.4	1:1.6	34.7	1:0.6
	8.0	91.5	56.5	1:1.6	35.0	1:0.6
	8.4	89.8	54.0	1:1.7	35.8	1:0.7
	8.8	88.2	49.4	1:1.8	38.8	1:0.8
(17)	7.5	98.0	62.3	1:1.6	35.7	1:0.6
	8.0	97.7	59.2	1:1.7	38.5	1:0.7
	8.4	96.9	56.0	1:1.7	40.9	1:0.7
	8.8	96.0	52.3	1:1.8	43.7	1:0.8
(18)	7.5	84.9	48.8	1:1.7	36.1	1:0.7
	8.0	80.4	49.1	1:1.6	31.3	1:0.6
	8.4	76.2	48.0	1:1.6	28.2	1:0.6
	8.8	71.5	44.6	1:1.6	26.9	1:0.6

Table 4 (Cont'd)

Comparisons of the Phosphate Retention shown by fluoride treated and "untreated" Soils at Four Selected pH values in the Alkaline Range.

Serial No.	pH	(a) Retention of "untreated" soils	(b) Retention of NH_4F-treated soils	Ratio of retention of NH_4F - treated to "untreated" soils	(c) Retention by soil components other than iron (a) - (b)	Ratio of iron - bound to aluminium - bound phosphate $^{(b)}/(c)$
		%	%		%	
(19)	7.5	60.3	54.1	1:1.1	6.2	1:0.1
	8.0	57.0	51.4	1:1.1	5.6	1:0.1
	8.4	54.0	48.6	1:1.1	5.4	1:0.1
	8.8	51.8	45.3	1:1.1	6.5	1:0.1
(20)	7.5	41.4	47.0	1:0.9		
	8.0	38.0	44.5	1:0.9		
	8.4	34.2	41.5	1:0.8		
	8.8	30.1	47.5	1:0.6		
(21)	7.5	81.5	92.5	1:0.9		
	8.0	82.0	89.9	1:0.9		
	8.4	81.7	87.5	1:0.9		
	8.8	80.7	80.0	1:1.0		
(22)	7.5	51.6	65.6	1:0.8		
	8.0	48.9	67.5	1:0.7		
	8.4	45.6	67.0	1:0.7		
	8.8	42.3	64.6	1:0.7		
(23)	7.5	24.8	38.0	1:0.7		
	8.0	22.5	37.0	1:0.6		
	8.4	20.2	35.3	1:0.6		
	8.8	17.4	32.5	1:0.5		
(24)	7.5	31.4	40.0	1:0.8		
	8.0	29.6	38.0	1:0.8		
	8.4	28.0	35.5	1:0.8		
	8.8	26.0	33.0	1:0.8		

7. Correlation of Phosphate Retention values of the fluoride treated Soils with the Free Iron Oxide Contents of the Soils.

The extent of correlation between the amounts of phosphate retained by fluoride treated soils at the four selected alkaline pH levels and the iron oxide contents of the soils were calculated. An r value of + 0.41 was obtained from the statistical calculations presented in Appendix V. The result is significant at 5 per cent level thus indicating some association between phosphate retention at alkaline pH levels of "dealuminated" soils following fluoride treatment and the iron oxide contents.

V. GENERAL DISCUSSION

Comparisons of the phosphate retention patterns at alkaline pH levels of the NaOH - treated and fluoride treated soils (figures 1, 2, 3 and 5) indicate that the former exhibits higher retention patterns than the latter in all the soils investigated except in Tekapo silt loam and Arapohue clay. This could be explained in part by the fact that NaOH is more effective than NH_4F in organic matter removal thus exposing more adsorption sites for phosphate on the free iron oxide surfaces. Furthermore, NaOH dissolves Al_2O_3 as sodium aluminate whereas although aluminium is in part dissolved by fluoride (Fife, priv. comm.) thus possibly exposing some otherwise protected iron oxide surfaces, an insoluble fluoaluminate is also probably formed which may continue to protect iron oxide surface which would be exposed by NaOH treatment. The general pattern of retention behaviour shown by NaOH - treated soils as compared with that of the fluoride treated soils is in keeping with this. Waiwera clay loam (figure 2) and Oparawa gritty silt loam (figure 3) are examples of soils showing this effect.

Tekapo silt loam (figure 1) does not show phosphate retention pattern of NaOH - treated sample higher than that of fluoride treated sample due possibly to its low contents of Al_2O_3 and organic matter. In Arapohue clay it has been deduced previously that the fluoride treated clay behaves as a calcium clay thus showing sharp rise in phosphate retention with increasing pH as shown in figure 1 (Heck 1934, Scarseth and Tidmore 1934, Ravikovitch 1934, Gilligan 1938, Chandler 1941 and Pratt and Thorne 1948). The conversion of this soil to a Na - clay by NaOH treatment has removed this pronounced effect (figure 1).

In the extreme cases even the fluoride treated soils have higher phosphate fixing capacity than the untreated soils. This is shown in figure 5 by Middlehurst silt loam, Maunu loam, Mangakahia clay loam, Hastings clay loam and Manawatu silt loam. The various factors which may contribute to increased phosphate retention by the free iron oxide components of soils are presumably acting in some degree in all the soils tending therefore to exaggerate the roles of iron in phosphate fixation of that which are probably occurring in the field and in the particular instances noted above are operating to such an extent that the phosphate fixing capacity of the "untreated" soils is exceeded by that of the fluoride treated soils.

SUMMARY.

A study was made of the relative incidence of iron - and aluminium - bound phosphates in soils representative of the main New Zealand genetic groups, by the procedure for their separate determination developed by Fife (1962, priv. comm.). The free iron oxide contents of the soils were determined by the dithionite - citrate - bicarbonate method of Jackson, (Jackson 1958, pg. 168 -).

The amounts of iron oxide in soils did not bear a constant relationship to the amounts of iron - bound soil phosphate. The free iron oxide contents appeared to depend on the properties and nature of the soil - forming processes of the soils.

Soils were subjected to "dealumination" either by treatment with 0.5 M NH_4F at pH 8.5 for three days or 1 N NaOH for forty hours, and the amounts of phosphate retained at different pH levels in 0.5 M NH_4Cl were determined for the "untreated", NH_4F - treated and NaOH - treated soils. Reasonably good correlations exist between the amounts of phosphate retained at alkaline pH levels by fluoride treated soils with the amounts of free iron oxide of the soils. The NaOH treatment of soils gave greater activation to the free iron oxide component of the soils in binding phosphate than the fluoride treatment.

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APPENDIX

APPENDIX I

Phosphate Retention Shown by the Soils at Different pH values in 0.5 M NH_4Cl following "de-alumination" by 0.5 M NH_4F

(Results expressed as interpolated percentage retention.)

Serial No.	Final pH	p.p.m. P.	interpolated retention
			%
(1)	3.44	4.12	59.4
	4.26	5.09	49.5
	5.24	5.57	44.7
	5.49	5.50	45.7
	5.58	5.57	44.5
	6.01	5.42	45.8
	7.22	5.46	45.4
	7.73	5.13	48.8
	7.96	5.46	45.5
	8.43	5.69	43.3
	8.63	5.95	40.7
	8.94	6.31	36.1
	4.73	0.02	
	5.75	0.01	
	7.23	0.01	
	8.93	0.02	
(2)	3.42	6.96	31.4
	4.44	7.44	27.6
	5.40	7.44	26.5
	5.59	7.28	28.1
	5.68	7.28	28.1

Phosphate Retention Shown by the Soils at Different pH values in 0.5 M NH_4Cl following "de-alumination" by 0.5 M NH_4F

(Results expressed as interpolated percentage retention.)

Serial No.	Final pH	p.p.m. P.	interpolated retention
			%
	6.00	7.20	28.6
	7.10	6.96	30.5
	7.61	7.12	28.9
	7.89	7.28	27.4
	8.36	7.36	26.7
	8.58	7.61	24.3
	8.89	7.69	23.7
	5.16	0.09	
	5.74	0.06	
	7.10	0.01	
	8.87	0.05	
(3)	3.69	2.58	75.0
	5.00	4.00	60.8
	5.61	4.40	56.3
	5.81	4.41	56.4
	5.98	4.08	59.6
	6.17	4.20	58.4
	7.28	4.61	54.0
	7.77	5.07	49.5
	7.99	5.06	49.6
	8.47	5.62	44.0

APPENDIX I (Cont'd)

Phosphate Retention Shown by the Soils at Different pH values in 0.5 M NH_4Cl following "de-alumination" by 0.5 M NH_4F

(Results expressed as interpolated percentage retention.)

Serial No.	Final pH	p.p.m. P.	interpolated retention %
	8.69	5.83	41.9
	9.00	6.13	38.9
	5.50	0.06	
	5.99	-	
	7.26	0.02	
	8.98	0.02	
(4)	3.58	6.79	33.0
	4.78	7.20	28.9
	5.56	7.12	29.6
	5.75	7.04	30.0
	5.84	6.96	30.5
	6.14	6.86	31.5
	7.17	6.86	31.5
	7.66	7.12	29.0
	7.86	7.12	29.0
	8.34	7.18	28.6
	8.56	7.28	28.1
	8.88	7.28	28.1
	5.24	0.08	
	5.91	0.01	
	7.14	0.02	

APPENDIX I (Cont'd)

Phosphate Retention Shown by the Soils at Different pH values in 0.5 M NH_4Cl following "de-alumination" by 0.5 M NH_4F

(Results expressed as interpolated percentage retention.)

Serial No.	Final pH	p.p.m. P.	interpolated retention %
	8.87	0.04	
(5)	4.19	6.51	35.8
	5.15	7.08	30.0
	5.81	7.40	26.8
	6.04	7.16	29.0
	6.08	7.00	30.5
	6.43	6.92	31.1
	7.25	6.92	31.1
	7.70	7.00	30.3
	7.93	7.16	28.8
	8.39	7.49	25.5
	8.59	7.49	25.5
	8.90	7.73	23.1
	5.85	0.08	
	6.12	0.02	
	7.23	0.06	
	8.91	0.04	
(6)	3.83	6.45	35.2
	4.99	6.77	33.0
	5.73	7.00	30.6
	5.80	6.93	31.3

APPENDIX I (Cont'd)

Phosphate Retention Shown by the Soils at Different pH values in 0.5 M NH_4Cl following "de-alumination" by 0.5 M NH_4F

(Results expressed as interpolated percentage retention.)

Serial No.	Final pH	p.p.m. P.	interpolated retention
			%
	5.97	6.69	33.7
	6.23	6.61	34.4
	7.25	6.28	37.3
	7.72	6.45	35.6
	7.95	6.53	34.8
	8.42	6.85	31.6
	8.63	6.85	31.6
	8.94	6.93	30.8
	5.58	0.06	
	6.05	0.06	
	7.21	0.01	
	8.92	0.01	
(7)	3.14	9.25	9.5
	4.22	9.18	9.2
	5.51	9.18	9.2
	5.61	9.10	10.0
	5.68	9.10	10.0
	6.16	9.02	10.6
	7.31	9.10	10.6
	7.76	9.25	9.8
	8.03	9.35	7.7

Phosphate Retention Shown by the Soils at Different pH values in 0.5 M NH_4Cl following "de-alumination" by 0.5 M NH_4F

(Results expressed as interpolated percentage retention.)

Serial No.	Final pH	p.p.m. P.	interpolated retention
			%
	8.50	9.35	6.7
	8.70	9.43	6.7
	9.01	9.43	5.0
	5.64	0.1	
	6.10	0.07	
	7.26	0.02	
	8.99	0.06	
(8)	3.38	6.90	31.6
	4.43	7.47	25.9
	5.30	7.55	25.1
	5.38	7.63	24.3
	5.59	6.82	32.3
	6.02	6.84	31.6
	7.34	6.90	31.0
	7.80	7.06	29.4
	8.05	7.14	28.6
	8.52	7.31	26.9
	8.74	7.47	25.3
	9.01	7.79	22.1
	5.52	0.06	
	5.86	-	

APPENDIX I (Cont'd)

Phosphate Retention Shown by the Soils at Different pH values in 0.5 M NH_4Cl following "de-alumination" by 0.5 M NH_4F

(Results expressed as interpolated percentage retention.)

Serial No.	Final pH	p.p.m. P.	interpolated retention %
	7.31	0.03	
	9.00	0.01	
(9)	3.12	8.27	18.0
	3.83	8.37	17.0
	4.76	8.37	17.0
	5.31	8.27	18.0
	5.35	8.21	18.0
	5.94	7.77	22.3
	7.24	6.88	31.2
	7.77	7.29	27.1
	8.00	7.45	25.5
	8.45	7.94	20.6
	8.68	8.10	19.0
	9.00	8.45	15.6
	4.21	0.07	
	5.55	0.01	
	7.19	-	
	8.99	0.01	
(10)	5.03	0.01	99.7
	5.84	0.06	99.2

APPENDIX I (Cont'd)

Phosphate Retention Shown by the Soils at Different pH values in 0.5 M NH_4Cl following "de-alumination" by 0.5 M NH_4F

(Results expressed as interpolated percentage retention.)

Serial No.	Final pH	p.p.m. P.	interpolated retention
			%
	6.03	0.07	99.0
	6.15	0.1	98.6
	6.16	0.08	98.9
	6.40	0.1	98.6
	7.22	0.20	97.3
	7.72	0.37	95.9
	7.95	0.52	94.4
	8.40	0.70	92.7
	8.62	0.86	91.2
	8.95	1.14	88.4
	5.86	0.02	
	6.14	0.04	
	7.20	0.04	
	8.92	0.02	
(11)	5.53	7.07	29.7
	6.05	6.18	38.5
	6.23	4.88	51.5
	6.61	4.51	55.2
	6.72	4.02	60.1
	7.00	3.25	67.8
	7.38	2.03	80.0

APPENDIX I (Cont'd)

Phosphate Retention Shown by the Soils at Different pH values in 0.5 M NH_4Cl following "de-alumination" by 0.5 M NH_4F

(Results expressed as interpolated percentage retention.)

Serial No.	Final pH	p.p.m. P.	interpolated retention %
	7.76	1.50	85.2
	8.00	1.34	86.8
	8.44	1.25	87.7
	8.66	1.11	89.1
	9.00	1.05	89.7
	6.49	0.03	
	6.54	0.03	
	7.25	0.02	
	8.98	0.02	
(12)	4.54	4.43	56.2
	5.26	5.08	49.6
	5.81	5.00	50.3
	5.90	5.20	48.3
	5.98	5.16	48.5
	6.33	4.88	51.3
	7.26	5.04	49.3
	7.76	5.12	48.5
	8.10	5.20	47.7
	8.46	5.40	46.7
	8.71	5.49	44.8
	9.00	5.77	42.0

APPENDIX I (Cont'd)

Phosphate Retention Shown by the Soils at Different pH values in 0.5 M NH_4Cl following "de-alumination" by 0.5 M NH_4F

(Results expressed as interpolated percentage retention.)

Serial No.	Final pH	p.p.m. P.	interpolated retention %
	5.85	0.03	
	6.19	0.01	
	7.25	0.03	
	8.99	0.03	
(13)	5.30	0.98	90.9
	5.97	3.12	69.4
	6.18	3.95	61.1
	6.22	4.06	59.9
	6.41	3.87	61.7
	6.87	3.61	64.3
	7.20	2.61	74.3
	7.52	2.15	78.9
	7.82	2.24	77.9
	8.37	3.34	66.9
	8.58	3.34	66.9
	8.90	4.06	59.6
	6.16	0.06	
	6.26	0.04	
	7.01	0.04	
	8.90	0.01	

APPENDIX I (Cont'd)

Phosphate Retention Shown by the Soils at Different pH values in 0.5 M NH_4Cl following "de-alumination" by 0.5 M NH_4F

(Results expressed as interpolated percentage retention.)

Serial No.	Final pH	p.p.m. P.	interpolated retention
			%
(14)	4.92	3.26	68.0
	5.49	4.31	57.4
	5.94	4.11	49.4
	6.02	4.56	54.8
	6.12	4.72	53.1
	6.16	4.40	56.2
	7.19	4.31	56.9
	7.59	4.36	56.5
	7.94	4.80	52.2
	8.41	4.93	51.0
	8.62	5.01	50.3
	8.95	5.62	44.3
	5.95	0.05	
	6.10	0.02	
	7.13	-	
	8.93	0.05	
(15)	4.10	5.95	40.9
	5.27	7.00	30.4
	5.76	7.09	29.4
	5.98	7.33	27.0
	6.09	7.30	27.3

APPENDIX I (Cont'd)

Phosphate Retention Shown by the Soils at Different pH values in 0.5 M NH_4Cl following "de-alumination" by 0.5 M NH_4F

(Results expressed as interpolated percentage retention.)

Serial No.	Final pH	p.p.m. P.	interpolated retention
			%
	6.36	6.35	36.8
	7.21	5.06	49.6
	7.72	5.37	46.5
	7.99	6.66	33.6
	8.45	6.76	32.6
	8.66	6.84	32.8
	8.97	7.33	26.9
	6.07	0.03	
	6.11	0.03	
	7.21	0.02	
	8.97	0.02	
(16)	4.92	2.54	75.6
	5.70	3.41	66.9
	6.04	3.66	64.4
	6.15	3.72	62.0
	6.19	3.80	59.6
	6.38	3.82	58.5
	7.18	4.05	59.6
	7.60	4.25	57.6
	7.89	4.37	56.4

APPENDIX I (Cont'd)

Phosphate Retention Shown by the Soils at Different pH values in 0.5 M NH_4Cl following "de-alumination" by 0.5 M NH_4F

(Results expressed as interpolated percentage retention.)

Serial No.	Final pH	p.p.m. P.	interpolated retention
			%
	8.36	4.86	51.5
	8.56	5.06	49.5
	8.87	5.35	46.7
	6.11	0.01	
	6.40	0.03	
	7.14	0.01	
	8.87	0.02	
(17)	4.39	2.37	76.9
	5.40	3.55	65.0
	5.78	3.65	64.0
	5.88	3.71	63.2
	5.94	3.80	62.8
	6.24	3.59	64.2
	7.29	3.66	63.4
	7.77	3.96	60.4
	8.00	4.27	57.3
	8.48	4.43	55.7
	8.70	4.61	53.9
	8.98	5.14	48.8
	5.91	0.03	
	6.10	0.01	

APPENDIX I (Cont'd)

Phosphate Retention Shown by the Soils at Different pH values in 0.5 M NH_4Cl following "de-alumination" by 0.5 M NH_4F

(Results expressed as interpolated percentage retention.)

Serial No.	Final pH	p.p.m. P.	interpolated retention %
	7.23	-	
	9.00	0.02	
(18)	4.89	5.25	48.2
	5.74	5.37	47.0
	6.10	5.49	46.2
	6.18	5.45	45.6
	6.22	5.41	45.9
	6.40	5.37	46.3
	7.19	5.33	46.9
	7.68	5.13	48.9
	7.94	5.04	49.7
	8.38	5.33	46.8
	8.63	5.53	44.8
	8.96	5.69	43.2
	6.18	0.06	
	6.41	-	
	7.16	0.02	
	8.94	0.01	
(19)	5.37	4.84	51.7
	5.79	5.16	48.8

APPENDIX I (Cont'd)

Phosphate Retention Shown by the Soils at Different pH values in 0.5 M NH_4Cl following "de-alumination" by 0.5 M NH_4F

(Results expressed as interpolated percentage retention.)

Serial No.	Final pH	p.p.m. P.	interpolated retention
			%
	6.28	5.04	49.8
	6.42	5.01	50.0
	6.45	5.01	50.0
	6.51	4.68	53.2
	7.19	4.60	54.0
	7.77	4.93	50.7
	8.00	5.09	49.1
	8.47	5.16	48.5
	8.70	5.41	46.0
	9.00	5.66	43.6
	6.16	0.04	
	6.37	0.01	
	7.20	-	
	8.97	0.02	
(20)	4.52	7.89	22.0
	5.18	8.01	20.8
	5.56	7.82	22.6
	5.75	7.49	25.9
	5.76	7.41	26.6
	6.09	6.52	35.3
	7.14	4.61	54.0

APPENDIX I (Cont'd)

Phosphate Retention Shown by the Soils at Different pH values in 0.5 M NH_4Cl following "de-alumination" by 0.5 M NH_4F

(Results expressed as interpolated percentage retention.)

Serial No.	Final pH	p.p.m. P.	interpolated retention
			%
	7.67	4.93	50.8
	7.92	5.38	46.3
	8.40	5.54	44.7
	8.61	5.75	42.5
	8.93	5.83	41.7
	5.66	0.08	
	6.15	0.05	
	7.11	0.01	
	8.91	-	
(21)	6.53	1.88	81.5
	6.60	1.97	80.6
	6.62	2.40	75.2
	6.63	2.16	78.6
	6.72	2.28	77.4
	6.99	2.23	77.8
	7.04	1.91	80.9
	7.44	2.16	78.4
	7.67	2.13	78.8
	8.30	1.76	82.6
	8.60	1.88	81.4
	8.94	1.80	81.2

APPENDIX I (Cont'd)

Phosphate Retention Shown by the Soils at Different pH values in $0.5\ M\ NH_4Cl$ following "de-alumination" by $0.5\ M\ NH_4F$

(Results expressed as interpolated percentage retention.)

Serial No.	Final pH	p.p.m. P.	interpolated retention %
	6.61	0.03	
	6.69	-	
	7.12	-	
	8.94	0.02	
(22)	4.94	5.65	43.5
	5.46	6.39	36.1
	5.90	6.31	36.9
	6.02	5.98	40.2
	6.04	6.06	39.4
	6.22	5.55	44.5
	7.19	3.59	64.2
	7.73	3.27	67.4
	7.97	2.93	70.8
	8.46	3.30	67.1
	8.68	3.62	63.9
	8.99	3.70	63.1
	5.85	-	
	6.16	-	
	7.18	0.01	
	8.99	0.01	

APPENDIX I (Cont'd)

Phosphate Retention Shown by the Soils at Different pH values in 0.5 M NH_4Cl following "de-alumination" by 0.5 M NH_4F

(Results expressed as interpolated percentage retention.)

Serial No.	Final pH	p.p.m. P.	interpolated retention
			%
(23)	3.95	7.79	23.0
	4.98	7.96	21.2
	5.71	7.79	22.8
	5.90	7.63	24.2
	5.98	7.47	25.7
	6.37	6.49	35.3
	7.37	6.49	35.1
	7.80	6.09	39.3
	8.04	6.33	37.0
	8.51	6.49	35.5
	8.71	6.74	33.1
	9.01	7.14	29.2
	5.61	0.07	
	6.25	0.02	
	7.31	0.02	
	9.00	0.06	
(24)	3.62	6.25	38.3
	5.01	6.48	35.9
	5.64	6.64	34.2
	5.71	6.56	34.9

APPENDIX I (Cont'd)

Phosphate Retention Shown by the Soils at Different pH values in 0.5 M NH_4Cl following "de-alumination" by 0.5 M NH_4F

(Results expressed as interpolated percentage retention.)

Serial No.	Final pH	p.p.m. P.	interpolated retention
			%
	5.96	6.48	35.6
	6.38	5.99	40.2
	7.31	5.99	40.2
	7.74	6.15	38.5
	7.99	6.56	34.7
	8.44	6.56	34.7
	8.66	6.64	34.0
	8.97	6.80	32.5
	5.63	0.07	
	6.18	0.01	
	7.27	-	
	8.95	0.05	

APPENDIX II

Phosphate Retention of "untreated" Soils at Alkaline pH values in 0.5 M NH_4Cl

(Results expressed as interpolated percentage retention.)

Serial No.	Final pH	p.p.m. P.	interpolated retention %
(1)	7.14	4.29	57.2
	7.80	4.68	53.3
	7.94	4.84	51.7
	8.36	5.01	50.0
	8.66	5.25	47.7
	8.94	5.57	44.5
	5.02	0.07	
	5.38	0.01	
	7.29	0.01	
	8.97	0.02	
(2)	3.62	8.26	19.4
	4.12	7.61	25.5
	4.76	7.21	28.9
	5.34	7.13	29.4
	5.38	6.82	32.5
	7.10	6.55	34.5
	7.74	6.44	36.4
	8.01	6.72	33.7
	8.38	6.80	33.0
	8.64	6.97	31.4
	8.92	7.29	29.4

Phosphate Retention of "untreated" Soils

at Alkaline pH values in 0.5 M NH_4Cl

(Results expressed as interpolated percentage retention.)

Serial No.	Final pH	p.p.m. P.	interpolated retention %
	4.56	0.16	
	5.13	0.07	
	7.16	0.07	
	9.01	0.13	
(3)	7.00	0.90	91.0
	7.72	1.11	88.9
	7.88	1.16	88.4
	8.31	1.35	86.5
	8.59	1.44	85.6
	8.86	1.76	82.4
	5.18	1.79	
	5.42	0.01	
	7.15	-	
	8.96	0.01	
(4)	6.69	3.93	61.0
	7.55	4.30	57.4
	7.86	4.46	55.8
	8.38	4.91	51.4
	8.68	5.68	44.0
	8.96	6.25	38.4

Phosphate Retention of "untreated" Soils

at Alkaline pH values in 0.5 M NH_4Cl

(Results expressed as interpolated percentage retention.)

Serial No.	Final pH	p.p.m. P.	interpolated retention
			%
	4.12	0.11	
	4.68	0.04	
	6.97	0.03	
	8.99	0.09	
(5)	7.04	4.91	51.3
	7.78	5.19	48.5
	7.88	5.48	45.6
	8.42	6.00	40.4
	8.70	6.13	39.2
	8.96	6.42	36.4
	4.64	0.04	
	5.24	0.04	
	7.17	0.04	
	8.98	0.06	
(6)	7.21	5.25	47.5
	7.78	5.33	46.7
	7.94	5.58	44.2
	8.34	5.62	43.8
	8.66	6.06	39.4
	8.95	6.22	37.9

Phosphate Retention of "untreated" Soils

at Alkaline pH values in 0.5 M NH_4Cl

(Results expressed as interpolated percentage retention.)

Serial No.	Final pH	p.p.m. P.	interpolated retention %
	3.78	0.01	
	5.12	-	
	7.24	-	
	8.96	0.01	
(7)	7.02	8.10	20.1
	7.66	8.23	18.6
	7.80	8.34	17.5
	8.28	9.10	10.0
	8.55	9.10	10.0
	8.85	9.26	8.5
	3.98	0.17	
	4.94	0.15	
	7.06	0.09	
	8.89	0.11	
(8)	7.08	5.15	48.5
	7.67	5.62	43.9
	7.85	5.71	43.0
	8.29	5.91	41.0
	8.47	6.31	37.1

APPENDIX II (Cont'd)

Phosphate Retention of "untreated" Soils

at Alkaline pH values in 0.5 M NH_4Cl

(Results expressed as interpolated percentage retention.)

Serial No.	Final pH	p.p.m. P.	interpolated retention
			%
	8.88	6.55	34.7
	4.21	0.02	
	5.20	0.01	
	7.18	0.01	
	8.91	0.02	
(9)	7.12	6.29	37.5
	7.68	6.71	33.4
	7.83	6.79	32.6
	8.30	6.98	30.9
	8.58	7.42	26.6
	8.86	7.61	24.7
	4.07	0.05	
	5.00	0.05	
	7.20	0.05	
	8.91	0.08	
(10)	6.26	0.09	99.1
	7.45	1.00	99.0
	7.64	0.11	98.9
	8.17	0.20	98.0
	8.56	0.24	97.6

APPENDIX II (Cont'd)

Phosphate Retention of "untreated" Soils

at Alkaline pH values in 0.5 M NH_4Cl

(Results expressed as interpolated percentage retention.)

Serial No.	Final pH	p.p.m. P.	interpolated retention %
	8.84	0.26	97.4
	5.00	0.01	
	5.20	-	
	6.70	-	
	8.92	0.01	
(11)	7.28	6.10	39.0
	7.84	6.39	36.2
	8.00	6.47	35.5
	8.40	6.63	34.0
	8.66	6.67	33.7
	8.93	7.04	30.2
	5.78	0.01	
	6.20	0.01	
	7.37	-	
	9.00	0.06	
(12)	7.18	2.85	71.5
	7.78	2.99	70.2
	7.91	3.10	69.1
	8.30	3.54	64.7
	8.66	3.67	63.4
	8.94	3.99	60.2

APPENDIX II (Cont'd)

Phosphate Retention of "untreated" Soils at Alkaline pH values in 0.5 M NH_4Cl

(Results expressed as interpolated percentage retention.)

Serial No.	Final pH	p.p.m. P.	interpolated retention %
	4.93	0.01	
	5.39	-	
	7.21	0.01	
	8.97	0.01	
(13)	6.96	0.33	96.7
	7.64	0.50	95.0
	7.80	0.52	94.8
	8.28	0.63	93.7
	8.60	0.73	92.7
	8.82	0.79	92.1
	5.31	-	
	5.46	-	
	7.06	-	
	8.93	-	
(14)	7.06	0.81	92.9
	7.65	0.88	91.2
	7.84	1.02	89.8
	8.33	1.23	87.7
	8.63	1.43	85.7
	8.91	1.67	83.1
	5.36	-	

APPENDIX II (Cont'd)

Phosphate Retention of "untreated" Soils

at Alkaline pH values in 0.5 M NH_4Cl

(Results expressed as interpolated percentage retention.)

Serial No.	Final pH	p.p.m. P.	interpolated retention %
	5.50	-	
	7.01	-	
	8.94	0.02	
(15)	7.04	5.21	47.9
	7.64	5.49	45.1
	7.80	5.82	41.8
	8.26	6.10	39.0
	8.52	6.47	35.4
	8.83	6.63	33.9
	4.61	0.02	
	5.49	-	
	7.20	-	
	8.85	0.02	
(16)	6.92	0.55	94.5
	7.52	0.65	93.5
	7.74	0.71	92.9
	8.05	0.88	91.2
	8.59	0.96	90.4
	8.82	1.10	89.0
	5.63	-	
	5.90	-	

APPENDIX II (Cont'd)

Phosphate Retention of "untreated" Soils

at Alkaline pH values in 0.5 M NH_4Cl

(Results expressed as interpolated percentage retention.)

Serial No.	Final pH	p.p.m. P.	interpolated retention
			%
	6.93	-	
	8.85	-	
(17)	6.90	0.13	98.7
	7.57	0.19	98.1
	7.70	0.20	98.0
	8.20	0.28	97.2
	8.60	0.33	96.7
	8.95	0.37	96.3
	5.67	-	
	5.52	-	
	6.95	-	
	8.95	-	
(18)	5.74	2.16	78.6
	6.87	0.12	98.0
	7.14	1.30	87.3
	7.97	1.93	81.0
	8.39	2.32	77.2
	8.76	2.89	71.7
	4.57	0.06	
	4.58	0.02	
	5.69	0.02	

APPENDIX II (Cont'd)

Phosphate Retention of "untreated" Soils

at Alkaline pH values in 0.5 M NH_4Cl

(Results expressed as interpolated percentage retention.)

Serial No.	Final pH	p.p.m. P.	interpolated retention %
	8.78	0.06	
(19)	7.01	3.71	63.0
	7.67	4.05	59.6
	7.81	4.12	58.9
	8.28	4.52	54.9
	8.58	4.69	53.2
	8.84	5.10	49.0
	4.84	0.04	
	5.44	0.02	
	7.16	0.01	
	8.88	0.01	
(20)	7.23	5.66	43.9
	7.80	6.06	39.6
	7.98	6.31	37.2
	8.41	6.46	35.8
	8.71	6.88	31.7
	8.96	7.20	29.1
	5.86	2.58	
	5.50	0.07	
	7.38	0.05	
	9.00	0.11	

APPENDIX II (Cont'd)

Phosphate Retention of "untreated" Soils
at Alkaline pH values in 0.5 M NH_4Cl

(Results expressed as interpolated percentage retention.)

Serial No.	Final pH	p.p.m. P.	interpolated retention %
(21)	7.22	0.63	93.7
	7.86	0.91	90.9
	7.96	0.98	90.2
	8.40	1.18	88.2
	8.66	1.32	86.8
	8.98	1.65	83.6
	5.48	-	
	5.75	-	
	7.36	-	
	9.01	0.01	
(22)	7.14	4.68	53.2
	7.78	4.84	51.6
	7.90	5.01	49.9
	8.36	5.33	46.8
	8.62	5.58	44.4
	8.89	5.98	40.5
	4.93	0.05	
	5.50	0.03	
	7.30	-	
	8.96	0.03	

APPENDIX II (Cont'd)

Phosphate Retention of "untreated" Soils

at Alkaline pH values in 0.5 M NH_4Cl

(Results expressed as interpolated percentage retention.)

Serial No.	Final pH	p.p.m. P.	interpolated retention
			%
(23)	7.12	7.53	25.4
	7.72	7.77	23.3
	7.84	8.02	21.8
	8.30	8.11	21.4
	8.56	8.36	19.8
	8.86	8.61	17.3
	4.96	0.16	
	5.60	0.12	
	7.20	0.07	
	8.90	0.34	
(24)	7.19	6.97	31.7
	7.80	7.05	30.9
	7.81	7.29	29.1
	8.33	7.45	28.5
	8.59	7.86	25.6
	8.96	7.88	25.4
	5.07	1.38	
	5.51	0.16	
	7.20	0.14	
	8.91	0.42	

APPENDIX III

Phosphate Retention of NaOH - treated Soils

at Alkaline pH values in 0.5 M NH_4Cl

(Results expressed as interpolated percentage retention.)

Serial No.	Final pH	p.p.m. P.	interpolated retention %
(1)	7.18	5.40	46.0
	7.74	5.72	42.8
	7.89	5.97	40.3
	8.24	6.17	38.4
	8.59	6.45	35.6
	8.88	6.86	31.5
	5.02	-	
	6.07	-	
	7.36	-	
	8.97	0.01	
(3)	7.30	2.82	71.9
	7.72	3.33	66.8
	7.88	3.68	63.3
	8.26	4.18	58.3
	8.53	4.57	54.4
	8.82	4.81	52.0
	5.85	-	
	6.32	0.01	
	7.36	0.01	
	8.83	0.01	

APPENDIX III (Cont'd)

Phosphate Retention of NaOH - treated Soils
at Alkaline pH values in 0.5 M NH_4Cl

(Results expressed as interpolated percentage retention.)

Serial No.	Final pH	p.p.m. P.	interpolated retention %
(4)	7.24	5.71	43.0
	7.74	6.44	35.7
	7.90	6.60	34.1
	8.26	6.76	32.5
	8.58	7.17	28.4
	8.84	7.25	27.6
	6.08	-	
	6.52	-	
	7.37	0.01	
	8.85	0.01	
(5)	7.30	6.45	35.6
	7.90	7.09	32.5
	8.01	7.14	32.0
	8.41	7.18	31.5
	8.71	7.26	27.5
	8.98	7.42	25.9
	5.95	0.01	
	6.55	0.01	
	7.45	0.01	
	9.00	0.01	

APPENDIX III (Cont'd)

Phosphate Retention of NaOH - treated Soils

at Alkaline pH values in 0.5 M NH_4Cl

(Results expressed as interpolated percentage retention.)

Serial No.	Final pH	p.p.m. P.	interpolated retention %
(6)	7.46	4.70	53.0
	7.88	5.14	48.6
	8.00	5.31	46.9
	8.42	5.68	43.3
	8.68	5.92	40.9
	8.96	6.32	36.9
	5.95	-	
	6.50	-	
	7.46	-	
	9.00	0.01	
(10)	7.36	0.03	100.0
	7.89	0.04	99.9
	7.97	0.07	99.6
	8.38	0.11	99.1
	8.65	0.15	98.7
	8.98	0.22	98.0
	6.54	-	
	6.85	-	
	7.48	0.03	
	8.98	0.02	

APPENDIX III (Cont'd)

Phosphate Retention of NaOH - treated Soils

at Alkaline pH values in 0.5 M NH_4Cl

(Results expressed as interpolated percentage retention.)

Serial No.	Final pH	p.p.m. P.	interpolated retention %
(11)	7.59	4.74	52.7
	7.89	5.04	49.7
	7.98	5.13	48.8
	8.49	5.39	46.2
	8.68	5.52	44.9
	8.97	5.96	40.5
	6.86	0.01	
	7.16	0.01	
	7.52	0.01	
	8.98	0.01	
(22)	7.41	2.59	74.2
	7.84	2.93	70.8
	7.97	3.17	68.4
	8.36	3.69	63.2
	8.62	3.77	62.4
	8.89	4.22	57.9
	8.94	-	
	7.46	0.01	
	6.78	0.01	
	6.21	0.01	

APPENDIX IV

Phosphate Retention Shown by NaOH - treated Soils in 0.5 M NH_4Cl at Different pH levels.

Serial No.	Final pH	p.p.m. P.	Phosphate retention %
(1)	3.52	0.04	99.6
	4.65	0.07	99.3
	6.02	0.12	98.8
	6.21	0.14	98.6
	6.22	0.15	98.5
	6.26	0.15	98.5
	6.34	0.16	98.4
	6.49	0.20	98.0
	6.74	0.21	97.9
	6.94	0.23	97.7
	7.14	0.28	97.2
	7.64	0.37	96.3
	7.88	0.50	95.0
	9.04	0.57	94.3
(2)	3.58	0.26	97.4
	5.09	0.37	96.3
	6.18	0.37	96.3
	6.26	0.39	96.1
	6.34	0.37	96.3
	6.40	0.41	95.9
	6.44	0.44	95.6
	6.50	0.45	95.5

APPENDIX IV (Cont'd)

Phosphate Retention Shown by NaOH - treated Soils in 0.5 M NH_4Cl at Different pH levels.

Serial No.	Final pH	p.p.m. P.	Phosphate retention %
	6.62	0.49	95.1
	6.92	0.50	95.0
	7.12	0.69	93.1
	7.50	0.71	92.9
	7.61	0.73	92.7
	8.10	0.81	91.9
	8.57	0.85	91.5
	9.04	1.10	89.0
(3)	4.67	0.01	99.9
	6.56	0.03	99.7
	6.62	0.06	99.4
	6.67	0.04	99.6
	6.82	0.07	99.3
	7.13	0.07	99.3
	7.58	0.08	99.2
	8.34	0.15	98.5
	8.99	0.23	97.7
(4)	5.75	0.35	96.5
	6.69	0.40	96.3
	6.77	0.37	96.0
	6.85	0.52	95.2

APPENDIX IV (Cont'd)

Phosphate Retention Shown by NaOH - treated Soils in 0.5 M NH_4Cl at Different pH levels.

Serial No.	Final pH	p.p.m. P.	Phosphate retention
			%
	7.19	0.48	94.8
	8.20	0.65	93.5
	8.98	1.02	89.8
(5)	5.68	0.20	98.0
	6.66	0.37	96.3
	6.75	0.40	96.0
	6.94	0.41	95.9
	7.19	0.49	95.1
	7.70	0.50	95.0
	8.36	0.71	92.9
	9.01	1.17	88.3
(6)	4.74	0.08	99.2
	6.56	0.12	98.8
	6.64	0.12	98.8
	6.76	0.13	98.7
	7.16	0.15	98.5
	7.80	0.25	97.5
	8.33	0.35	96.5
	9.00	0.59	94.1
(8)	4.50	0.07	99.3

APPENDIX IV (Cont'd)

Phosphate Retention Shown by NaOH - treated Soils in 0.5 M NH_4Cl at Different pH levels.

Serial No.	Final pH	p.p.m. P.	Phosphate retention
			%
	5.47	0.11	98.9
	6.37	0.12	98.8
	6.48	0.13	98.7
	6.54	0.17	98.3
	6.54	0.17	98.3
	6.79	0.19	98.1
	6.92	0.20	98.0
	7.14	0.20	98.0
	7.47	0.30	97.0
	8.57	0.70	93.0
	9.01	0.76	92.4
(9)	3.38	0.93	90.7
	4.38	0.86	91.4
	5.66	0.84	91.6
	5.99	0.80	92.0
	6.06	0.84	91.6
	6.08	0.84	91.6
	6.21	0.85	91.5
	6.33	0.89	91.1
	6.63	0.94	90.6
	6.67	0.94	90.6
	6.80	0.95	90.5

APPENDIX IV (Cont'd)

Phosphate Retention Shown by NaOH - treated Soils in 0.5 M NH_4Cl at Different pH levels.

Serial No.	Final pH	p.p.m. P.	Phosphate retention %
	7.45	1.00	90.0
	7.60	1.10	89.0
	8.08	1.30	87.0
	8.54	1.40	86.0
	9.03	1.52	84.8

APPENDIX V

Correlation Coefficient (r).

Serial No.	Fe_2O_3 (x)	Mean Amount of retention of NH_4F - treated soil (y)	Serial No.	Fe_2O_3 (x)	Mean Amount of retention of NH_4F - treated soil (y)
	%	%		%	%
(1)	0.86	44.3	(13)	1.76	71.2
(2)	0.46	26.6	(14)	2.11	52.6
(3)	1.43	55.0	(15)	1.10	36.0
(4)	1.67	28.8	(16)	2.42	54.6
(5)	0.94	27.3	(17)	1.84	57.5
(6)	2.19	33.8	(18)	1.10	47.6
(7)	0.11	8.3	(19)	1.53	49.9
(8)	1.41	26.5	(20)	2.51	45.1
(9)	0.29	23.7	(21)	1.45	87.5
(10)	2.15	94.0	(22)	0.80	66.2
(11)	1.10	83.1	(23)	0.78	35.7
(12)	2.70	47.0	(24)	0.76	36.6

Calculations.

$$SS_x = E_x^2 - \frac{(E_x)^2}{n} \quad ; \quad n = 22$$

$$= 11.7760$$

$$SS_y = E_y^2 - \frac{(E_y)^2}{n}$$

$$= 10512.24$$

$$SP_{xy} = E_{xy} - \frac{(E_x)(E_y)}{n}$$

$$= +145.269$$

$$r_{xy} = \frac{+145.269}{123792.13} \qquad \frac{SP_{xy}}{(SS_x)(SS_y)}$$

$$= \frac{+145.269}{351.841} = +0.413$$

Result *

$$(y - 47.45) = +12.336\,(x - 1.395)$$

$$y = +30.241 + 12.336x$$

therefore regression coefficient = 12.34

$$s^2_b = \frac{SS_y - \frac{(SP_{xy})}{SS_x}}{(n)\ (SS_x)}$$

$$= 33.659$$

therefore $b \pm s_b = +12.34 \pm 5.80$