Changes in the Forms and Availability of Applied Phosphate Over a Twelve-Month Period in Two Soils of the Manawatu-Rangitikei Sand Country

A thesis presented in partial fulfilment
of the requirements for the degree of
Master of Agricultural Science
at Massey University

by

K.W. Steele
1972

TABLE OF CONTENTS

Page

Page

2. Analytical procedures

CHAPTER THREE - RESULTS

Page

CHAPTER FOUR

A. DISCUSSION

LIST OF TABLES

LIST OF FIGURES

INTRODUCTION

A feature of New Zealand agriculture is the requirement for regular applications of phosphate fertilizer to maintain high producing pastures. This is reflected in the large amounts of phosphate fertilizer sold annually, which for the 1971-72 season reached a level of 2,041,000 tonnes.

The soils of the Manawatu-Rangitikei sand country, being naturally deficient in phosphate, are no exception to this requirement for regular applications of phosphate. However, these soils, especially those of the sand plains are potentially fertile. Thus trials conducted by the Department of Agriculture have shown that, on Himatangi sand, pasture production in the range 15,700-16,800 kg D.M./ha can be realized (Blackmore, pers. comm.).

The need for regular, preferably at least annual, application of phosphate to these sand country soils implies a fall in the level of availability of the applied phosphate within the zone of action of the pasture roots due either to:-

(i) actual loss of phosphate from this zone by leaching a distinct possibility in such light-textured soils; or

(ii) a change in the soil/soil solution equilibrium distribution of phosphate as a result of changes in the nature of the fixed forms with time; or

(iii) a combination of these factors.

The object of the present study was to investigate the operation of these factors for two representative sand country soils, the differing moisture regime and pH status of which might be expected to exert some influence on the course of phosphate fixation. At the same time, it was hoped to reach some conclusion as to the relative sensitivity of a number of commonly used chemical "quick tests" for evaluation of phosphate availability in these soils and to determine whether changes in these values were paralleled by demonstrable changes in the forms of phosphate binding.

* * * * * *

CHAPTER ONE

A. Introduction to the Manawatu-Rangitikei Sand Country

(1) Location: The Manawatu-Rangitikei sand country (Figure 1.1) comprises a complex of dunes, sand plains and peaty swamps bordering the coast and extending inland up to 14.5 km. It is part of an extensive complex bordering the west coast of the lower part of the North Island of New Zealand, extending from Paekakariki in the south to Patea in the north. The total area involved is over 109,300 hectares of which approximately 68,800 hectares are in the Manawatu and Rangitikei districts (Cowie, et al. 1967).

(2) Climate: The Manawatu-Rangitikei sand country falls within the western Wellington climatic district, its climate being characterised by warm summers and mild winters (Robertson, 1959). March tends to be the driest month (54.15 mm) and June the wettest month (91.01 mm), the average annual rainfall being in the range of 847-904 mm (Appendix 1(a)).

Data recorded at Flock House Farm of Instruction shows that there is no great extreme in temperature, the air temperatures being highest in February and lowest in July (Appendix 1(b)).

Strong north-west and westerly winds, frequently reaching gale force are common during spring and early summer. These winds decrease in frequency and strength during late summer and autumn and easterlies become more frequent. From late autumn to spring light winds prevail and calm spells are common (Cowie, et al. 1967).

LEGEND FOR FIGURE 1.1

TOWNS

1 Turakina
2 Marton
3 Bulls
4 Ohakea
5 Sanson
6 Carnarvon
7 Clydesdale
8 Rongotea
9 Tangimoana

10 Glen Oroua
11 Oroua Downs
12 Himatangi Beach
13 Himatangi
14 Rangiotu
15 Foxton
16 Waitarere
17 Koputaroa
18 Hokio

DUNE PHASES

Waitarere

Motuiti ░

Foxton ▨

Koputaroa ⁘

Alluvium ▥

Loess
Gravels
Greywacke ▥

Tertiary
rocks

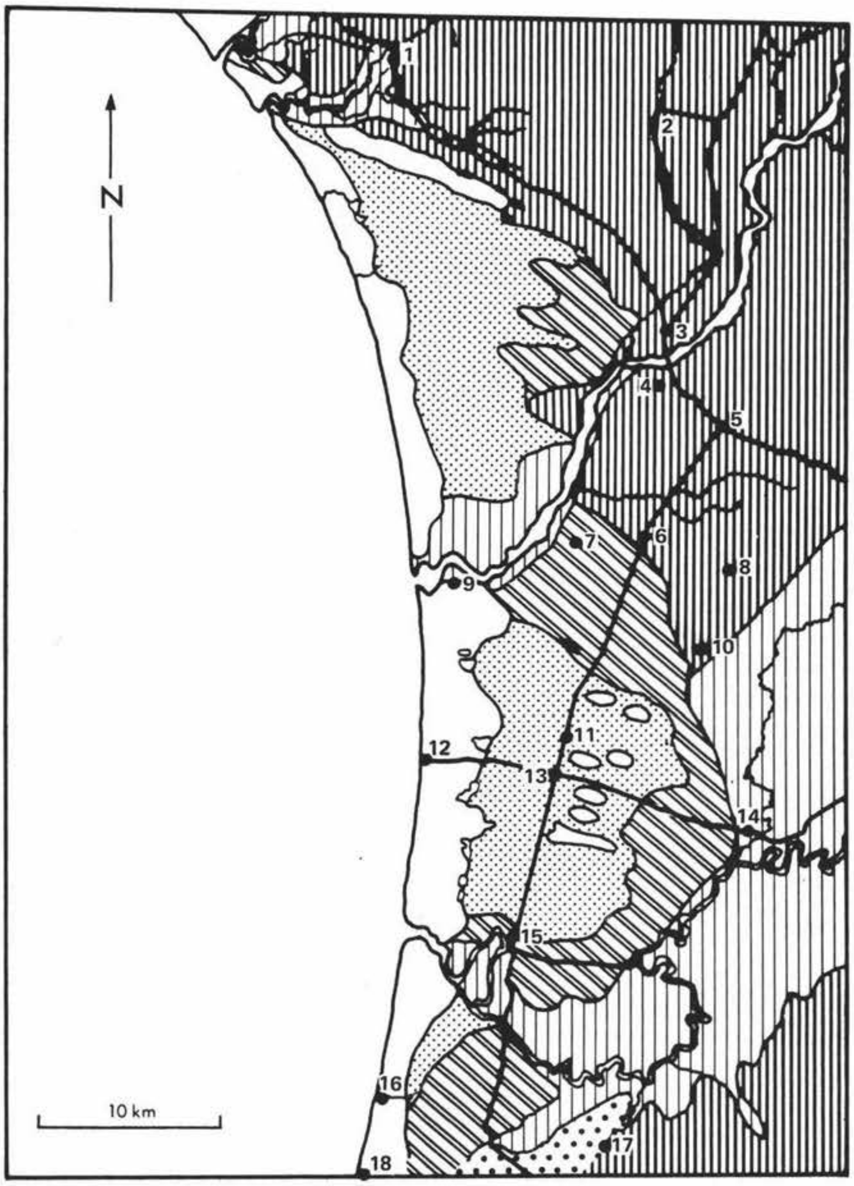


Figure 1.1 Map showing extent of dune-building phases in the Manawatu district

(3) Vegetation: Scrub, fern or swamp vegetation originally covered most of the sand country, although there is evidence that considerable areas of forest existed especially on the more inland parts. Most of the sand plains have now been cleared and sown to pasture, but in some places there has been reversion to scrub, and some of the wetter swamp areas still maintain original vegetation.

Detailed reports of the vegetation are to be found in Appendix 1(c) and 1(d).

(4) Parent Material: The parent material of the Manawatu-Rangitikei sand country soils is wind-blown sand derived chiefly from greywacke of the central ranges, tertiary sandstones and mudstones flanking these ranges and volcanic materials from the Taupo and Taranaki districts (Cowie, et al. 1967).

The dominant characteristics of the wind-blown sand are its coarse texture (a large proportion of the sand grains fall within the size range 0.15-0.3 mm diameter) and its negligible amounts of silt and clay (Cowie, 1968).

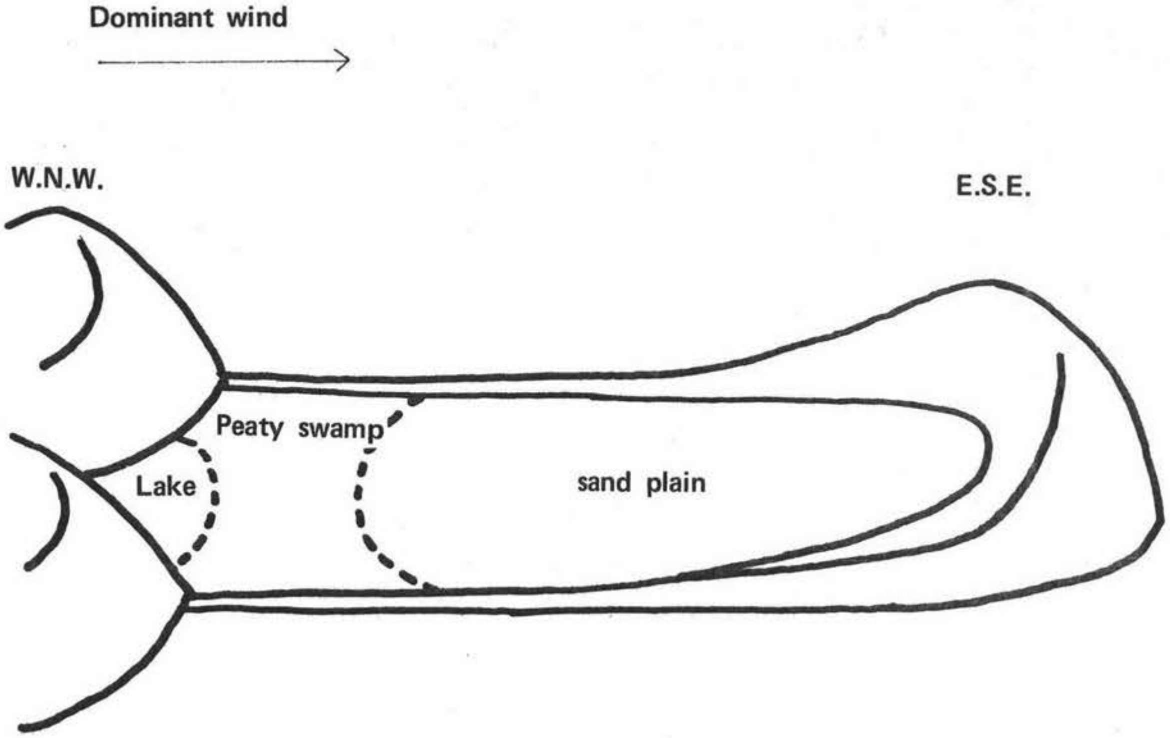
Claridge (1961) stated that the dominant clay mineral in these soils is illite, together with partially expanded micas and vermiculites. He suggested that the assemblage of clays is consistent with the hypothesis that most of the clay in these soils is derived from loess-like material blown in from the beaches after being eroded from soils in the vicinity.

(5) Physiography: From sea-level the sand country rises to the terraces of the Marton-Turakina district, the altitude of the inland margin being approximately 30 m near

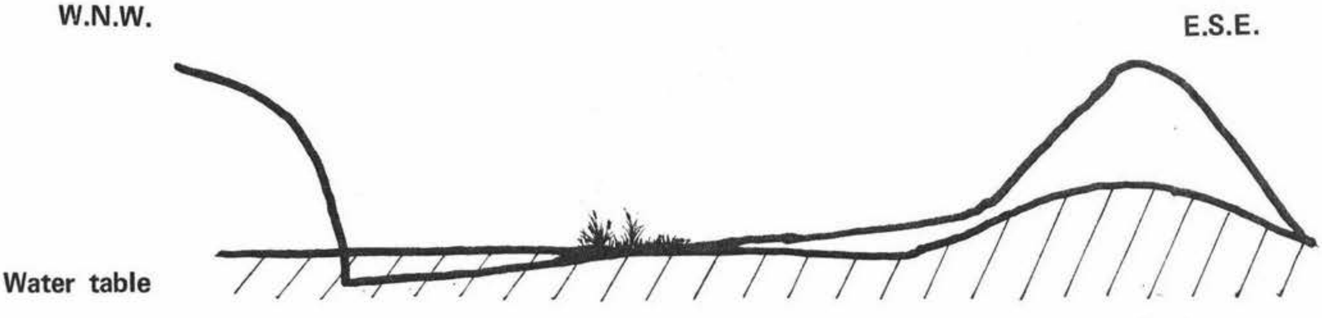
Turakina and 105 m near Bulls. The land between the Rangitikei and Manawatu rivers rises to an altitude of between 12 and 45 m and then falls away to the margin of the flats and terraces of the Oroua and Manawatu rivers. This rise is less pronounced south of the Manawatu river, where the land rises to between 15 and 30 m before it falls away towards the flats and terraces of the Levin-Koputaroa district (Cowie, et al. 1967).

Cowie (1957, 1968) notes that at first sight the arrangement of dunes seems chaotic, but closer examination reveals a well-defined dune unit as the fundamental constituent of the overall pattern. This fundamental unit consists of a windrift dune of two long narrow parallel ridges united at their eastern end to form an apex with an enclosed sand plain (Figure 1.2). The sand plain slopes down from east to west so that the water table is low at the higher, eastern end but becomes closer to the surface towards the lower western end. In the extreme western end of the sand plain it is at, or near the surface during winter and spring. Where the flow of this surface water away from the sand plains is prevented by the next dune to the west, peaty swamps and lakes have been formed.

Although examples of this basic unit of dune, sand plain and peaty swamp can be found in many places, it is in fact, often more complex. Several subsidary apices may be present along the wings, the dunes may be crescent shaped and arranged in festoons, or, as in the extreme southern part of the district, the wings are shortened and the festoons compressed so that the dune apices are the dominant features of the landscape and peaty swamps occupy most of the area between dunes.



Oblique view



Longitudinal Section

Figure 1.2: Diagram of basic unit of dune ridge, sand plain and peaty swamp.
(From Cowie, 1968.)

(6) Dune Successions: The Manawatu-Rangitikei dunes appear to have formed during four distinct dune-building phases (Cowie, 1963). These phases, in order of increasing age are named Waitarere, Motuiti, Foxton and Koputaroa.

The Waitarere phase, extending from the coast inland for a distance of from 0.4 to 3.2 km, is thought to be less than 120 years old and the advance is attributed partly to overgrazing and burning of the vegetation on previously stabilized dunes, and partly to accelerated erosion inland due to clearing and burning (Cowie, 1963).

Inland from the Waitarere phase, the Motuiti phase forms a belt up to 10 km wide. The dunes of this phase are believed to have begun advancing 750 years ago and consideration of the degree of soil profile development indicates that stabilization took place about 500 years ago (Cowie, 1963).

A 3-6 km wide belt of Foxton phase dunes lie inland from those of the Motuiti phase and Cowie (1963) suggests these dunes are between 2,000 and 4,000 years old.

Dunes of the Koputaroa phase, according to Cowie (1963) are between 10,000 and 15,000 years old, and they occur only in a few areas of the northern and southern parts of the Manawatu district inland from the Foxton dunes.

(7) Soils: Soils of differing degrees of profile development correspond to the four dune phases. Within each dune phase differences between soils are due either directly or indirectly to differences in relief.

Sequences of soils arranged according to age and drainage are shown in Table 1.1 and further detail is provided by Cowie (1957, 1968); Cowie and Smith (1958); Cowie and Hall (1965); and Cowie, et al. (1967).

* * * * * *

TABLE 1.1

Manawatu-Rangitikei Sand Country Soils

Arranged According To Age And Drainage

Topographic Position	Drainage	Increasing Age And Soil Profile Development →				
Dune	Excessive Somewhat excessive Free	Waitarere sand	Motuiti	Foxton black sand Foxton brown sand* Foxton brown mottled sand*		Koputaroa sandy loam*
	Somewhat excessive	Hokio weakly mottled sand	Himatangi weakly mottled sand, shallow topsoil phase Himatangi weakly mottled sand Himatangi sand, shallow topsoil phase			
	Free	Hokio strongly mottled sand	Himatangi sand	Pukepuke brown sand*	Awahou loamy sand Awahou loamy sand	
Sand plain	Imperfect	Hokio sand	Pukepuke black sand Pukepuke black loamy sand	Pukepuke brown loamy sand*	Carnarvon black loamy sand ~~Carnarvon~~ brown loamy sand	
	Poor	Hokio sand, peaty phase	Pukepuke black sand with concretions	Pukepuke brown sandy loam* Pukepuke brown sandy loam, peaty phase*	Carnarvon brown loamy sand Omanuka peaty loam, shallow phase	
Peaty swamp	Very poor		Omanuka peaty sandy loam	Omanuka peaty silt loam	Omanuka peaty loam	
Corresponding dune phases		Waitarere	Motuiti	Foxton		Koputaroa

Soils marked with an asterisk are formed under forest; remainder are formed under scrub, sedges, and rushes. Position of peaty soils in time sequence tentative only.

B. LITERATURE REVIEW

(1) Phosphate Fractionation And The Forms Of Inorganic Phosphate In Soils:

Although extensive literature has been published on the phenomenon of retention of phosphate by soils, first demonstrated by Way (1850), and the possible mechanisms involved, interest in the subject remains undiminished. This is demonstrated not only by the large number of recent publications on this subject, but also by review articles such as those of Dean (1949), Wild (1950), Hemwall (1957), and Smith (1965a).

It is generally agreed that in acid soils, phosphate is present in chemical combination as, or in association with, iron and aluminium compounds, while calcium compounds are important in calcareous soils (Smith, 1969b).

Many workers have attempted to fractionate inorganic phosphate (Fraps, 1906; Fisher and Thomas, 1935; Truog and Dean, 1935; Williams, 1937; Dean, 1938; Bray and Dickman, 1942; Ghani, 1943; Fraps and Fudge, 1945; Chirikov and Volkova, 1945; Williams, 1950; Bhangoo and Smith, 1957; Chang and Jackson, 1957a; and Saunders, 1959a) with varying degrees of success. The method proposed by Chang and Jackson (1957a), although often criticised, has gained wide acceptance, although it has been modified by Khin and Leeper (1960); Fife (1959a, 1959b, 1962, 1963); Glen, et al. (1959); Chang and Liaw (1962); Smith (1965c); Williams (1965); Peterson and Corey (1966), and Williams, et al. (1967).

The method as proposed by Chang and Jackson (1957a) provides a procedure for fractionation of soil inorganic phosphate into the following categories:

(i) Water-soluble and loosely-bound phosphate
(ii) Aluminium phosphate
(iii) Iron phosphate
(iv) Calcium phosphate
(v) Reductant-soluble iron phosphate
(vi) Occluded aluminium phosphate
(vii) Occluded iron phosphate

However, the procedure has limitations. Yuan and Fiskell (1959) found that the citrate-dithionite extraction for reductant-soluble iron phosphate extracted large amounts of aluminium from soils, and Saunders (1959b) showed that for a range of twelve New Zealand soils, the citrate was responsible for most of the aluminium extracted. Khin and Leeper (1960) were of the opinion that ambiguity must always remain in the distinction between (a) aluminium and iron phosphates, due to resorption of phosphate by iron oxides during extraction of aluminium phosphate by fluoride, and (b) between calcium phosphate and reductant-soluble phosphate, due to extraction of reductant-soluble phosphate in the calcium phosphate extraction. Corrections for the resorption of phosphate by iron oxides during extraction with fluoride have been proposed by Fife (1962), and Smith (1965a), but Bromfield (1970) concluded that neither of these corrections could be used with confidence. Smith (1972), however, stated that although the corrections of Fife (1962) and Smith (1965a) may not give the actual values of iron and aluminium phosphate, there is a noticeable improvement over no correction at all. Patel and Mehta (1961) criticised the fractionation procedure on the grounds that no one form of soil phosphate was a definite fraction of total phosphate. In soils containing $CaCO_3$, formation of CaF_2 during extraction with NH_4F may effectuate the iron plus aluminium phosphate to be greatly underestimated, due to the resorption of released phosphate by CaF_2 during extraction with NH_4F and NaOH, and subsequent fractions to be overestimated, due to the release of phosphate from CaF_2 (Syers, et al. 1972). In resorption studies of a range of British and Indian soils using ^{32}P, Rajendran and Sutton (1970) found 68 to 87% resorption of phosphate during the extraction for loosely-bound phosphate, along with a tendency for the Chang and Jackson procedure to overestimate occluded phosphate due to resorption of phosphate during the preceding extractions. Corrections to the remaining fractions differed between soils, the overall result being to accentuate soil differences rather than to change the original pattern. If dicalcium phosphate is present in soils, as may occur after fertilizer application, this will be included in the aluminium phosphate fraction due to its solubility in NH_4F (Laverty and McLean, 1961; Kaila, 1961a, 1963a). Terpugov and Yuzhakov (1969) noted that the aluminium phosphate fraction may also contain some magnesium phosphate; they also pointed out that the soil may contain mixed phosphates of the $CaAlH(PO_4)_2.6H_2O$ type, (Lehr, et al. 1959), which cannot be characterised simply as aluminium or as calcium phosphate compounds.

Some authors prefer to discuss results of fractionation studies in terms of the extracting solutions used, i.e. NH_4F- soluble phosphate, NaOH- soluble phosphate or acid-soluble phosphate, rather than by the names of discrete compounds (aluminium phosphate, iron phosphate and calcium phosphate) in the manner of Chang and Jackson. In the present review, the terms aluminium phosphate, iron phosphate and calcium phosphate will be used with the proviso that they may not be discrete fractions. Comparisons of results published by different authors may not be strictly valid and should be made with certain reservations, as it appears, inter alia, corrections for resorption of released phosphate during the determination of aluminium phosphate have not always been made; in such a circumstance it is obvious that the aluminium phosphate will be underestimated.

(2) <u>The Effects of Degree of Weathering, Time, Soil Type and pH on the Forms of Phosphate in Soils</u>: Chang and Jackson (1958) suggested that the distribution of inorganic phosphates in soils reflected the degree of chemical weathering and followed the sequence calcium phosphate, aluminium phosphate, iron phosphate and occluded phosphate. In proposing this theory they consider that aluminium phosphates in soils are predominantly in the form of discrete crystalline phases and transformation of the various phosphate species is determined by the solubility products of these species. This theory has been criticised by Hsu (1964) and by Williams and Walker (1969) who extended the view of Bauwin and Tyner (1957) and proposed an alternative theory. They suggested that iron and aluminium phosphates in soils consist of phosphate ions which are either chemisorbed on the surfaces or occluded within the matrices of phosphate-retaining soil components such as gibbsite, goethite and amorphous alumino-silicates. Whereas Chang and Jackson (1958)

implied that the relative amounts of aluminium and iron phosphate should be influenced by soil maturity and not by soil composition, Williams and Walker (1969) predicted that secondary inorganic phosphates would be distributed between the various soil mineral phases in amounts directly related to the phosphate-retaining capacity of each phase.

There is evidence that the forms of inorganic phosphate in soils alter with increasing age of the soils. Thus as soils age, calcium phosphate has been shown to decrease in El Salvador soils developed from volcanic material (Dahnke, et al. 1964), New Zealand basaltic soils (Williams and Walker, 1969), New Zealand soils developed from greywacke alluvium (Syers, et al. 1969), New Zealand soils developed from wind blown sand (Syers and Walker, 1969b), Canadian soils developed from river alluvium (John and Gardner, 1971), and in chernozen soils of South Dakota as compared with younger chestnut soils (Westin and Buntley, 1966). This decline in calcium phosphate with increased age is usually accompanied by an increase in the iron phosphate (Westin and Buntley, 1966; Syers, et al. 1969), and reductant soluble phosphate (Syers, et al. 1969). The accumulation of non- occluded secondary inorganic phosphate appears to be characteristic of weakly weathered soils (Syers, et al. 1969; Syers and Walker, 1969; Williams and Walker, 1969), while in highly weathered soils iron phosphate, particularly occluded iron phosphate, is dominant (Chang and Jackson, 1958).

Trends in the amounts of aluminium phosphate in soils of differing ages are variable. Dahnke, et al. (1964), found that aluminium phosphate decreased with age in El Salvador volcanic soils, but Syers and Walker (1969) noted that in the course of

10,000 years of soil development in a chronosequence of soils developed from wind-blown sand, aluminium phosphate showed a slight increase. John and Gardner (1971) also noted an increase of aluminium phosphate with increasing soil age in a chronosequence of Canadian soils developed from river alluvium. Westin and Buntley (1966) found no significant differences between aluminium phosphate in chernozem and chestnut soils, but Williams and Walker (1969) noted that as the age of the basaltic soils studied by them increased, aluminium phosphate increased to a maximum and then declined. The apparently different trends of aluminium phosphate observed above may, at least in part, be attributed to differences in the age and degree of weathering of the soil sequences.

Of the phosphate fractions studied by Williams and Walker (1969), only calcium phosphate showed a trend free from marked irregularities with increasing maturity, and it was suggested that the values of secondary phosphate fractions were dependent on factors other than the degree of maturity.

Some general conclusions have been made with respect to phosphate fractions and soil type. Iron phosphate is the dominant unoccluded form in Terra Rossa soils (Ahmad and Jones, 1967), volcanic soils (Appelt and Schalscha, 1970; Fassbender, 1968), latosols (Sing, et al. 1966, Fassebender, 1968), alluvial soils in Costa Rica (Fassebender, 1968), tropical soils (Blasco and Bohorquez, 1968), chestnut soils (Westin and Buntley, 1966), and podzolic soils (Chang and Jackson, 1958; Halstead, 1967). Manning and Salomon (1965), however, found aluminium phosphate to be the dominant form in a brown podzolic soil from Rhode Island. Aluminium phosphate is the dominant form in grumusols

(Ahmad and Jones, 1970), but calcium phosphate dominates dark grey gleysolic soils and brown forest soils (Halstead, 1967), chernozem soils (Chang and Jackson, 1958; Westin and Buntley, 1966; Halstead, 1967), and a gleyed luvisol (Massey, et al. 1970).

After completing a fractionation study of six calcareous soils from the south-east of England, Sen Gupta and Cornfield (1962) noted that from values given in the literature, aluminium phosphate, iron phosphate and non-apatitic calcium phosphate accounted for a smaller proportion of total soil phosphate in calcareous soils than in non-calcareous soils, but that the inert phosphate (total phosphate - (NH_4Cl soluble phosphate + aluminium phosphate + iron phosphate + organic phosphate)) and apatitic fractions accounted for a greater proportion of the phosphate in calcareous than in non-calcareous soils. This difference, however, may be due to CaF_2 formation in calcareous soils during extraction with NH_4F, leading to the underestimation of the aluminium plus iron phosphate fractions, and the over-estimation of the subsequent phosphate fractions.

Organic phosphate, as a percentage of total phosphate, generally decreases with particle size, whereas total phosphate tends to be maximal in the clay separates of soils (Williams and Saunders, 1956; Hanley, et al. 1965; Syers, et al. 1969). Syers, et al. (1969), found calcium phosphate levels were greatest in silt and sand separates of two New Zealand alluvial soils and this agrees with the findings of Williams and Saunders (1956) that apatite as a percentage of total phosphate decreased with decreasing particle size. Syers, et al. (1969), also found a pronounced increase in both aluminium and unoccluded iron phosphate with a decrease in particle size in one soil, but in the other soil the coarse sand contained greater amounts of these two fractions. In both profiles silt and clay contributed significantly to the aluminium phosphate and the unoccluded iron phosphate. Occluded iron phosphate and residual inorganic phosphate fractions were highest in the clay fractions of both soils.

The association between pH and the dominant forms of phosphate in soils is well documented in the literature. Morillo and Fassebender (1968) found a significant correlation (+ 0.769) between calcium phosphate and pH in ten soil series in the lower basin of Choluteca, Honduras. Calcium phosphate dominated a range of Indian soils of pH 7.1 to 8.2 (Tripathi, et al. 1970) and also two other Indian soils of pH 8.3 and 8.6 (Khanna and Mahajan, 1968). Khanna and Datta (1968) found that calcium phosphate dominated soils of pH>7 while aluminium and iron phosphate dominated soils of pH<7. A similar conclusion was reached by Du Plessis and Burger (1966). However, Al-Abbas, et al. 1966, found that iron phosphate dominated in soils up to pH 6.7 and calcium phosphate above 6.7. However, these conclusions must be considered with some reserve, as soils with high pH are likely to contain $CaCO_3$, the presence of which will affect the relative amounts of each phosphate fraction determined.

Hsu and Jackson (1960) and Mackenzie (1962) found curvilinear relationships between pH and aluminium phosphate, iron phosphate and calcium phosphate, when these individual fractions were expressed as a percentage of their sum. Later, Williams, et al. (1971), in reference to these studies noted that an increase in soil pH was associated with an increase in $CaCO_3$ content, and they suggested that this would lead to an increasing underestimation of aluminium phosphate and even more markedly to an underestimation of iron phosphate because of readsorption of phosphate by CaF_2 during extraction with NH_4F and NaOH. This implies that aluminium, iron and calcium phosphate fractions do not vary as much between samples of differing $CaCO_3$ content as was previously estimated. In contrast to the evidence presented above, Kaila (1964a) found calcium phosphate to be dominant in several acid soils (pH 4.6 to 6.3) of Finland and she ascribed this to a low degree of weathering. The increase in calcium phosphate with depth found by Kaila (1963b) in an earlier study would seem to corroborate this assumption,

Pratt (1961) showed that when soils containing relatively large amounts of calcium phosphate were acidified to pH 3.5, the calcium phosphate fraction decreased and this was largely balanced by an increase in aluminium phosphate. It was suggested that lowering the pH increased the exchangeable aluminium in solution and with dissolution of calcium phosphate at lower pH values, this led to the precipitation of aluminium phosphate. Hsu and Jackson (1960) showed that aluminium, iron and calcium phosphates, represented by variscite, strengite and hydroxyapatite, had approximately equal solubilities between pH 6 and 7, depending on the magnitude of cation activities from various solid phases such as gibbsite, aluminosilicates, hydrous iron oxides, $CaCO_3$, exchangeable calcium and possibly from soluble salts. Above this pH range the calcium phosphates were more stable than aluminium or iron phosphates, particularly in the presence of $CaCO_3$, while below this range the aluminium and iron phosphates were more stable than calcium phosphates.

It was concluded by Chai and Caldwell (1959) that the pH of a soil need not be a good indication of the forms of phosphate present, for although the pH values of two sandy soils and a silt loam soil they studied were similar, the distribution of inorganic phosphate in the phosphate fractions was different.

(3) Limitations of Phosphate Fractionation Procedures as an Aid to the Study of the Fate of Phosphate Added to Soil:

Many studies have been made on the identification of individual reaction products formed when soluble phosphates are added to soil. A discussion of the identification of individual compounds is outwith the scope of this review. Nevertheless, it is worth drawing attention to reviews by Huffman, (1962, 1968), Huffman and Taylor (1963), and Mattingly and Talibudeen (1967) as these authors deal with the identification of the phosphate compounds included in the phosphate fractions discussed in more detail below.

Although chemical phosphate fractionation procedures have been widely used to determine the fate of soluble phosphate applied to the soil, they are not without criticism. Laverty and McLean (1961) state that the procedures fail to distinguish differences in solubilities between freshly formed phosphates and more aged crystalline compounds, but, nevertheless, these authors acknowledge that there is no valid reason why the methods should not be used empirically until better means are devised.

The possibility of changes in the forms of soil phosphate during fractionation procedures, which may be important when phosphate has been applied recently to a soil under investigation, has been raised by Kaila (1963a), although no indication has been given as to the extent of these changes. It is also unknown to what extent the addition of a fairly high amount of phosphate will change the solubility of the native soil phosphate. Thus the difference between the phosphate content of a certain phosphate fraction in the fertilized and unfertilized soils may not give a reliable estimate of the content of fertilizer phosphate in this fraction (Kaila, 1963a). In soils which have been recently fertilized, it is likely that the aluminium phosphate may be overestimated due to the extraction of dicalcium phosphate by the ammonium fluoride solution (Laverty and McLean, 1961; Kaila, 1961a; 1963a). Lindsay and Stephenson (1959) found that dicalcium phosphate dihydrate may persist in soils for a period of several months. This, however, would be more likely in calcareous than acid soils.

The amounts of added phosphate recovered by fractionation procedures vary. Yuan, et al. (1960) studying three acid sandy soils recovered on average 80% of the added phosphate but the range of percentage recovery was 20 to 180. Bapat and Bedekar (1965) recovered 21 to 84% of added phosphate while other workers (Laverty and McLean, 1961; Volk and McLean, 1963) recovered more phosphate than was added.

It is generally agreed that when soluble phosphates are applied to acid soils the reaction products are recovered predominantly in the aluminium and iron phosphate fractions, with normally little or no increase in the calcium phosphate fraction (Chang and Jackson, 1958; Yuan, et al. 1960; Laverty and McLean, 1961; Chang and Chu, 1961; Weir and Sopher, 1963;

Volk and McLean, 1963; Kaila, 1964b; 1965a; 1969; Hsu, 1964; Kurtz and Quirk, 1965; Fassbender, 1968; Shelton and Coleman, 1968; Bezuglaya, 1969; Massey, et al. 1970). In spite of this wealth of evidence, exceptions have been found in an acidic lowland rice soil high in total and active Fe_2O_3 where the reductant soluble phosphate showed a significant increase (Mandal and Das, 1970); in two latosols after one hundred days flooding where it was thought that phosphate was occluded by iron oxide during drying after flooding (Chang and Chu, 1961); and in West Bengal soils where an appreciable increase in occluded iron and aluminium phosphate was noted (Kar and Chakravarti, 1969). In the case of soils high in $CaCO_3$, the bulk of added phosphate has been recovered from the calcium phosphate fraction (Sen Gupta and Cornfield, 1963; Mackenzie and Amer, 1964; Bapat and Bedekar, 1965; Chai and Caldwell, 1959). However, when determining the fate of applied fertilizer phosphate, due regard must be given to the type of phosphate fertilizer used. For example, addition of rock phosphate may significantly increase the calcium phosphate fraction (Kaila, 1961a; 1969; Manning and Salomon, 1965; Smith, 1968), but this could be due largely to residual apatite present in the fertilizer.

(4) Factors Affecting the Binding of Inorganic Phosphate by Soils: The appearance of added phosphate in either the aluminium or iron phosphate fractions depends to some extent on the time interval between application and sampling. Chang and Jackson (1958) and Chang and Chu (1961) found that on addition of phosphate to soil, the aluminium phosphate at

first increased more than iron phosphate, but later the calcium phosphate and aluminium phosphate levels gradually decreased while iron phosphate, being the least soluble, (Chang and Jackson, 1957b) increased. Other workers have also noted a change from aluminium phosphate to iron phosphate with time (Hsu, 1964; Smith, 1965b, 1967; 1969a; Kaila, 1967), and Mathan and Durairaj (1967) found an increase in occluded phosphate with time. Shelton and Coleman (1968) detected an increase in reductant soluble phosphate three to five years after the initial application of phosphate to a red clay soil; the soils which received the highest amounts of fertilizer phosphate showed this increase earlier than those which received smaller amounts of fertilizer. Humphreys and Pritchett (1971) found that seven to eleven years after application of superphosphate to sandy forest soils, two of the soils showed an increase in the phosphate fraction remaining after extraction of the easily-soluble phosphate, aluminium phosphate, iron phosphate and calcium phosphate fractions. Appelt and Schalscha (1970) noted a relative decrease of aluminium phosphate and a relative increase of iron phosphate with time in a range of volcanic soils of Chile, but they concluded that the pattern was peculiar to each soil.

Water logging has been shown to accelerate the conversion of aluminium phosphate to iron phosphate (Chang and Chu, 1961; Mahapatra and Patrick, 1969), and to increase the calcium phosphate fraction in a clay-loam soil (Smith, 1969a). The latter found that although the extent of the increase in iron phosphate was dependent on the amount of phosphate added to the soil, the extent of the increase in calcium phosphate depended on the length of time of water logging, but was independent of the rate of application of fertilizer phosphate.

The relative proportions of the forms to which applied phosphate is converted appears to be influenced by the amount of phosphate added. Fiskell and Spencer (1964) found that when 896kg per hectare of triple superphosphate was added over a period of six years to Lakeland fine sand (in which native phosphate was largely iron phosphate) most of the added phosphate accumulated as aluminium phosphate along with lesser amounts of iron and calcium phosphates; but when 14,336kg per hectare were applied, although the predominant increase still occurred in the aluminium phosphate fraction, there was also an increase in the proportion of iron and calcium phosphates. Kaila (1965a) found an increase in the proportion of aluminium to iron phosphate when the rate of application of soluble phosphate was increased. This was apparent even in samples in which the pattern of phosphate retention was dominated by iron. Similar findings have been reported by Yuan, et al. 1960, and by Shelton and Coleman (1968). Smith (1965c) showed that this effect may be due, at least, in part, to the decreasing ability of ferric oxides to sorb phosphate due to their partial saturation with fertilizer phosphate.

Another aspect which may affect the form in which added phosphate is retained is the fixation capacity of the soil. Laverty and McLean (1961) found a definite relationship between the fixation capacity of soils and the amounts of iron and aluminium phosphate formed. Soils with high fixation capacity retained almost twice as much phosphate in the form of iron phosphate as in the form of aluminium phosphate. This situation was more than reversed in soils with low fixation capacity while soils between these extremes retained progressively more phosphate in the form of aluminium phosphate relative to iron phosphate, as the fixation capacity of the soil decreased. Similar results have been reported by Volk and McLean (1963) and by Kaila (1963a; 1965a).

Singh, et al. (1966) found that in a reddish brown lateritic soil with a high iron content, most of the phosphate applied over a sixteen year period occurred as iron phosphate. Other workers (Robertson, et al. 1966; Mandal and Das, 1970) have noted significant increases in the occluded phosphate fraction of soil high in iron after addition of phosphate over a period of years. Perhaps the explanation for these observations lies with the suggestion of Kaila (1964a) that the ratio of aluminium to iron contents is more important than the absolute amounts in determining the distribution of phosphate between the aluminium- and iron-bound fractions.

The literature contains contradictory reports on the effect of pH on the forms in which applied phosphate is retained in soils. Chang and Jackson (1958) found that liming soils to pH levels of 4.7 to 6.7 had little effect on the relative abundance of different forms of phosphate in unfertilized soil, but when phosphate fertilizer was applied, the calcium phosphate fraction tended to increase more in the limed than in the unlimed soils. On the other hand, Chang and Chu (1961) found that lime applied together with fertilizer phosphate over a period of thirty-one years did not significantly alter the distribution of added phosphate in the soils. Fiskell and Spencer (1964) showed that as the amounts of phosphate and lime added to Lakeland fine sand increased, the relative amounts of calcium phosphate formed increased with a corresponding decrease in the proportions of iron and aluminium phosphate formed. Hortenstine (1966) noted that liming had different effects on three soils. In one soil, water-soluble phosphate and calcium phosphate fractions increased linearly with each increment of lime while the iron phosphate decreased. There was no significant effect on the aluminium phosphate. In another soil, water-soluble phosphate decreased and calcium phosphate increased with liming, while in the third soil, which had a high fixation capacity, the aluminium and iron phosphate fractions remained unchanged while the calcium phosphate fraction increased. Addition of phosphate to the first two of these soils after liming produced a decrease in the calcium phosphate fraction and an increase in aluminium phosphate and to a lesser extent in iron phosphate, while in the third soil all three fractions increased.

After studies on Finnish soils, Kaila (1961b; 1965b) reached the conclusion that the effect of liming was to increase the aluminium phosphate and calcium phosphate fractions at the expense of the iron phosphate fraction. However, in a later study Kaila (1967) found that although incubation for four months with $CaCO_3$ increased the aluminium phosphate, calcium phosphate and easily-soluble phosphate fractions in both fertilized and unfertilized soils and decreased the iron phosphate fraction, incubation for eight months tended to increase iron phosphate at the expense of aluminium phosphate. The small amounts of fertilizer phosphate recovered in the acid soluble form did not depend on the rate of liming even at pH 7. Laverty and McLean (1961) investigating a range of soils of silt-loam texture found a tendency for iron phosphate to decrease and calcium phosphate to increase with liming.

Mahapatra (1969) added lime to an air dry soil and also to soil kept water logged and anaerobic during incubation at 35°C for sixty days. In the former situation aluminium phosphate and iron phosphate decreased while calcium phosphate increased slightly, whereas in the latter situation the reverse was the case.

(5) Phosphate Fractions Extracted by Olsen's and Truog's Methods:

Several workers have demonstrated correlations between the phosphate fractions in soils and the phosphate extracted by Truog's reagent (0.002N H_2SO_4 buffered to pH 3 with $(NH_4)_2SO_4$) and by Olsen's*reagent (0.5M $NaHCO_3$ at pH 8.5). Positive significant correlations have been shown to occur between the amounts of phosphate extracted by Truog's reagent and (i) NH_4Cl-soluble phosphate and calcium phosphate (Srivastava and Pathak (1969) and (ii) aluminium and calcium phosphates (Susuki, et al. 1963; Grigg, 1965a; 1965b; Sherrell, 1970). Similarly, significant correlations have been shown to exist between the amounts of phosphate extracted by Olsen's reagent and (i) NH_4Cl-soluble phosphate (Patel and Mehta, 1961; Pratt and Garber, 1964); (ii) NH_4Cl-soluble phosphate and iron phosphate (Khanna, 1967), (iii) aluminium phosphate (Chai and Caldwell, 1959; Grigg, 1965; Susuki, et al. 1963; Sherrell, 1970),

*The reagent of Olsen, et al. (1954), designated in this review as Olsen's reagent.

and (iv) NH_4Cl-soluble phosphate, aluminium phosphate and iron phosphate (Datta and Kehra, 1969; Srivastava and Pathak, 1969).

According to Bray and Kurtz (1945), Olsen's reagent solubilizes aluminium and iron phosphates, and similar conclusions were drawn by Pratt and Garber (1964). However, Grigg (1966), Susuki, et al. (1963), and Datta and Kehra (1969) agree that Olsen's reagent solubilizes mainly aluminium phosphate.

Pratt and Garber (1964) found that with increasing clay content of soils, the efficiency with which Olsen's reagent extracts NH_4Cl-soluble phosphate, aluminium phosphate, and iron phosphate appears to decrease. Srivastava and Pathak (1969) found a negative correlation between Olsen's soluble phosphate and the clay content, and also between Truog's soluble phosphate and the clay content of twenty-three Indian soils. Pratt and Garber (1964) suggested that two factors were involved; first that the ineffectiveness of the Olsen's reagent in removing phosphate from clayey soils as compared with sandy soils was a result of reaction of the reagent with minerals other than phosphates, and secondly that there was dissolution of one phosphate fraction with subsequent reprecipitation in another fraction. It is interesting to note the work of McConaghy and Stewart (1963) who found that water-soluble phosphate classified nine Irish soils in much the same order as did Olsen extractable phosphate.

Chang and Juo (1963), and Srivastava and Pathak (1969) found that Truog's reagent dissolved predominantly calcium phosphate, but Chang and Juo (1963) noted that it also dissolved small amounts of aluminium and iron phosphates. Susuki, et al. (1963), considered that Truog's reagent removed portions of both aluminium and calcium phosphate.

It appears that the phosphate fractions removed by Truog's and Olsen's reagents depend to a large extent on the soil. For example, Grigg (1965) found significant correlations between phosphate extracted by Truog's reagent and calcium phosphate for all the soils he studied, but found significant correlations with aluminium phosphate only for gley soils derived from greywacke alluvium. In a later study on the Lismore stony silt loam, Grigg (1966) found that partial correlation on calcium phosphate was negligible for the Truog's reagent, and this contrasts with his earlier findings. Chang and Juo (1963) divided soils from Taiwan into (i) soils dominant in iron phosphate, (ii) soils dominant in iron and calcium phosphate, and (iii) soils dominant in calcium phosphate. They found that Olsen's phosphate was correlated with aluminium phosphate in soils dominant in calcium phosphate, whereas in soils dominant in iron phosphate the highest correlation was between Olsen's reagent and aluminium phosphate but significant correlations were also found between Olsen extractable phosphate and calcium and iron phosphate. Similarly, Truog's phosphate correlated significantly with calcium and iron phosphates at the 1% level and with aluminium phosphates at the 5% level in soils dominant in iron phosphate, but in soils dominant in calcium phosphates, Truog's phosphate correlated only with calcium phosphate, and then only at the 5% level. Weir and Soper (1963) found that in four soils ranging in $CaCO_3$ content from 0.7 to 42%, only a very small fraction of the total acid extracted phosphate was exchangeable. However, an increased percentage of the aluminium phosphate and an even larger fraction of the iron phosphate exchanged with ^{32}P. Thus, they concluded that the iron phosphate constituted a labile fraction of soil phosphate. Tripathi, et al. (1970), also found that calcium phosphate, although constituting 41% of total phosphate, made insignificant contributions to labile phosphate as estimated by Olsen's method and by isotopic exchange. Most of the variation in Olsen's phosphate was accounted for by aluminium phosphate whereas iron phosphate accounted for most of the variations in isotopically exchangeable phosphate.

(6) Changes in the "Availability" of Soluble Phosphate Applied to Soil:

It has been recognized for many years that when soluble phosphates are brought into contact with soil, they generally decrease in solubility with increasing time of contact. This has been demonstrated using extractants such as water (Smith and Simpson, 1950), dilute sulphuric acid (Scarseth and Tedmore, 1934; Hibbard, 1935; Moser 1941), calcium lactate, magnesium bicarbonate, acetic acid, potassium bisulphate, citric acid and sodium hydroxide (Williams and Stewart, 1943). The initial increase in "available" phosphate after phosphate addition and the subsequent decrease in "available" phosphate are both dependent on the rate of application (Sell and Olsen, 1946; Mattingly, 1963).

Lynch and Davies (1964) found that four years after cessation of phosphate top-dressing, pasture production on a New Zealand yellow-grey earth fell to about two-thirds the original level and then decreased further until a fairly stable low-production level was reached seven years after the last application of fertilizer. Larsen, et al. (1965), studying a range of twenty-four British soils for four years after the application of phosphate, found that when the difference in L value between the treated and control plots (ΔL) was plotted against the time that had elapsed since application, ΔL showed an exponential decrease with time, Determination of a half-life parameter from the slope of the plot of ΔL against time gave half-life values which varied widely between soils. The half-life values ranged from one to six years in eighteen soils, while for another soil a value of over fifty years was gained. A peak in the distribution occurred at approximately two and one half years.

Kurtz and Quirk (1965), studying samples of field plots with different fertilizer treatments from three groups of soils (red-brown earths, lateritic podzols and brunizemic) found that the values for total phosphate were misleading in estimating the phosphate status of fertility plots. Relatively little change was sometimes found in total phosphate although the more soluble phosphate fractions had been increased appreciably. Williams (1950) working with red-brown earths found that although 170 ppm phosphate had been added to plots, the increase in total phosphate was about 42 ppm. Similar findings have been reported by Ensminger and Cope (1947) and by Ozanne, et al. (1961). Moschler, et al. (1957), found that after application of 76 kg P_2O_5 per hectare each year for forty years, about three-quarters was still present in the 0 to 15 cm layer.

Ceceoni (1960) showed that the initial products of phosphate applied to soil often have short range order and possess a high ability to exchange phosphate, but this ability decreases with increasing range of order during ageing. Juo and Ellis (1968) showed that, under the same environmental conditions, iron phosphate crystallises at a much faster rate than aluminium phosphate and colloidal iron and aluminium phosphates are more "available" to plants than the corresponding crystalline forms. However, pH is an important factor with respect to the availability of various phosphate compounds. Whereas Juo and Ellis (1968) reported that colloidal aluminium phosphate was considerably more "available" than variscite in a sand culture, Taylor, et al. (1963) reported colloidal aluminium phosphate and variscite to be equally "available" in a calcareous soil at pH 8.5.

Although the "availability" of phosphate in soils is complex, it is evident that the "availability" of phosphate applied to soil decreases with increasing time of contact, and to maintain a high level of phosphate"availability", continued application is required on most soils.

* * * * * * *

CHAPTER TWO

(A) MATERIALS

Two contrasting sand country soils, Pukepuke brown sandy loam and Foxton black sand, were chosen for this study. Both soils lie in the Pukepuke-Omanuka association which covers approximately 5,470 hectares (Cowie et al. 1967). This association is part of the Foxton dune phase and the soils are believed to be between 2,000 and 4,000 years old (Cowie, 1963).

The Pukepuke brown sandy loam is formed on low-lying sand plains where the drainage is poor, the water table being at or near the surface for much of the winter and spring. Although the water table may fall considerably during summer droughtiness is uncommon. Figure 2.1 indicates the extent of the sand plain from which the soil samples were collected, while Figure 2.2 shows the profile, which is fully described in Appendix 2.

In contrast, the Foxton black sand is formed on the dune where drainage is somewhat excessive. Consequently, it is prone to droughtiness in the summer. Provided that the surface cover and topsoil are preserved, the dunes are relatively stable, but once the cover of the dune is broken, "blow-outs" may occur with an accelerated sand loss. Two small "blow-outs" are shown in Figure 2.3 and situations such as this are fairly common in the district. The profile is shown in Figure 2.4 and is described in Appendix 2.

Figure 2.5 shows the association of sand dune and sand plain, and Figure 2.6 illustrates the way in which water lies at the lower end of the sand plain during winter. The sites on which the experimental plots were established were:-

FIGURE 2.1

Sand Plain On Which The Pukepuke Brown Sandy Loam Experimental Site Was Situated

FIGURE 2.2

Pukepuke Brown Sandy Loam Profile

FIGURE 2.3

Foxton Black Sand Experimental Site Showing Two Small "Blow-Outs" On The Dune

FIGURE 2.4

Foxton Black Sand Profile

FIGURE 2.5

Association Of Sand Dune And Sand Plain

FIGURE 2.6

Water Lying On The Lower Parts Of The Sand Plain

At The Foxton Black Site During Winter

(a) on a large sheep and cattle farm in the case of the Foxton black soil, and

(b) on an intensive dairy farm in the case of the Pukepuke brown sandy loam soil.

The particular area chosen on the Foxton black soil had received no fertilizer addition in the past, but the area chosen on the Pukepuke brown sandy loam soil had received 250 kg/ha of 30% potassic super annually for ten years, as well as considerable amounts of lime.

* * * * * * *

(B) METHODS

1. Experimental Design

(a) Estimate of Phosphate Variability: A phosphate variability test was carried out on the two soils as follows: a 50 m line was fixed diagonally across the proposed sampling area and at 5 m intervals, two single core samples, 30 cm apart, were collected. All samples were analysed for "0.5N H_2SO_4 soluble phosphate" and "1N NaOH soluble phosphate" to gain an index of two different soil phosphate fractions.

On the basis of this preliminary study, the number of plots and also the number of samples per plot required to allow a statistical analysis of the results were determined.

(b) Plot Design: Ten plots each 1.5 x 3 m were marked out on both soils a block design being used on the sand plain (Figure 2.7) while on the sand dune the plots were arranged in a line along the face of the dune to prevent the possibility of run-off water moving phosphate from one plot to another (Figure 2.8).

(c) Soil Sampling: A sampling depth of 0-5 cm was chosen as this was considered adequate to recover the bulk of the applied phosphate without excess dilution with unenriched soil. At each sampling (March 5, April 16, May 19, July 14, September 8, November 2, December 24, 1971 and February 23, 1972), two samples, each consisting of twelve 2.5 cm diameter

FIGURE 2.7

Plot Design On The Pukepuke Brown Sandy Loam Soil

FIGURE 2.8

Plot Design On The Foxton Black Sand

cores, were collected from each plot. The samples were air-dried in the laboratory, passed through a 2 mm sieve, and stored in air-tight jars.

(d) Addition of Phosphate: To ensure significant increases in the amounts of the several phosphate fractions over and above those already present in the soil, it was considered that a 50-60 percent increase in the total phosphate in the top 5 cm would be required from fertilizer additions. The addition of commercial superphosphate at the rate of $25g/m^2$ to the Foxton soil and $50g/m^2$ to the Pukepuke soil was calculated as the amount of fertilizer required. The fertilizer was applied on March 5, 1971, at these rates, to five plots chosen at random at each site, the remaining plots being used as controls. The extent of phosphate enrichment of the fertilized plots was taken as that amount appearing in the top 5 cm calculated by difference between total phosphate determined on the plot samples collected prior to addition of phosphate, (March 5), and on samples collected six weeks after the addition of phosphate (April 16), (Tables 2.1 and 2.2).

TABLE 2.1

Amounts Of Total Phosphate Determined Prior To And Six Weeks After The Addition Of $50g/m^2$ Of Superphosphate To Five Plots On The Pukepuke Soil

Plot/Sample Number	Total Phosphate Before Addition of Superphosphate mgP%	Total Phosphate After Addition of Superphosphate mgP%	Amount of Phosphate Added (By Difference) mgP%
1 A	169.9	263.9	94.0
B	172.6	278.7	106.2
4 A	173.9	247.8	74.0
B	161.2	246.6	85.3
6 A	160.6	272.6	112.1
B	163.9	267.3	103.4
9 A	164.6	276.6	112.1
B	183.9	204.6	100.7
10 A	163.9	269.3	105.4
B	163.9	262.6	98.7
Standard Error	2.3	6.9	3.8
Coefficient of Variation	4.3	8.5	12.1
Average Calculated Increase			99.2
Percentage Increase			54.3

TABLE 2.2

Amounts Of Total Phosphate Determined Prior To And Six Weeks After The Addition Of $25g/m^2$ Of Superphosphate To Five Plots On The Foxton Soil

Plot/Sample Number	Total Phosphate Before Addition of Superphosphate mgP%	Total Phosphate After Addition of Superphosphate mgP%	Amount of Phosphate Added (By Difference) mgP%
1 A	61.2	102.0	40.8
B	63.6	102.0	38.4
4 A	62.7	107.9	45.2
B	63.6	94.4	30.7
6 A	62.1	102.8	40.7
B	61.2	107.6	46.4
7 A	60.0	103.8	43.8
B	61.2	106.1	44.9
9 A	61.2	99.2	38.0
B	64.3	102.0	37.7
Standard Error	0.4	1.3	1.5
Coefficient of Variation	2.3	3.9	11.6
Average Calculated Increase			40.7
Percentage Increase			65.5

2. Analytical Procedures

(a) Determination of Phosphate: Phosphate in solution was determined by the method of Murphy and Riley (1962), as outlined by Watanabe and Olsen (1965). The method involves the formation and reduction of the phosphomolybdic acid complex using an acidic molybdate solution containing ascorbic acid; it was chosen because of its sensitivity and the stability of the blue colour. Colour development was measured on a Beckman model D.U. quartz spectrophotometer at 890 mμ.

Several authors, (Woods and Mellon, 1941; Kurtz, 1942; Jackson, 1958; John, 1970) have reported interference by various ions in the development of the molybdate blue colour in the colorimetric determinations of phosphate. In the present study experiments were conducted to assess the limits of tolerance of the method to NH_4^+, Cl^- and F^-. While no interference from Cl^- (added as HCl) was observed even at a concentration of 17,250 ppm, a pronounced effect was observed with NH_4^+ (added as NH_4Cl) at 2,880 ppm (Table 2.3), the interference being characterised by the formation of a fine precipitate and a fading of the blue colour. That the observed effect was due to NH_4^+ alone and not to a combination of NH_4^+ and Cl^- is evident from Table 2.3 which shows that an identical interference level applied when $(NH_4)_2SO_4$ was substituted for NH_4Cl. As a result of these preliminary tests, the molarity of extracting solutions containing NH_4^+ was reduced to the extent that even when large aliquots of such solutions were taken, no interference by NH_4^+ on colour development would be experienced.

TABLE 2.3

The Influence Of NH_4^+ On Colour Development In The Determination Of Phosphate In Solution By The Method Of Watanabe And Olsen (1965)

Concentration of NH_4^+ in final solution ppm	Optical Density (0.4 ppm phosphate in final solution) using 1N NH_4Cl as source of NH_4^+	Optical Density (0.4 ppm phosphate in final solution) using $(NH_4)_2SO_4$ as source of NH_4^+
72	0.295	0.295
360	0.295	0.295
720	0.295	0.295
1080	0.295	0.295
1440	0.295	0.295
1800	0.295	0.295
2166	0.295	0.295
2880	0.108	0.108

Fluoride present in excess of 90 ppm in the final solution caused a depression of colour intensity (Table 2.4). This interference was eliminated by the boric acid procedure of Kurtz (1942).

All extractions of phosphate which involved shaking were carried out on an end-over-end shaker at 38 rpm maintained at a temperature of approximately 22°C.

(b) Determination of Total Soil Phosphate: Williams (1965) and Syers et al. (1968) found that fusion with Na_2CO_3 by the method of Muir (1952) was the most reliable method for determining total phosphate in sandy and highly weathered soils in New Zealand. This procedure was adopted in this study with the modification that the Na_2CO_3 melt was taken up in 10N H_2SO_4 rather than in water as in the original method.

(c) Measurement of Available Phosphate: The methods of Truog (1930), (0.002N H_2SO_4 buffered to pH 3 with $(NH_4)_2SO_4$; soil:extractant ratio 1:200; 30 minute extraction), Olsen et al. (1954), (0.5M $NaHCO_3$, pH 8.5; soil:extractant ratio 1:20; 30 minute extraction) and Schofield (1955), (0.01M $CaCl_2$; soil:extractant ratio 1:20; 16 hour extraction) were used to determine estimates of the available phosphate. All extractions were carried out on 2 mm air-dry soil.

(d) Phosphate Fractionation Procedure: The soil samples used in this section of the work

TABLE 2.4

The Influence Of F^- On Colour Development For The Determination Of Phosphate In Solution By The Method Of Watanabe And Olsen (1965) With And Without The Addition Of Saturated Boric Acid (Kurtz, 1942)

Concentration of Fluoride in final solution ppm	Optical Density (0.4 ppm phosphate in final solution)	Optical Density (0.4 ppm phosphate in final solution) + 10 ml saturated Boric acid
20	0.295	0.295
40	0.295	0.295
60	0.295	0.295
80	0.295	0.295
90	0.295	0.295
100	0.281	0.295
200	0.018	0.295
400	n.c.	0.295
800	n.c.	0.295

n.c. - no colour development.

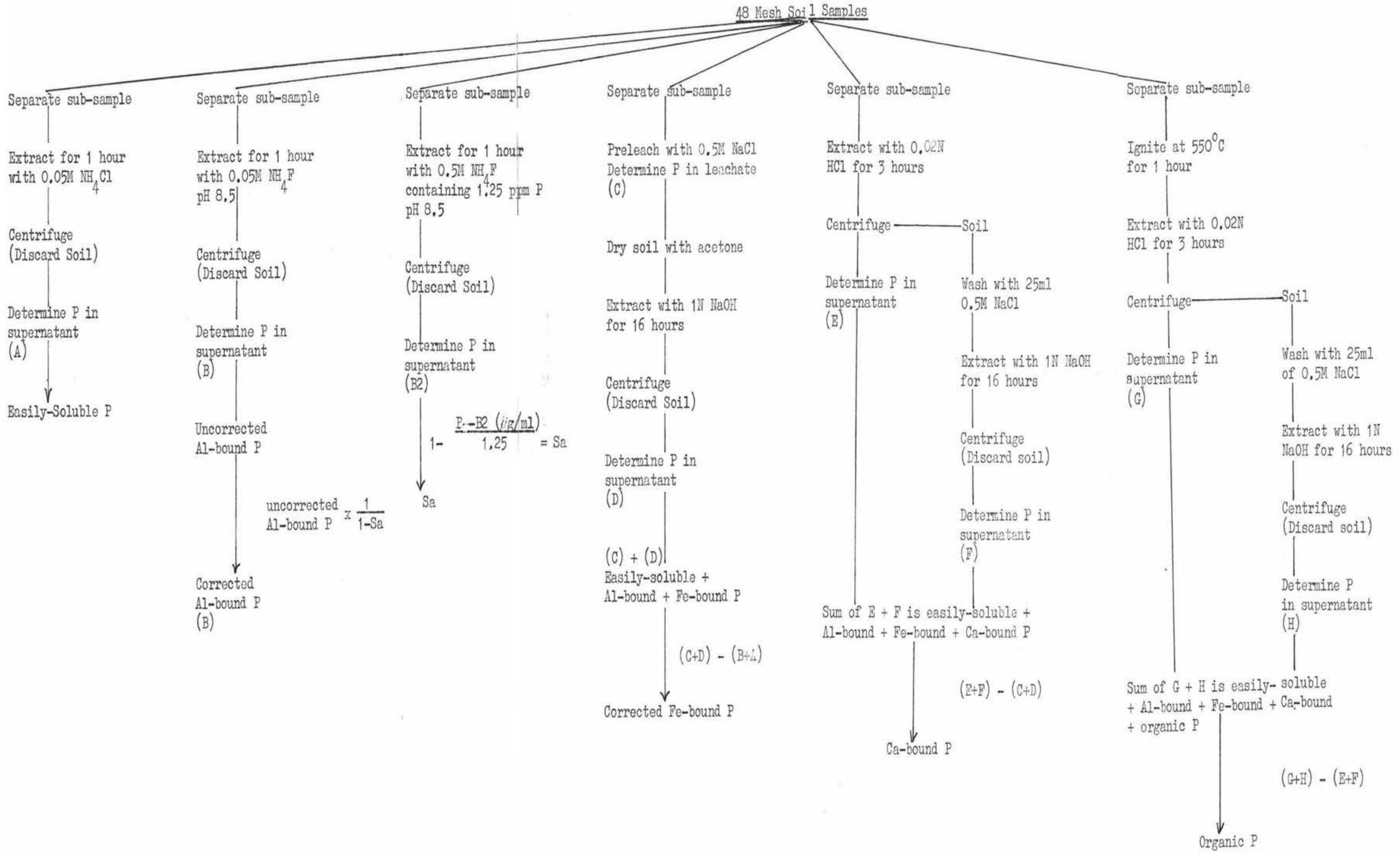
were ground to pass a 48 mesh sieve. The fractionation procedure used was that of Fife (pers. comm.) and it is detailed in Figure 2.9. It is recognized that there is some uncertainty concerning the selectivity of the methods employed in fractionation studies, and that the various categories of phosphate may generally be more correctly specified in terms of the extracting agents used than as specific forms of chemically-bound phosphate. This approach works well for fractionation schemes such as those of Chang and Jackson (1957a) and Williams (1965), where the fractions are removed systematically from one sub-sample. Thus, for example, in the procedure of Williams (1965) "the acid-soluble" fraction can be equated closely with calcium-bound phosphate, whereas in the procedure of Fife as used in the present study, the latter would have to be described as "acid-soluble" minus "alkali soluble" phosphate. Similarly, the "alkali-soluble" fraction in the procedure of Fife represents the sum of aluminium-bound plus iron-bound forms, whereas in the procedure of Williams (1965) it represents (in its corrected form) largely iron-bound phosphate. To save the possibility of confusion, it was decided to characterize the four main fractions delineated in the present study as aluminium-bound, iron-bound, calcium-bound and residual phosphate, with full recognition that sharp delineation of forms is probably not realized under the conditions of the extraction procedures employed.

(i) Determination of Easily-Soluble Phosphate

Chang and Jackson (1957a) extracted soils with 1N NH_4Cl to remove "water-soluble" and "loosely-bound phosphate". As this NH_4^+ ion concentration was too high for convenient use with the Watanabe and Olsen (1965) method

FIGURE 2.9

Fractionation Flow Sheet



when large aliquots were taken, a 0.05M NH_4Cl solution was substituted. The extraction period adopted was one hour. It was thought desirable to remove as much NH_4Cl soluble phosphate as possible from the soils of the treated plots, so that as high a proportion as possible of the phosphate removed in the subsequent extraction could be regarded as being released by the complexing activity of the fluoride ion. It was concluded, using the data presented in Table 2.5, that a 1:250 soil: solution ratio for the Foxton soil and a 1:300 soil: solution ratio for the Pukepuke soil would efficiently remove a large proportion of the NH_4Cl soluble phosphate and provide a sufficient concentration of phosphate for easy measurement.

(ii) Determination of Aluminium-Bound Phosphate

Fife (1962) used 0.5M NH_4F at pH 8.5 to determine aluminium-bound phosphate, and this method was adopted in the present study after preliminary experiments established the most suitable extraction period and soil: extractant ratios. Using the data shown in Table 2.6, it was decided to use a soil:extractant ratio of 1:250 for the Foxton soil and 1:500 for the Pukepuke soil. Although further widening of the soil:extractant ratio produced a more efficient extraction, the difficulty of measuring low phosphate concentrations made such a step undesirable. Even at the extreme soil:extractant ratios, resorption of liberated phosphate by iron oxide was considerable and to correct for this, the method outlined by Williams, Syers and Walker (1967) was adopted. This involved

TABLE 2.5

Amounts Of Phosphate Extracted By 0.05M NH_4Cl From The Foxton And Pukepuke Treated Soils Over A Range Of Soil:Extractant Ratios

(One Hour Extraction Period)

Soil:Extractant Ratio	Foxton Treated Soil mgP%	Pukepuke Treated Soil mgP%
1:50	6.6	5.3
1:100	8.7	9.3
1:150	9.5	12.6
1:200	10.1	15.4
1:250	10.1	17.2
1:300	10.1	18.6
1:350	n.d.	18.8
1:500	n.d.	19.0

n.d. - not determined.

TABLE 2.6

Amounts Of Phosphate Extracted By 0.5M NH_4F (pH 8.5) From The Foxton And Pukepuke Soils Over A Range Of Soil:Extractant Ratios (One Hour Extraction Period)

Soil:Extractant Ratio	Foxton Treated Soil mgP%	Pukepuke Treated Soil mgP%
1:50	31.9	26.1
1:100	33.6	35.2
1:200	36.8	43.6
1:300	36.9	48.0
1:400	36.6	52.4
1:500	37.0	55.0
1:800	38.9	57.6

shaking a second soil sample with 0.5M NH_4F (pH 8.5) containing 1.25 ppm P and determining, from the difference in phosphate levels in the fluoride extracts with and without added phosphate, the proportion of added phosphate that had been absorbed by the soil during extraction. The term "corrected aluminium-bound phosphate" is used to describe the aluminium-bound phosphate after correction for resorption. No attempt was made to correct for the relatively small zero order hydrolysis of iron-bound phosphate during fluoride extraction as was done by Fife (1962).

The short (one hour) extraction period used in this study, when compared with the recommended twenty-four extraction of Fife, appears reasonable after consideration of the work of Tandon (1969). Extracting three soils of differing clay content (4%, 12% and 46% clay) Tandon found that the soil which had the lowest clay content showed the highest initial rate of extraction, and equilibrium was reached earlier than with the other soils. Apparent equilibrium in the low clay soil was reached after twenty minutes, whereas in the high clay soil, no apparent equilibrium was reached even after one hundred and sixty minutes of extraction.

When the extracts were highly coloured, the acid-precipitable organic matter was removed by mixing equal volumes of the extract and a solution saturated with respect to H_3BO_3 and normal with respect to H_2SO_4. After shaking, the precipitate of organic matter was separated by centrifugation. This method provided not only the acidity needed to precipitate the organic matter, but also the H_3BO_3 required at a later stage to prevent fluoride interference in the development of the molybdate blue colour. When the colour of the extracts was low and removal of the organic matter was unnecessary, the H_2SO_4 addition was omitted and 10 ml of saturated H_3BO_3 were added to an aliquot of the fluoride extract prior to colour development.

(iii) Determination of Iron-Bound Phosphate

As a preliminary step to the extraction of NaOH-soluble phosphate, the soil samples were leached with 0.5M NaCl to remove exchangeable Ca^{++} and thus prevent precipitation of phosphate by Ca^{++} during the NaOH extraction.

It was found (Table 2.7) that a soil:extractant ratio of 1:250 over a four hour extraction period was sufficient to remove the NaOH-soluble phosphate fractions. In practice, a sixteen hour extraction period was adopted to fit in with laboratory schedules. The differences between the NaOH-soluble phosphate and the corrected aluminium-bound phosphate previously determined on a separate soil sample gave a value for iron-bound phosphate.

(iv) Determination of Calcium-Bound Phosphate

Unless, as in the fractionation procedure developed by Williams (1965), the reductant soluble phosphate is removed prior to the acid extraction, the concentration of the acid should be kept to the minimum value required for complete dissolution of apatite.

During extraction of soils with acid, some resorption of released calcium-bound phosphate by iron

TABLE 2.7

Amounts Of Phosphate Extracted By 1M NaOH From The Foxton And Pukepuke Soils Over A Range Of Soil:Extractant Ratios (16 Hour Extraction Period)

Soil:Extractant Ratios	Foxton Treated Soils mgP%	Pukepuke Treated Soils mgP%
1:50	31.4	97.5
1:100	34.5	101.3
1:200	35.8	106.1
1:250	36.0	106.6
1:300	35.7	106.6
1:400	36.0	106.4
1:500	36.0	106.7

and aluminium compounds occurs. According to Fife (pers. comm.), extraction with 1N NaOH following such acid extraction releases this resorbed phosphate into solution. Hence the difference between the sum of these two extractions and the NaOH extraction previously carried out on a separate soil sample should give a value for calcium-bound phosphate.

Preliminary experiments were carried out to determine the effect of extracting the soils used in this study with varying strengths of acid and also to determine the strength of acid required to give an equilibrium pH below 2.38 in the presence of the soil. Ballard (1968) found this to be the equilibrium pH value obtained in an HCl extract just sufficiently acid to dissolve apatite in the absence of soil. Table 2.8 shows that acid strength had very little effect on the HCl + NaOH-soluble phosphate extracted from the fertilised Foxton soil, whereas Table 2.9 shows that the comparable values for the fertilised Pukepuke soil depended on the strength of the acid used. Further extractions were carried out to determine if the same effect would occur with the Pukepuke untreated soil (Table 2.10) and it was found here also that the total phosphate extracted increased with increasing acid strength. Tables 2.9 and 2.10 show that of the acid strengths studied 0.02N HCl provided the nearest approach to a final equilibrium pH below 2.38 for the Pukepuke soil, and as acid strength had very little effect on the amount of phosphate extracted from the Foxton soil, it was decided to adopt

TABLE 2.8

Amounts Of Phosphate Extracted From The Fertilised Foxton Soil By Extraction With Varying Strengths Of HCl For 3 Hours (Soil:Acid Ratio 1:100) Followed By A 16 Hour Extraction With 1N NaOH (Soil:NaOH Ratio 1:250)

Normality of HCl	Initial pH	Final pH	P Extracted by HCl (a) mgP%	P Extracted by NaOH (b) mgP%	Total P Extracted (a) + (b) mgP%
1.0	0.41	0.50	47.8	5.0	52.8
0.5	0.59	0.88	46.6	6.3	52.9
0.1	1.20	1.35	45.3	7.5	52.8
0.08	1.38	1.42	43.9	8.2	52.1
0.06	1.49	1.52	43.9	9.3	53.2
0.04	1.58	1.68	42.7	10.1	52.8
0.02	1.81	2.02	41.6	11.3	52.9
0.01	2.10	2.23	40.7	12.0	52.7

TABLE 2.9

Amount Of Phosphate Extracted From The Fertilised Pukepuke Soil By Extraction With Varying Strengths Of HCl For 3 Hours (Soil:Acid Ratio 1:100) Followed By A 16 Hour Extraction With 1N NaOH (Soil:NaOH Ratio 1:250)

Normality of HCl	Initial pH	Final pH	P Extracted by HCl (a) mgP%	P Extracted by NaOH (b) mgP%	Total P Extracted (a) + (b) mgP%
1.0	0.41	0.68	149.7	23.9	173.6
0.5	0.59	0.75	130.4	33.6	164.0
0.1	1.20	1.42	72.6	85.5	158.1
0.08	1.38	1.49	57.1	100.8	157.9
0.06	1.49	1.58	44.9	113.0	157.9
0.04	1.58	1.81	25.0	131.3	156.3
0.02	1.81	2.08	12.2	139.4	151.6
0.01	2.10	2.50	9.8	140.2	150.0

TABLE 2.10

Amount Of Phosphate Extracted From The Pukepuke Untreated Soil By Extraction With Varying Strengths Of HCl For 3 Hours (Soil:Acid Ratio 1:100) Followed By A 16 Hour Extraction With 1N NaOH (Soil:NaOH Ratio 1:250)

Normality of Acid	Initial pH	Final pH	P Extracted by HCl (a) mgP%	P Extracted by NaOH (b) mgP%	Total P Extracted (a) + (b) mgP%
1.0	0.41	0.45	45.7	18.1	63.8
0.5	0.59	0.68	36.2	27.3	63.5
0.1	1.20	1.28	4.5	55.1	59.6
0.08	1.38	1.40	3.0	56.0	59.0
0.06	1.49	1.51	1.9	56.8	58.7
0.04	1.58	1.63	1.5	55.6	57.1
0.02	1.81	2.01	0.7	53.5	54.2
0.01	2.10	2.40	0.6	53.5	54.1

this strength of acid for the extraction of both soils. The effect of strength of acid on the amount of phosphate extracted from the Pukepuke soil is further discussed on page 81. On the basis of these preliminary experiments, a 1:100 soil:acid ratio and a three hour extraction period was adopted for the acid extraction stage of the acid-soluble plus alkali soluble phosphate determinations on the soils.

(v) Determination of Organic Phosphorus

Organic phosphorus may be determined by extraction or by ignition methods. Williams, et al. (1970) pointed out that in contrast to extraction procedures which have only negative errors, ignition procedures may have both positive and negative errors. Steward and Oades (1972) commented that no extraction method is consistently superior to any other in removing organic phosphorus from soils.

Two ignition methods, that of Fife (pers. comm., Figure 2.9 , and Williams and Saunders (1956) and one extraction method, Mehta, et al. (1954), were compared in this study (Table 2.11). All three methods gave similar results for the Foxton soil but the extraction method gave lower values for the Pukepuke soil than were obtained by the ignition methods. This may have been due to incomplete extraction and hydrolysis of organic phosphorus as the Pukepuke soil has a high organic matter content. On the basis of this preliminary work, the method of Fife was adopted as the most convenient for use in the present investigation, having due

TABLE 2.11

Amounts Of Organic Phosphorus Present In The Foxton And Pukepuke Soils As Determined By The Methods Of Fife (Pers. Comm.), Williams And Saunders (1955) And Mehta, et al. (1954)

Method	Foxton Soil mgP%	Pukepuke Soil mgP%
Fife (pers. comm.)	30.25	67.42
Williams and Saunders (1955)	30.62	68.75
Mehta, et al. (1954)	30.51	60.00

regard for the problems associated with ignition methods as discussed by Black and Goring (1953).

(vi) Total Phosphate Fractionated and Residual Phosphate

In subsequent discussions, the sum of phosphate extracted by HCl and NaOH on the ignited soil in the determination of organic phosphorus is referred to as the "total phosphate fractionated", and the difference between this value and the total phosphate value determined by Na_2CO_3 fusion is referred to as "residual phosphate".

(e) Measurement of Phosphate Sorption Capacity: The phosphate sorption capacities of the untreated soils were measured according to the method of Ozanne and Shaw (1967). This involved shaking the soil with 0.01M $CaCl_2$ solution containing varying amounts of added phosphate, for 17 hours, using a soil:extractant ratio of 1:20.

(f) Determination of 'Free' Iron Oxide: The 'free' iron oxide contents of the 2 mm soils were determined after two extractions using the dithionite-citrate method of Aguilera and Jackson (1953) as modified for inclusion of $NaHCO_3$ buffer by Mehta and Jackson (1960). After each dithionite-citrate-bicarbonate extraction, the soils were washed with 10 ml 0.05N HCl (Mitchell and Mackenzie, 1954), for three minutes at 40°C to remove any coatings of iron sulphide which may have formed.

The iron in solution was measured by the thioglycollate method (Sandell, 1944), the density of the solution being measured on a model DU Beckman quartz spectrophotometer at 535 mμ. It was shown that at 18°C the colour developed fully after eleven minutes and it was then stable for at least one hour. To standardise the procedure, the density was measured twenty minutes after addition of the thioglycollate reagent.

(g) Determination of 'Free' Alumina: Follett, et al. (1965) showed that treatment of the clay fractions of selected Scottish soils with cold and hot 5% Na_2CO_3 removed amorphous and poorly-ordered alumino-silicate materials while the well crystallized components were relatively unaffected. This method was modified slightly and used to remove 'free' (highly active) alumina from the Foxton and Pukepuke soils. Five successive two hour digestions of 250 mg of unperoxidised soil with 80 ml 5% Na_2CO_3 were carried out in a boiling water bath. The aluminium removed was determined by the aluminon method (Robertson, 1950), using thioglycollic acid to prevent interference by iron in the red lake. The percentage transmission was determined with a Hilger and Watts Spekker spectrophotometer using the green 604 filter.

(h) Determination of Exchangeable Calcium and Magnesium: Exchangeable Ca and Mg were removed by shaking 10 g of 2 mm air-dried soil with 150 ml of neutral 1N NH_4OAc and allowing to stand overnight. The soil was filtered and leached with NH_4OAc until no positive test for Ca was obtained in the effluent solution.

The amounts of Ca and Mg in solution were determined with a Techtron AA5 atomic absorption spectrophotometer, using $SrCl_2$ to prevent PO_4^{3-} interference in the Ca determination and Al interference in the Mg determination.

(i) Determination of Organic Matter Content: The organic matter contents of the soils were determined by the method of Mitchell (1932). The soils were heated in a muffle furnace at 350-400°C for 8 hours, the difference between the oven dry weight (105°C) and the weight after ignition being taken as the weight of organic matter.

3. Other Measurements

All results are expressed on an oven dry (105°C) basis.

The pH values were measured electrometrically at a soil:water ratio of 1:2.5 after overnight equilibration.

Bulk densities were calculated as:

$$\text{Bulk Density} = \frac{\text{oven dry weight}}{\text{field volume of sample}} \text{ g/cc}$$

on soils sampled to a depth of 5 cm.

Mechanical analyses were carried out according to the procedure outlined by Piper (1942).

The mineralogy of the clay fractions were investigated by x-ray diffraction techniques using a Philips 1011 generator with diffractometer recording. The clay fractions were saturated with various cations and heat treatment applied as necessary (Mitchell, 1966).

Rainfall measurements were recorded each morning at the Pukepuke site.

CHAPTER THREE

RESULTS

1. Introduction

In this section the results are presented in the form of tables and graphs. The graphs are derived from the tables in Appendix 3, the table number being shown under each graph.

A two-tailed test was used to test for statistical differences, calculations being made on a programmable Canola 164P electronic calculator. Coefficients of variation, standard errors, and means were also calculated using a programme: all these statistical data are included in the appropriate tables in Appendix 3.

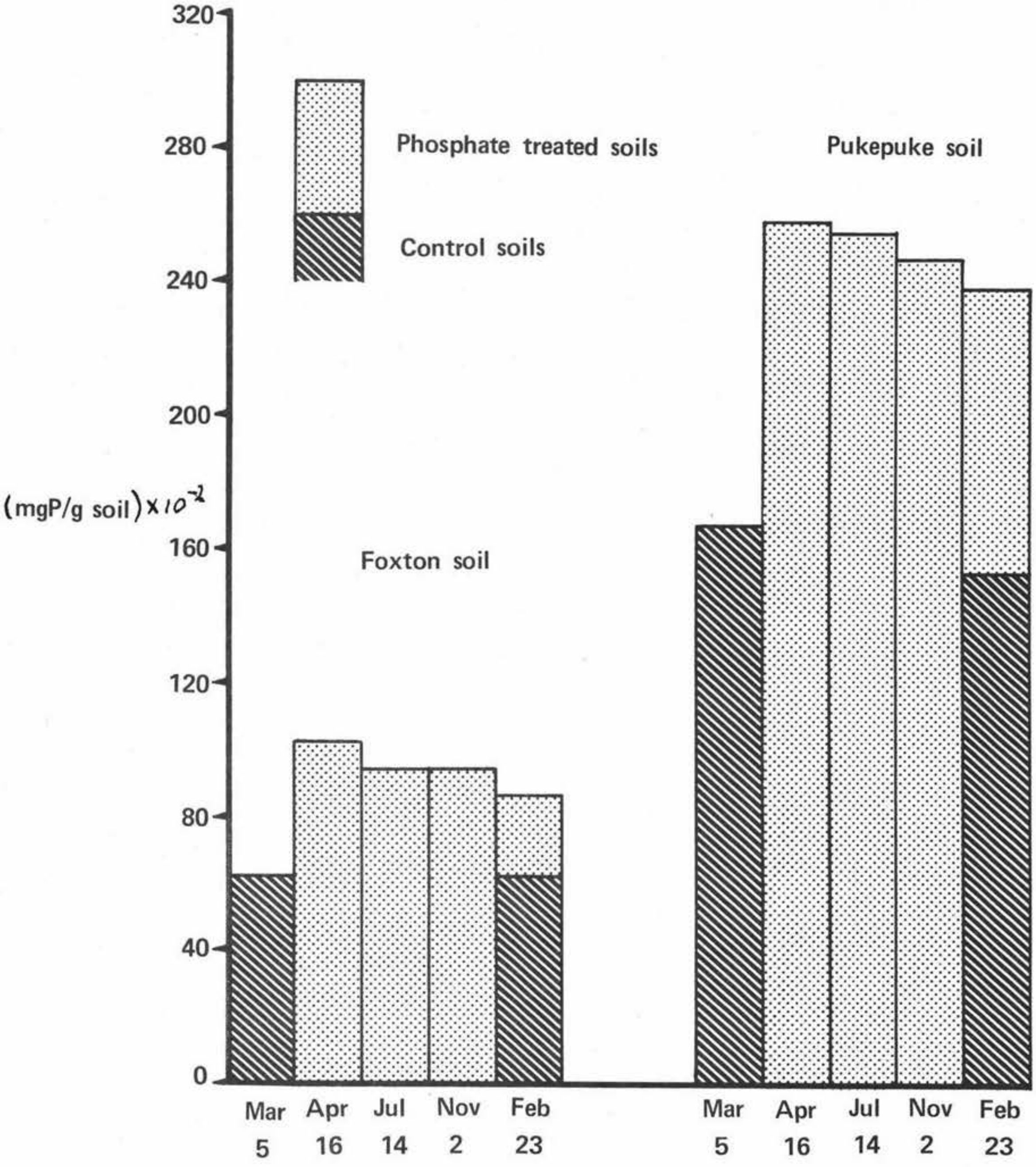
2. Total Phosphate

The means of total phosphate determinations, expressed on a weight basis, carried out at the commencement and conclusion of the experiment on control plots, and at intervals throughout the experiment on the phosphate treated plots are shown in Figure 3.1. It is evident that the total phosphate in the Foxton control plots underwent no significant change over the experimental period, whereas the Pukepuke control plots decreased by 8.45 mgP%.

Figure 3.1 shows that addition of 50 g/m^2 of superphosphate to the Pukepuke soil resulted in an increase in the total phosphate content of 91.2 mgP% six weeks after application, while addition of 25 g/m^2 to the Foxton soil resulted in an increase in total phosphate of 40.7 mgP% after the same time interval.

The total phosphate level in the treated Foxton soil underwent a significant decline at the .01 level (Table 2, Appendix 3) between the April 16 and July 14 samplings, and also between the November 2 and February 23 samplings, with an overall decrease between the April 16 and February 23 samplings of 15.2 mgP%. Although the overall decrease in total phosphate reported (Figure 3.1) for the Pukepuke treated plots between April 16 and February 23 of 20.7 mgP% is significant at the 0.01 level, there is no significant difference between successive samplings. When the amount of phosphate lost from the control plots of the Pukepuke soil is subtracted from that lost from the treated plots, the actual loss of phosphate over the experimental period is only 12.24 mgP%.

Figure 3.1: Total phosphate levels in the Foxton and Pukepuke control and phosphate treated plots determined throughout the experimental period.
(Appendix 3, Table 1).



Date of Sampling

3. Estimation of Phosphate Availability

The mean values of "available" soil phosphate determined at each sampling throughout the experiment, using the methods of Truog (1930), Olsen, et al. (1954) and Schofield (1955) are plotted in Figures 3.2, 3.3 and 3.4. It is clear that phosphate availability values for the treated plots on the Pukepuke and Foxton soils fell rapidly with time. Schofield's values moved towards the value of the untreated plots while the Truog and Olsen values appeared to be moving towards an equilibrium level above that of the untreated soils. Table 3.1 shows the rate of decrease of the Truog, Olsen and Schofield values for treated soils expressed as a percentage of the April 16 sampling.

The ratio of Olsen phosphate:Truog phosphate for each sampling is presented in Table 3.2. Although there is some variation in the ratios between samplings, they tend to be higher for the Pukepuke soil than for the Foxton soil.

Phosphate potentials calculated at each sampling using the value of 1.13 for $\frac{1}{2}$pCa in 0.01M $CaCl_2$ calculated by Murrmann and Peech (1968) from activity coefficients given by Cole and Olsen (1959), are presented in Table 3.3.

Figure 3.2: Mean values for Truog extractable phosphate determined at each sampling for the Foxton and Pukepuke control and phosphate treated soils.
(Appendix 3, Tables 4 and 5).

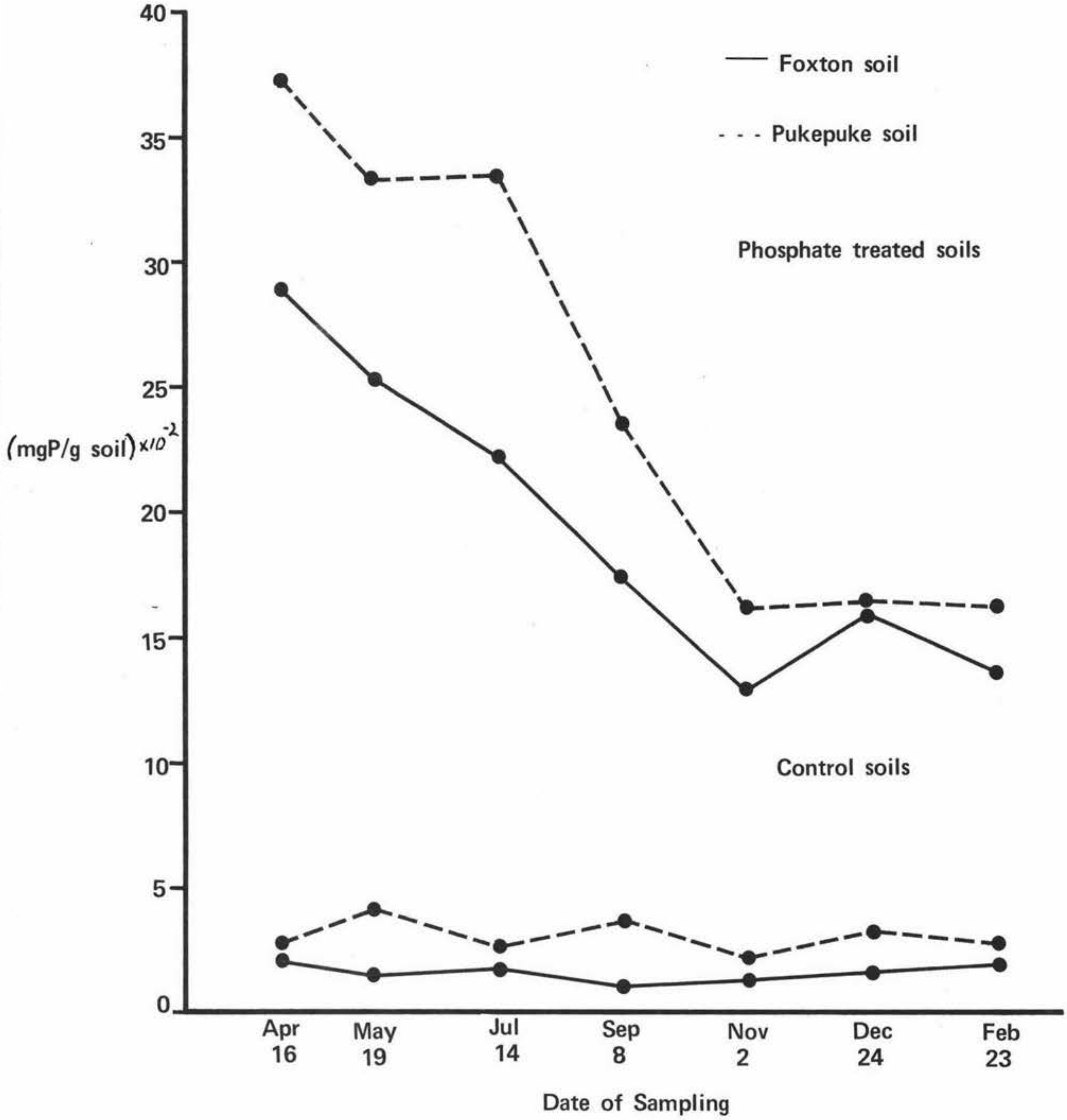


Figure 3.3: Mean values for Olsen extractable phosphate determined at each sampling for the Foxton and Pukepuke control and phosphate treated soils.

(Appendix 3, Tables 3 and 4).

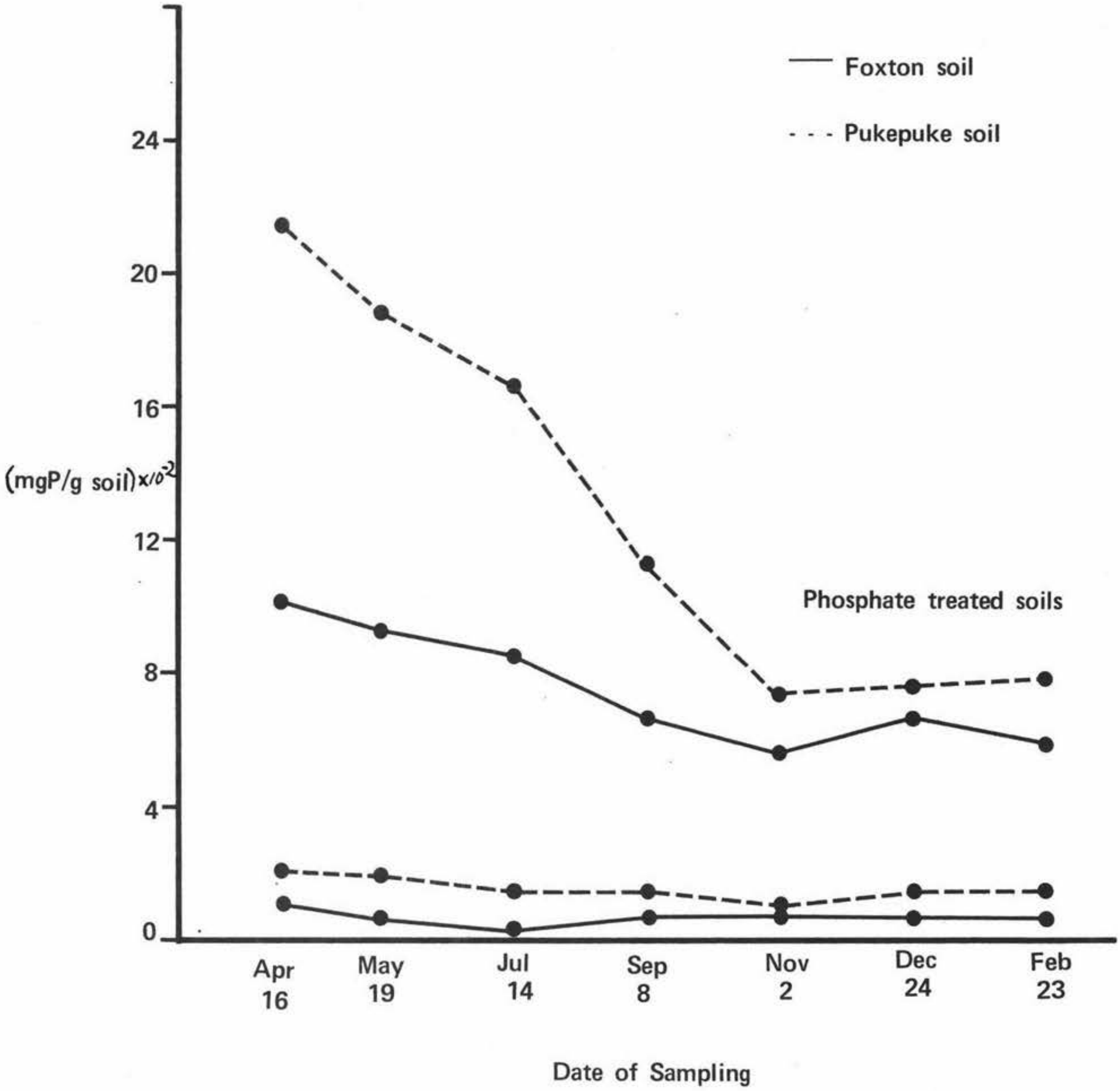


Figure 3.4: Mean values for Schofield extractable phosphate determined at each sampling for the Foxton and Pukepuke control and phosphate treated soils.

(Appendix 3, Table 3).

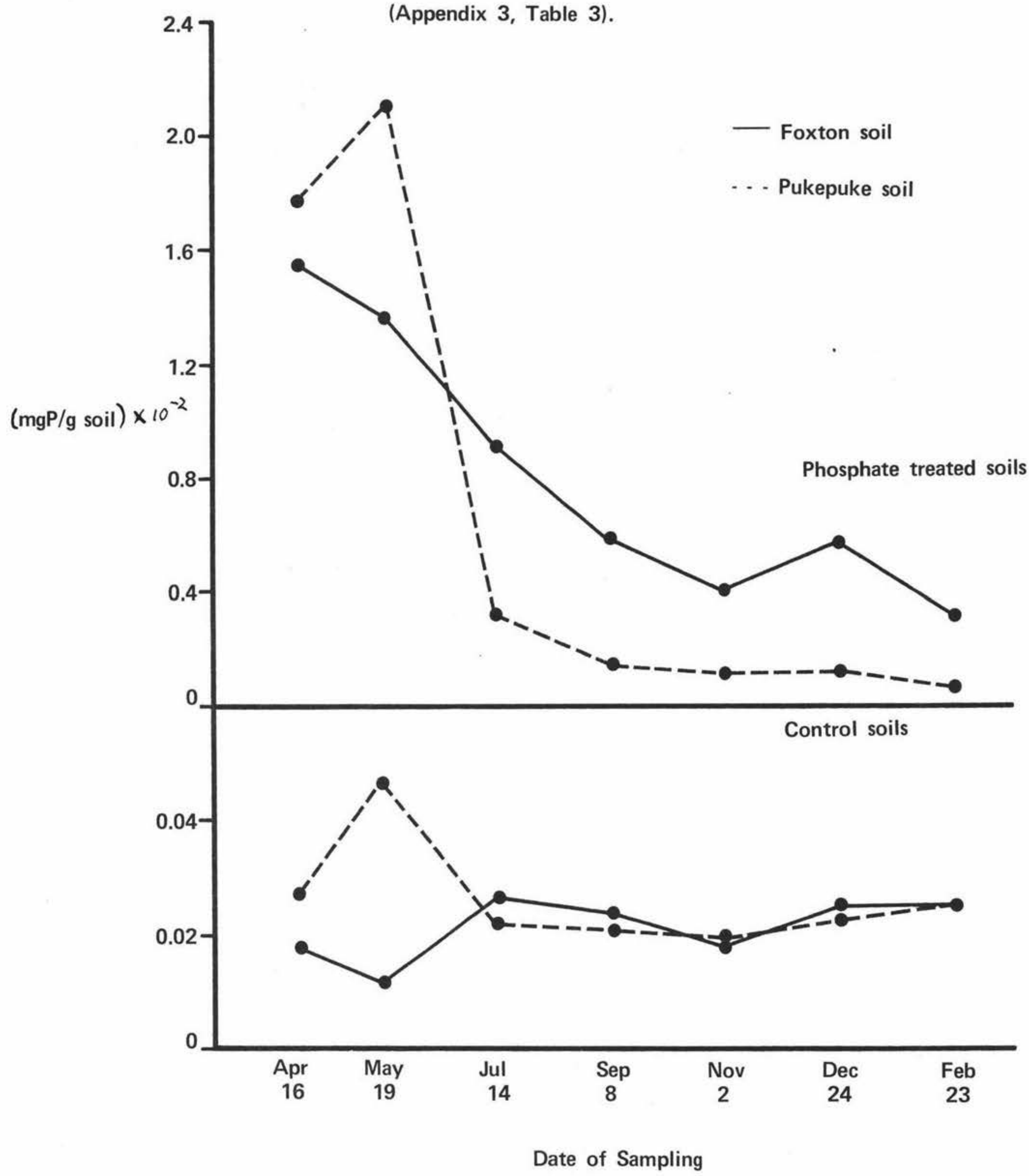


TABLE 3.1

The Mean Determined Truog, Olsen And Schofield Values For The Foxton And Pukepuke Treated Soils At Each Sampling Expressed As A Percentage Of The April 16 Sampling

Sampling Date	Pukepuke Treated Soil			Foxton Treated Soil		
	Truog	Olsen	Schofield	Truog	Olsen	Schofield
April 16	100	100	100	100	100	100
May 19	89.4	88.2	121.3	87.9	91.6	88.3
July 14	89.8	78.2	18.4	77.1	84.4	59.3
Sept 8	63.4	53.0	8.6	66.6	66.5	38.0
Nov 2	43.5	35.0	6.9	44.9	55.3	26.4
Dec 24	44.2	35.7	7.5	52.3	65.6	37.4
Feb 23	43.7	36.8	4.0	47.4	58.1	20.6

TABLE 3.2

The Ratio Of Olsen Phosphate:Truog Phosphate Calculated For Each Sampling For The Foxton And Pukepuke Control And Phosphate Treated Plots

Sampling Date	Pukepuke Soil Ratio Olsen:Truog Phosphate		Foxton Soil Ratio Olsen:Truog Phosphate	
	Control Plots	Treated Plots	Control Plots	Treated Plots
Apr 16	0.75	0.58	0.48	0.35
May 19	0.45	0.55	0.39	0.37
Jul 14	0.54	0.50	0.20	0.38
Sep 8	0.44	0.48	0.60	0.39
Nov 2	0.52	0.46	0.51	0.43
Dec 24	0.48	0.46	0.39	0.44
Feb 23	0.58	0.49	0.32	0.43
$\bar{x}$	0.53		0.41	

TABLE 3.3

Phosphate Potentials Calculated At Each Sampling For The Foxton And Pukepuke Control And Phosphate Treated Soils

Sampling Date	Foxton Soil		Pukepuke Soil	
	Control	Phosphate Treated	Control	Phosphate Treated
Apr 16	7.37	5.44	7.72	5.92
May 19	7.55	5.50	7.47	5.83
Jul 14	7.21	5.67	7.78	6.78
Sep 8	7.74	5.86	7.84	7.00
Nov 2	7.37	6.02	7.84	7.09
Dec 24	7.28	5.98	7.78	7.03
Feb 23	7.48	6.14	7.78	7.32

4. Phosphate Fractionation

The amounts of each phosphate fraction present at the commencement and end of the experimental period for the control soils, and at intervals throughout the duration of the experiment for the fertilized soils, are shown in Figures 3.5 and 3.6. For both the Pukepuke and Foxton control soils, organic phosphorus accounts for much of the total phosphate in the top 5 cm (43.6% and 52.8%, respectively).

The inorganic phosphate fractions show large differences, both in amount and relative importance of each fraction, between the two soils. The following table shows each inorganic phosphate fraction expressed as a percentage of total inorganic phosphate for the Foxton and Pukepuke control soils.

Phosphate Fraction	Foxton Control Soil	Pukepuke Control Soil
Aluminium-bound P	19.4%	6.9%
Iron-bound P	3.4%	27.8%
Calcium-bound P	29.3%	27.6%
Residual P	47.9%	37.7%

In both soils, residual phosphate is the largest inorganic phosphate fraction, and in order of importance with respect to amount, this is followed by calcium-bound phosphate, aluminium-bound phosphate, and iron-bound phosphate in the Foxton soil and iron-bound phosphate, calcium-bound phosphate and aluminium-bound phosphate in the Pukepuke soil.

Data calculated to show the mgP% increase in each phosphate fraction which had occurred six weeks after the addition of fertilizer, and also the increase expressed as a percentage of the fertilizer

Figure 3.5: Means of phosphate fractions determined for the Foxton control and phosphate treated soils. (Appendix 3, Tables 6 and 8).

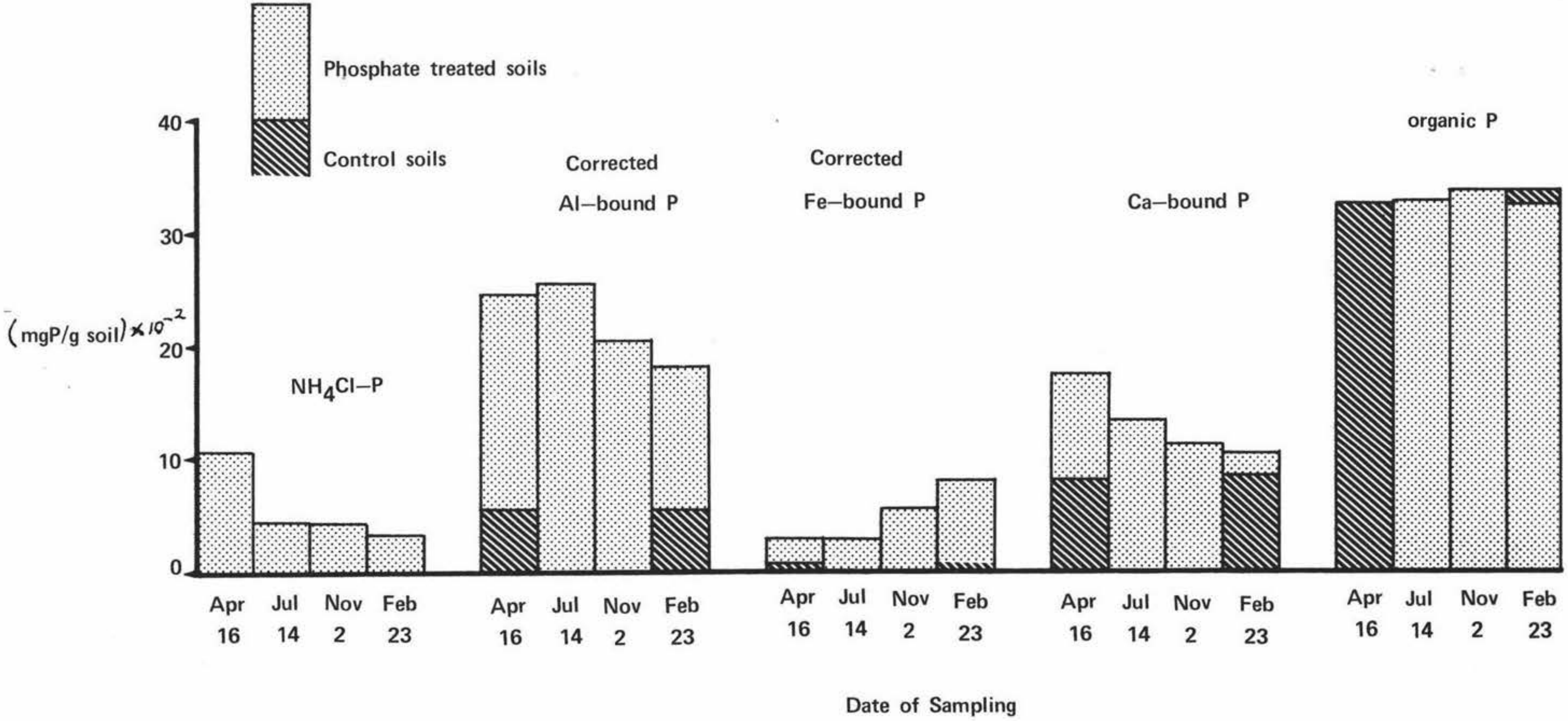
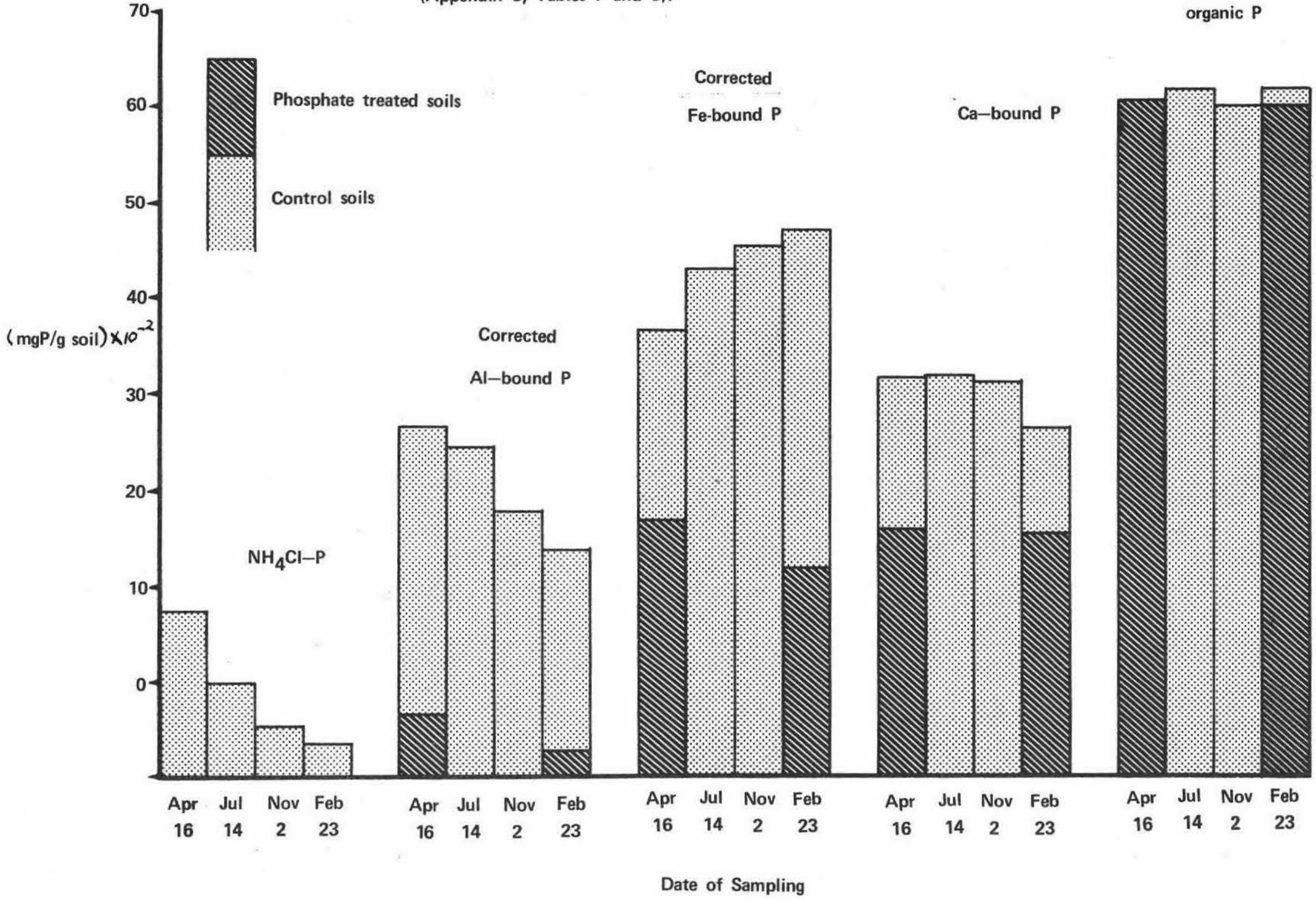


Figure 3.6: Means of phosphate fractions determined for the Pukepuke control and phosphate treated soils. (Appendix 3, Tables 7 and 8).



phosphate applied, are presented in Table 3.4. Equivalent data calculated at the end of the experimental period are presented in Table 3.5.

(i) Ammonium Chloride-Soluble Phosphate: Table 3.4 shows that 26.3% of the added phosphate remaining six weeks after the application of fertilizer to the Foxton soil appeared in the NH_4Cl-soluble phosphate fraction. This decreased over the experimental period and constituted only 14.0% (Table 3.5) of the added phosphate remaining in the top 5 cm at the end of the experimental period. Although the increase in the NH_4Cl-soluble phosphate fraction in the Pukepuke soil (17.6 mgP%) was greater than in the Foxton soil (10.8 mgP%), it comprised only 19.0% of the added phosphate remaining six weeks after application (Table 3.4) and fell to 4.5% of the added phosphate remaining at the end of the experimental period (Table 3.6).

In the Pukepuke soil, each sampling was significantly different from the preceding sampling at the 0.01 level (Table 10, Appendix 3). For the Foxton soil, the difference between the April 16 and July 14 samples, and also the difference between the November 2 and February 23 samples was significant at the 0.01 level, but there was no significant difference between the July 14 and November 2 samplings.

(ii) Corrected Aluminium-Bound Phosphate: In both soils the aluminium-bound phosphate showed the largest increase of any of the inorganic phosphate fractions after addition of phosphate. Of the added phosphate remaining in the Foxton and Pukepuke soils six weeks after application, 46.4% and 32.4% respectively

TABLE 3.4

The mgP% Increase In Each Phosphate Fraction And The Percentage Of Applied Phosphate Occurring In Each Phosphate Fraction Six Weeks After Application Of Phosphate To The Foxton And Pukepuke Phosphate Treated Plots

	Foxton Soil		Pukepuke Soil	
	mgP% Increase on Addition of Phosphate	Increase as Percentage of Phosphate Applied	mgP% Increase on Addition of Phosphate	Increase as Percentage of Phosphate Applied
NH_4Cl-soluble P	10.8	26.3	17.6	19.0
Corrected Aluminium-bound P	18.9	46.4	30.0	32.4
Corrected Iron-bound P	2.2	5.3	19.9	21.5
Calcium-bound P	9.0	22.0	15.3	16.4
Residual P	-	-	10.0	10.7
Total Increase	40.8	-	92.8	-
Increase in Na_2CO_3 P	40.7	-	91.2	-

TABLE 3.5

The Amount Of Added Phosphate (mgP%) Remaining In Each Phosphate Fraction And The Percentage Of Remaining Phosphate Occurring In Each Phosphate Fraction Of The Foxton And Pukepuke Treated Soils At The End Of The Experimental Period

	Foxton Soil		Pukepuke Soil	
	mgP% Difference Between Control and Treated Plots	Difference Between Control and Treated Plots as % of Total Difference	mgP% Difference Between Control and Treated Plots	Difference Between Control and Treated Plots as % of Total Difference
NH_4Cl-soluble P	3.4	14.0	3.6	4.5
Corrected Aluminium-bound P	12.5	51.0	21.0	25.7
Corrected Iron-bound P	7.5	30.8	35.3	43.3
Calcium-bound P	2.1	8.8	8.9	11.0
Residual P	-1.1	-4.6	12.6	15.5
Total Increase	24.6	-	81.6	-
Increase in Na_2CO_3 P	24.9	-	84.5	-

appeared in the aluminium-bound phosphate fraction (Table 3.4). With time, the aluminium-bound phosphate tended to fall faster in the Pukepuke soil than in the Foxton soil and at the end of the experimental period the aluminium-bound phosphate fraction contained only 25.7% of the added phosphate remaining in the Pukepuke soil, whereas in the Foxton soil, although the actual amount of aluminium-bound phosphate had decreased, the added phosphate remaining in this fraction had increased to 51% (Table 3.5). This would indicate that other fractions had declined in amount faster than the aluminium-bound phosphate.

Statistical analyses showed that in the Foxton soil there was no significant difference between the aluminium-bound phosphate in samples collected on April 16 and July 14, but the differences between the July 14 and November 2 samplings and also between the November 2 and February 23 samplings were significant at the 0.01 level. This also applied to the Pukepuke soil with the exception that the difference between the November 2 and February 23 samplings was only significant at the 0.05 level.

The readsorption determinations made in the interest of correcting the NH_4F-soluble values showed that even at the wide soil:extractant ratios used in this study, the readsorption was considerable. Addition of 1.25 μg/ml of phosphate to the NH_4F extractant showed that readsorption was in the region of 10% for the Foxton soil while the equivalent measurement for the Pukepuke soil was approximately 29%.

(iii) Corrected Iron-Bound Phosphate: Of the added phosphate remaining in the Foxton and Pukepuke soils six weeks after application, 5.3% and 21.5% respectively appeared as iron-bound phosphate (Table 3.5). In both soils, this fraction showed an increase with time (Figures 3.8 and 3.6).

With the exception of the difference between the April 16 and July 14 samplings, the values determined at successive samplings were significantly different at the 0.01 level for the Foxton soil. This was not the case, however, for the Pukepuke soil. Although the difference between the July 14 and November 2 samplings was significant at the 0.01 level, the difference between the April 16 and July 14 samplings was significant only at the 0.05 level and there was no significant difference between the November 2 and February 23 samplings.

(iv) Calcium-Bound Phosphate: Of the added phosphate remaining in the top 5 cm of soil six weeks after application, 22.0% and 16.4% appeared in the calcium-bound phosphate fractions of the Foxton and Pukepuke soil respectively, (Table 3.4). In both soils, this fraction showed a tendency to decrease with time (Figures 3.5 and 3.6) although over the experimental period this change was non-significant in the Pukepuke soil and significant only at the 0.05 level in the Foxton soil.

The effect of strength of HCl on the amount of phosphate and iron extracted from the Pukepuke soil is shown in Table 3.6, and it can be seen that as the normality of HCl increased, the amount of phosphate and iron extracted also increased. The difference in amount of phosphate extracted from Pukepuke control plots and Pukepuke treated plots with varying normality of acid is presented in Table 3.7. Although the differences are approximately equal for HCl normalities ranging from 0.01

TABLE 3.6

Amounts Of Phosphate And Fe_2O_3 Extracted From The Pukepuke Untreated Soil By Extraction With Varying Strengths Of HCl For 3 Hours (Soil:Acid Ratio 1:100) Followed By A 16 Hour Extraction With 1N NaOH (Soil:NaOH Ratio 1:250)

Normality of HCl	Phosphate Extracted by Acid mgP%	Phosphate Extracted by NaOH mgP%	Total Phosphate Extracted mgP%	mg Fe_2O_3/gram of Soil Appearing in Extract
1.0	45.68	18.14	63.82	40.5
0.5	36.17	27.36	63.53	31.5
0.1	4.51	55.13	59.64	16.5
0.08	3.02	55.98	59.00	10.0
0.06	1.94	56.76	58.70	7.75
0.04	1.51	55.62	57.13	4.50
0.02	0.72	53.51	54.23	1.02
0.01	0.58	53.50	54.08	0.02

TABLE 3.7

The Difference In Amount Of Phosphate Extracted From Pukepuke Control Soil And Pukepuke Phosphate Treated Soil By Extraction With Varying Strengths Of HCl For 3 Hours (Soils: Acid Ratio 1:100) Followed By A 16 Hour Extraction With 1N NaOH (Soil:NaOH Ratio 1:250)

Normality of Acid	Phosphate Extracted From Untreated Plots (a) mgP%	Phosphate Extracted From treated Plots (a) mgP%	Difference (b) - (a) mgP%
1.0	63.82	173.58	109.76
0.5	63.53	164.04	100.51
0.1	59.64	158.14	98.50
0.08	59.00	157.99	98.99
0.6	58.70	157.98	98.28
0.04	57.13	156.28	99.15
0.02	54.23	151.62	97.38
0.01	54.1	150.1	96.0

to 0.1, there was an increase in the difference when extractions were carried out with 0.5N and 1.0N HCl.

(v) Residual Phosphate: The residual phosphate, as described in this study, comprises the reductant soluble phosphate, occluded iron and aluminium phosphate and residual phosphate of Chang and Jackson's fractionation procedure and is equivalent to the sum of the residual phosphate, reductant soluble phosphate and second NaOH phosphate of the fractionation procedure of Williams, et al. fractionation procedure.

Figure 3.7 shows the means of the residual phosphate calculated at the commencement and conclusion of the experiment in the control plots, and at intervals throughout the experiment in the phosphate treated plots. There was no significant difference between the residual phosphate in the Foxton control and treated plots, and the levels of residual phosphate remained constant throughout the experimental period. However, the Pukepuke treated plots showed a significant increase (0.01 level) in residual phosphate over the control plots six weeks after application of phosphate. This residual phosphate in the treated plots showed a tendency to increase with time, but the increase was not significant.

(vi) Organic Phosphorus: No significant differences between the organic phosphorus in treated and control plots were found in either the Pukepuke or Foxton soil over the duration of the experiment.

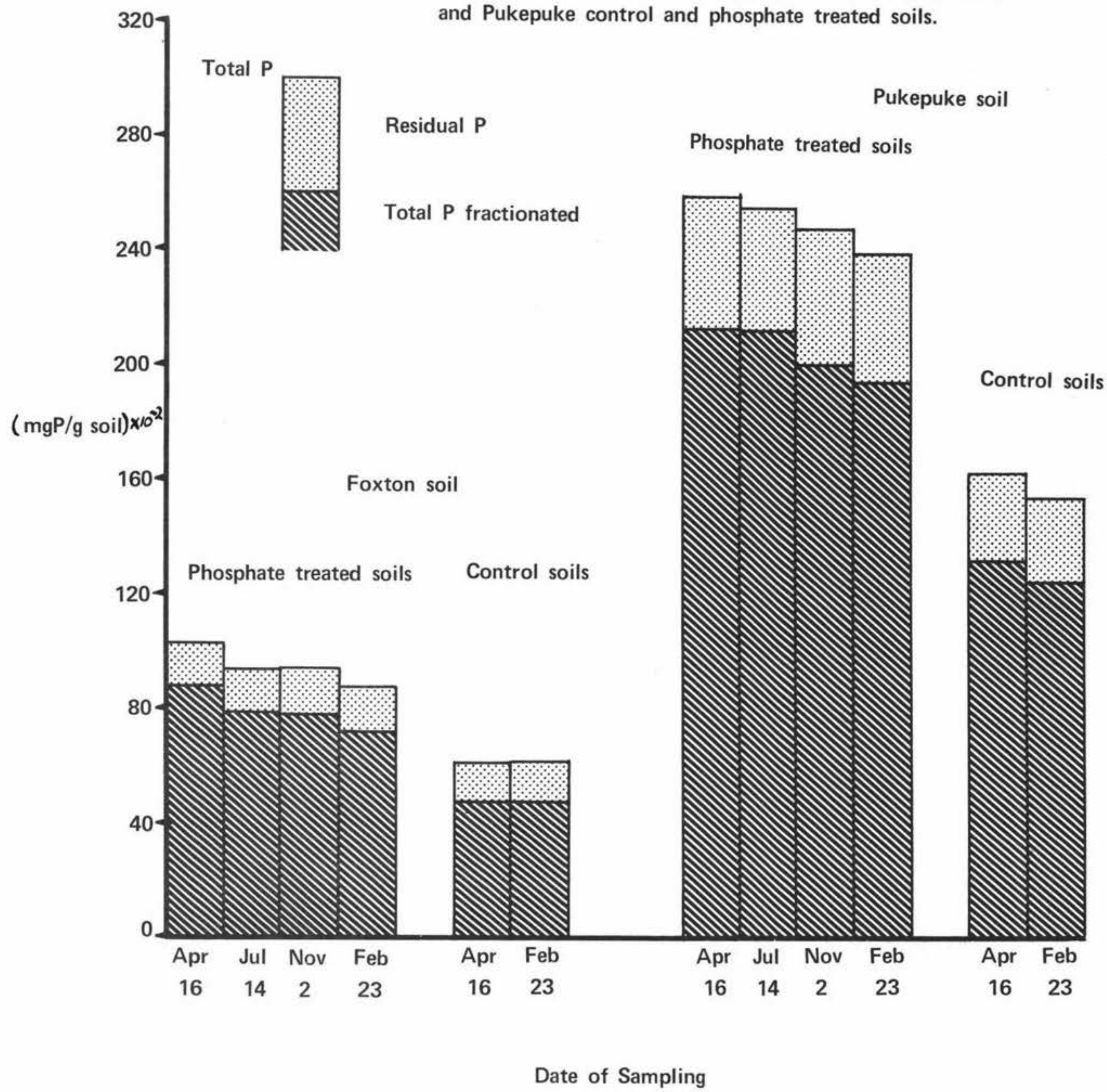


Figure 3.7: Residual phosphate shown as the difference between total phosphate (by Na_2CO_3 fusion) and the total phosphate fractionated (sum of NH_4Cl–soluble P, Al–bound P, Fe–bound P, Ca–bound P and organic P) for the Foxton and Pukepuke control and phosphate treated soils.

5. pH

The pH values determined at each sampling throughout the experiment are presented in Table 3.8. The high pH of the Pukepuke soil can be attributed to the liming policy of the farmer.

Application of 25 g/m^2 of superphosphate depressed the pH of the Foxton soil by 0.60 of a pH unit while addition of 50 g/m^2 of superphosphate to the Pukepuke soil depressed the pH by only 0.27. After sampling on December 24, there was no significant difference between the pH of control and treated plots on each soil.

TABLE 3.8

pH Values Determined For The Foxton And Pukepuke Control And Phosphate Treated Soils Determined At Each Sampling

Sampling Date	Foxton Soil		Pukepuke Soil	
	Control	Treated	Control	Treated
Apr 16	5.70	5.10	7.45	7.18
May 19	5.70	5.35	7.45	7.20
Jul 14	5.70	5.40	7.35	7.20
Sep 8	5.70	5.50	7.30	7.22
Nov 2	5.70	5.50	7.30	7.20
Dec 24	5.75	5.75	7.28	7.22
Feb 23	5.70	5.70	7.30	7.22

6. Phosphate Sorption Capacity

Phosphate sorption data for both soils are presented in Tables 3.9 and 3.10. It can be seen that there is a large difference between the two soils in their ability to retain added phosphate, the Pukepuke soil showing higher phosphate retention than the Foxton soil.

TABLE 3.9

Phosphate Sorbed By The Pukepuke Control Soil From Solutions Of Varying Phosphate Concentration Using A 1:20 Soil:Solution Ratio (16 Hour Shaking Period), Expressed As μgP/2.5g Soil And μgP/g Soil

Concentration of Phosphate Solution Added μg P per ml	μg P Added In 50ml Of Standard Phosphate Solution To 2.5gm Soil (a)	Equilibrium Phosphate Concentration μg P per ml	μg P In The Solution At Equilibrium (b)	P Sorbed (a) - (b) μg	μg P Sorbed Per Gram Of Soil
1.0	50	0.043	2.16	47.84	19.14
2.5	125	0.054	2.70	122.30	48.92
5.0	250	0.068	3.38	246.62	98.64
16.0	500	0.141	7.03	492.97	192.19
15.0	750	0.200	10.00	740.00	296.00
20.0	1,000	0.338	16.89	983.11	393.24
40.0	2,000	2.189	109.46	1,890.54	756.22
100.0	5,000	21.890	1,096.64	3,905.36	1,562.14
200.0	10,000	80.410	4,020.42	5,979.56	2,391.83
500.0	25,000	259.72	12,986.11	12,013.89	4,805.56

TABLE 3.10

Phosphate Sorbed By The Foxton Control Soil From Solutions Of Varying Phosphate Concentration Using A 1:20 Soil:Solution Ratio (16 Hour Shaking Period), Expressed As µP/2.5g Soil And µgP/g Soil

Concentration of Phosphate Solution Added µg P per ml	µg P Added In 50ml Of Standard Phosphate Solution To 2.5g soil (a)	Equilibrium Phosphate Concentration µg P per ml	µg P In The Solution At Equilibrium (b)	P Sorbed (a) - (b) µg	µg P Sorbed Per Gram Soil
1.0	50	0.051	2.57	47.43	18.97
2.5	125	0.154	7.70	117.30	46.92
5.0	250	0.389	19.46	230.54	92.22
10.0	500	1.703	85.35	414.65	165.86
15.0	750	3.960	198.20	551.80	220.72
20.0	1,000	6.950	347.98	652.02	260.81
40.0	2,000	22,290	1,114.90	885.1	354.04
100.0	5,000	78.550	3,927.51	1,072.49	428.99

7. Organic Matter, Bulk Density, Fe_2O_3, Al_2O_3, Exchangeable Ca And Exchangeable Mg Determinations

Results for these determinations for the Foxton and Pukepuke soils are shown in Table 3.11. The organic matter figures for both soils are high, due in part to the difficulty of sieving out all macro root fragments from the soil samples during preparation. This is particularly evident for the Pukepuke soil which supports a mat of roots formed during winter flooding.

The bulk densities determined for the top 5 cm of the Pukepuke and Foxton soils are 0.78 and 1.16 g/cc respectively. The value for the Pukepuke soil appears very low, but when the high root concentration in the top 5 cm of soil is considered, this figure does not seem unreasonable.

Whereas similar amounts of Al_2O_3 were extracted from both the Foxton and Pukepuke soils by hot dilute Na_2CO_3, the Pukepuke soils contain over ten times as much citrate-dithionite-bicarbonate extractable Fe_2O_3 as does the Foxton soil, and this explains partly the difference in colour of the soils in the field.

The exchangeable calcium content is considerably higher in the Pukepuke soil which also contains over twice as much exchangeable magnesium as the Foxton soil.

TABLE 3.11

Some Characteristics Determined For The Foxton And Pukepuke Control Soils

	Foxton Soil	Pukepuke Soil
Organic Matter (by ignition)	9.96%	21.68%
Bulk Density	1.16g/cc	0.78g/cc
Fe_2O_3 (citrate-dithionite-bicarbonate)	6.23mg Fe_2O_3/g soil	67.31mg Fe_2O_3/g soil
Al_2O_3 (hot dilute Na_2CO_3)	20.1mg Al_2O_3/g soil	16.6mg Al_2O_3/g soil
Exchangeable Ca (N NH_4OAc, pH 7)	1.05mg Ca/g soil	8.82mg Ca/g soil
Exchangeable Mg (N NH_4OAc, pH 7)	0.13mg Mg/g soil	0.34mg Mg/g soil
$CaCO_3$ % W/W	Nil	0.6

CHAPTER FOUR

A. DISCUSSION

(1) Movement and Losses of Phosphate, and the Phosphate Retention Property of the Soils:

The phosphate fertilizer was applied to the Foxton and Pukepuke soils towards the end of a drought, and the rainfall in the six weeks between application and the first sampling after application was only 25.1 mm (Table 3, Appendix 4), with no more than 11.9 mm falling within a twenty-four hour period. It is unlikely therefore, that any appreciable loss of added phosphate from the top 5 cm of soil would have occurred during this period. If the percentage loss between the April 16, 1971, and February 23, 1972, samplings is calculated on the basis of all of the added phosphate having remained in the top 5 cm at the April 16 sampling, then the loss from the Pukepuke treated soil was 13% and that from the Foxton soil was 37%. These results indicate that, in the Foxton soil, short term movement of phosphate may be appreciable. The high loss found in the present instance is in agreement with the finding of Jordan, et al. (1952). These workers indicated that on a short term basis there was an appreciable movement of phosphate in a fine sandy loam. The extent of movement was found to be dependent on the amount of water received by the soil. The results of Ozanne, et al. (1961) which showed that 17-81% of added phosphate was lost from sandy soils under low rainfall conditions, corroborates the above findings. Ozanne, et al. (1961) and Smith (1956) found that the rate of phosphorus application had little effect on percentage loss, and this would imply that comparisons between the two soils in the present study may be valid even though different phosphate application rates were used on each soil.

Saunders (1968) divided phosphate retention by New Zealand soils into four classes. These were derived from measurements of the percentage of added phosphate taken up in a twenty-four hour period by 5g of soil shaken at 20°C with 25 ml of NaOAc-HOAc buffer solution (pH 4.6) with an initial phosphate concentration of 0.032M KH_2PO_4. The four classes are low (0-30 percent), moderate (30-60 percent), high (60-90 percent) and very high (90-100 percent). According to this classification, the phosphate retention of the yellow-brown sands topsoil is low. The phosphate sorption data (Tables 3.9 and 3.10) show that the Pukepuke soil has a higher ability to absorb phosphate than the Foxton soil and this agrees with the findings that a larger percentage of the added phosphate was lost from the Foxton soil. The ability of the Pukepuke soil to retain added phosphate against leaching loss may be attributed to the high iron oxide content, and the amorphous nature of its clay content. Some loss of phosphate from the Pukepuke control plots was probably to be expected because of its history of fertilizer application.*

---

*It was not possible to trace the downward movement of phosphate in the Pukepuke soil as phosphate variability in samples collected from depths of 5-10 cm and 10-15 cm made any difference in phosphate levels in samples collected from control and treated plots non-significant. A similar sampling procedure was impracticable on the Foxton soil due to the unconsolidated nature of the soil which caused sampling difficulties.

(2) Phosphate Availability: At the initial sampling, the Truog phosphate value for the Pukepuke soil was 6.6 (expressed as by the New Zealand Department of Agriculture in parts per 50 million of extract) and that of the Foxton soil was 4.0. These values are low. The Pukepuke soil had received a total of 2,510 Kg/ha of superphosphate over the ten years prior to the commencement of this study, but evidently this had not increased the Truog phosphate value to a desirable level. Six weeks after application of superphosphate, the Truog phosphate value for the Pukepuke soil had risen to 89, and for the Foxton soil to 71, but at the final sampling these values had fallen to 39 and 33 respectively. Although the Truog value for each soil appears to decrease with time at a similar rate, the Olsen value decreases more rapidly for the Pukepuke than for the Foxton soil (Table 3.1). Whereas the final Truog value expressed as a percentage of the April 16 value is higher than the equivalent Olsen value for the Pukepuke soil, the Olsen value of the Foxton soil is higher than the Truog value. This evidence, coupled with the observation that the ratio of Olsen phosphate:Truog phosphate is different in the two soils (Table 3.2), indicates that Olsen's and Truog's reagents are extracting different fractions of phosphate. Whereas Bray and Kurtz (1945), Pratt and Garber (1964), Datta and Kehra (1969) and Srivastava (1971) found that Olsen's reagent solubilized aluminium and iron phosphates, Grigg (1966), Susuki, et al. (1963), and Datta and Kehra (1969) noted that this reagent solubilized mainly aluminium phosphate. Chang

and Juo (1963) found that Olsen's phosphate was correlated with aluminium phosphate in soils dominant in calcium phosphate. In soils dominant in iron phosphate the highest correlation again was between Olsen phosphate and aluminium phosphate, but significant correlations were also found between Olsen phosphate and calcium and iron phosphate. The evidence suggests that in the two soils of the present study, Truog's reagent extracted phosphate other than calcium-bound phosphate. For example, after application of phosphate to the Pukepuke soil, Truog phosphate increased by 34.57 mgP% whereas the sum of NH_4Cl-soluble phosphate and calcium-bound phosphate increased by only 32.87 mgP%. Therefore, even if all the 15.26 mgP% increase in calcium-bound phosphate after phosphate addition was soluble in Truog's reagent (which is unlikely), phosphate from other fractions must have been solubilized to account for the increase in Truog extractable phosphate found. A similar argument may be applied to the Foxton soil. If Olsen's reagent is assumed to remove largely the NH_4Cl-soluble and aluminium-bound fractions (Chang and Juo, 1963), then the more rapid decline in Olsen phosphate in the Pukepuke soil may be due to the more rapid decline of the NH_4Cl-soluble and aluminium-bound fractions found in the Pukepuke soil. The initial rapid decrease in Truog and Olsen phosphate levels may have been due to three factors: (a) the loss of phosphate by leaching, (b) a redistribution of phosphate within the soil phosphate fractions with a resulting decrease in extractability, and (c) decrease in extractability within the soil phosphate fractions. A fourth factor could possibly have been involved; this is suggested by the work of Evans and Syers (1971) which showed rapid penetration of added phosphate into soil crumbs from which seven days extraction with 0.1N $NaHCO_3$ resolubilized only 14-18% of the sorbed added phosphate. The suggestion that Truog's and Olsen's reagents extracted different fractions of phosphate is supported by the conclusion of Colwell and Donnelly (1971) that phosphate tests are affected by variation in soil composition, particularly with respect to compounds of iron, aluminium, magnesium and calcium. Borlan, et al. (1968) noted that the chemical properties of the soils they worked with accounted for up to eighty percent of the variance of the effect of fertilizer and lime.

The initial increase and subsequent decrease in "available" phosphate found in the present study agrees with the results of Grigg (1966), who showed that annual application of 564 Kg/ha of superphosphate to a yellow-grey earth gave an annual fluctuation from 0 to 17 units in Truog values. This emphasises the fact that soil phosphate status is a dynamic concept, and that interpretation of soil test values must take into account the time since fertilizer was previously applied and also seasonal growth conditions (Grigg, 1966). In the present study, the rapid decline in the phosphate concentrations in 0.01M $CaCl_2$ equilibrium solutions with time after application of superphosphate to the soils corroborates the findings of Larsen and Widdowson (1971) who showed that the ageing process of phosphate added to soil was indicated by falling solubility as time elapsed.

Schofield (1955) considered that it is not the amount of available phosphate in a soil that primarily controls the uptake of phosphate by plants but the work needed to withdraw it from the pool, and he proposed that the potential of monocalcium phosphate in soils may be expected to serve as an index of the availability of soil phosphate. Russell (1961) noted a lack of experimental evidence which could be used to discriminate between whether phosphate uptake by plants is controlled by the potential of monocalcium phosphate or by the phosphate ion concentration in the soil solution. However, it is the opinion of Wild (1964) that for solutions of about the same phosphate concentration as those in soil, it is the phosphate concentration and not the potential which determines phosphate uptake by plants. However, Wild also noted that it is not clear whether the concentration should refer to the total inorganic phosphate in solution or to that fraction present as $H_2PO_4^-$ ions. Nye (1968), considering the experimental finding of plant physiologists that the rate of uptake of an ion varies with its concentration in solution, was of the opinion that "to express this concentration as a concentration ratio with other ions, or to take the logarithm of the ratio and use thermodynamic terminology does not give the simple relation between concentration in solution and plant uptake any better theoretical justification". Hence the hypothesis of Schofield may not be entirely correct and may in fact not give any advantage over the simple measurement of phosphate concentration in solution.

In the present study, although the fertilized Pukepuke soil showed higher Truog and Olsen values than the fertilized Foxton soil, the amounts of phosphate at equilibrium in the $CaCl_2$ extracts were lower. This demonstrates that the level of phosphate maintained in the soil solution is lower in the treated Pukepuke soil than in the treated Foxton soil. Virtually all of the phosphate in solution in the Foxton soil will be in the form of $H_2PO_4^-$ because of the level of soil acidity; hence in calculation of phosphate potentials, the actual phosphate concentration in the equilibrium 0.01M $CaCl_2$ extracts was used. However, this is not the case for the Pukepuke soil where, because the equilibrium pH of 0.01M $CaCl_2$ extracts lies between 7.1 and 7.2, only approximately 31% of the total phosphate concentration is in the monovalent form, and only this fraction is considered in determination of phosphate potentials. Hence the phosphate potentials for the Pukepuke soil indicate a lower level of phosphate in the 0.01M $CaCl_2$ extracts than is indicated by measurement of the phosphate concentration. Consideration of the coefficients of variation (Tables 3-5, Appendix 3) shows that the order of coefficient of variation was Schofield values > Truog values > Olsen values.

Nye (1963) stressed the need for deeper understanding of the transfer of nutrients from soil to crop and concluded that without it "the future of soil testing will consist of an endless series of fertilizer trials designed for correlation with an ever increasing number of hit-or-miss extractions". Perhaps the comment of Ozanne and Shaw (1967) that "it is the amount of required phosphate that is of more concern than the existing supply" is relevant. These authors showed that the measurement of phosphate sorption by soil at some standard equilibrium concentration was closely and linearly related to the phosphate requirement of pasture plants growing on that soil. A standard equilibrium concentration of 0.3 ppm was chosen because this would ensure maximum yield without entering the zone of luxury consumption. However, Ozanne and

Shaw noted that because of a differing phosphate requirement between species, more accurate relationships between phosphate sorbed and phosphate required might be found in situations where only one species is dominant. Graphical representation of the sorption data presented in Tables 3.9 and 3.10 showed that to obtain an equilibrium phosphate concentration of 0.3 ppm required the addition of 82 μgP to each gram of the Foxton soil and 364 μg to each gram of the Pukepuke soil. Ozanne and Shaw found that where plants were grown in field soil to which a surface application of phosphate had been made, the ratio of phosphate sorbed in the laboratory test, to phosphate required by the plants, was 1/0.7, whereas when the phosphate was uniformly mixed through the soil, the ratio was 1/1.6.

(3) The Significance of Soil pH Changes Induced By The Field Application of Phosphate:

The difference in pH depression shown by the two soils (Table 3.8) as a result of the addition of superphosphate indicates different buffering capacities. A temporary depression of pH of about one unit within twenty-four hours following the application of superphosphate to yellow-brown loams was observed by Saunders (1958) who found that during a period of three to six weeks after topdressing, the pH of the phosphate treated soils moved towards that of the control soils. Saunders attributes the initial decrease of pH in the treated soils to the acid nature of the fertilizers and the replacement of exchangeable H^+ ions by Ca^{++} ions from the fertilizer. He considered that the extent of the pH change would be dependent on the buffering capacity and the nature of the phosphate-retaining complex of the soils. The tendency found in the present study for the pH of the phosphate treated plots to move towards that of the control plots within a few months after addition of superphosphate agrees with the view of Russell (1961) that superphosphate is not an acid fertilizer as demonstrated by the fact that long term fertilizer trials on the Rothamsted and Woburn soils had no appreciable effect on the pH. Part of the pH depression noted in this study may be due simply to the salt effect, as measurement of the equilibrium pH values in 0.01M $CaCl_2$ extracts showed that the pH difference between treated and control soils was only 0.1 for the Foxton soil and 0.08 for the Pukepuke soil at the first sampling after addition of phosphate.

(4) <u>The Trends Of Phosphate Fixation Revealed By The Fractionation Procedures</u>: The coefficient of variation for the estimation of the various phosphate fractions generally varied from 5-26% (Table 6-8, Appendix 3), depending upon the soil and the fraction. Khanna and Datta (1967) reported that the coefficient of variation in their study varied from 0-23%, and the maximum variation was observed with the estimation of the iron-bound phosphate. They suggested this was probably due to the hydrolysis of organic phosphorus extracted along with this fraction. Exceptionally high coefficients of variation were found in determination of iron-bound phosphate in the present study, the highest being 71%. This occurred in determination of iron-bound phosphate in the Foxton control soils, and may be partially due to the low level of phosphate in this fraction.

The value of 52.8% for the organic phosphorus content of the Foxton control soil (expressed as a percentage of total phosphate) is comparable to the value of 50% given by Syers and Walker (1969a) for the top horizon (0–14 cm). However, results obtained in the present study for the Foxton soil when compared with values of phosphate fractions expressed as a percentage of total inorganic phosphate calculated from the results of Syers and Walker (1969b), show that although the importance according to abundance is similar, the relative percentages vary. Percentages calculated from the results of Syers and Walker (1969b), and the percentages determined in this study (in brackets) are: residual phosphate 60.1% (47.9%), calcium-bound phosphate 18.7% (29.3%), aluminium-bound phosphate 12.6% (19.4%), and iron-bound phosphate 8.6% (3.4%). Differences are probably due to different sampling depths (0–5 cm in the present study and 0–14 cm in the study by Syers and Walker (1969b)), and to differences in the fractionation procedure used.

(i) Ammonium Chloride Soluble Phosphate: The phosphate extracted by NH_4Cl corresponds to water-soluble and weakly-bound phosphate (Chang and Jackson, 1957a). According to Fassbender (1968) this fraction decreases in soils with increasing degree of phosphate retention. Thus the higher phosphate retention capacity and the higher iron content of the Pukepuke soil could be used to predict that a smaller proportion of the added phosphate would remain in the NH_4Cl-soluble fraction; the results show that this was indeed the case (Table 3.4). The rate of decrease of the NH_4Cl-soluble fraction with time was more rapid in the Pukepuke soil than in the Foxton soil and at the end of the experimental period, the NH_4Cl-soluble fraction comprised 14.0% of the added phosphate remaining in the Foxton soil, whereas the equivalent figure for the Pukepuke soil was 4.5% (Table 3.5), despite the fact that the percentage loss of added phosphate was greatest in the Foxton soil.

Only a few workers have reported on and discussed the NH_4Cl-soluble phosphate fraction. Fassbender (1968), by shaking 0.5g samples of soil with a solution containing 100 ppm phosphate labelled with ^{32}P, found that the percentages of added phosphate recovered in the NH_4Cl-soluble fraction were 14.50, 11.05, and 2.95 for alluvial soils, latosols, and andosols respectively. Yuan, et al. (1960) added a solution containing 100 ppm phosphate to three acid sandy soils and reported that of the phosphate retained, 4.5, 2.1, and 3.8 percent was recovered in the NH_4Cl-soluble fraction. The percentages of added phosphate recovered in the NH_4Cl-soluble fraction in the present study are considerably greater than those reported in the literature, and this is true even six weeks after application of the phosphate fertilizer. This could be due to the high application rate being used and also to the fact that the soil: extractant ratio used here was considerably wider than that used by the authors reported above, and may be expected to extract more phosphate.

(ii) <u>Corrected Aluminium-Bound Phosphate</u>: Several authors, including Robertson and Hutton (1960), Chang and Chu (1961), Fiskell and Spencer (1964), Manning and Salomon (1965), Khanna and Datta (1968), Fassbender (1968), and Appelt and Schalscha (1970), have reported that the bulk of phosphate added to soils can be recovered in the aluminium-phosphate fraction. This was found to be the case in the present study and, furthermore, the initial increase in the aluminium-bound phosphate followed by a decline with time (Figures 3.5 and 3.6) agree with the findings of Chang and Jackson (1958) and Chang and Chu (1961).

Harter (1968) found that the portion of phosphate adsorbed by a lake sediment which was subsequently extracted by NH_4F, appeared to be bonded by two different mechanisms. When small amounts of phosphate were added, NH_4F extracted a tightly bonded form of phosphate probably occurring as an aluminium phosphate. When larger amounts of phosphate were added the additional phosphate was bound more loosely in a form which appeared to be independent of the aluminium content of the sediment, and could be removed by successive extraction with water. Tandon (1969) also noted that smaller additions of phosphate to soil resulted in a stronger bonding between phosphate and aluminium than did larger additions, assuming a constant amount of phosphate retention surface. He ascribed this to a variation in the distance between the phosphate ion and the retention site, which increased as the amount of added phosphate increased. From additional adsorption-extraction data on several soils, Harter (1969) postulated that the loosely adsorbed phosphate is primarily bonded to organic matter on anion exchange sites, and the mechanism involved is most likely a substitution of phosphate ions for hydroxyl ions. This proposal suggests that phosphate is initially bonded to anion exchange sites on organic matter, and subsequently transformed to less soluble iron and aluminium phosphates. It may be concluded, therefore, that as the amount of phosphate added to soil increases, there is a reduction in bonding strength of the phosphate. It would be expected that as the Pukepuke soil received twice as much phosphate as the Foxton soil, and since this soil contains less free alumina, more of the added phosphate will be held by the low energy bonds. The more rapid decline of the NH_4F-soluble phosphate in the Pukepuke soil supports this hypothesis. However, although the Pukepuke soil contains less free alumina, the degree of saturation of the alumina surfaces is not known.

One of the first reaction products of monocalcium phosphate in soil may be dicalcium phosphate, and its importance could be expected to increase as the calcium content of the soil is increased (Lindsay, et al. 1959). Such dicalcium phosphate is likely to be extracted mainly by the fluoride solution (Kaila, 1961b, 1963a; Laverty and McLean, 1961) and therefore, in the early samplings of the Pukepuke soil after phosphate application, the NH_4F-soluble phosphate may include some dicalcium phosphate.

The large difference in readsorption of phosphate found between the Foxton and Pukepuke soils during

NH_4F extraction, reflects the different free iron oxide contents. As suggested by Smith (1965c), it was found necessary to use separate correction factors for the control soils and the phosphate treated soils, the percentage adsorption of added phosphate being lower in the treated soils. As pointed out by Williams, et al. (1967), the use of recovery values obtained after the addition of 1.25 μgP per ml of NH_4F solution as a basis for correction to an adsorption-free basis, is not entirely adequate if the relationship between sorbed phosphate and phosphate in solution is non-linear. It would appear desirable to keep the concentration of phosphate added in the NH_4F solution as low as possible, but some difficulty was experienced in this study when low concentrations of phosphate were added to NH_4F solutions due to variability between samples in the amounts of phosphate adsorbed.

(iii) Corrected Iron-Bound Phosphate: The higher percentage of the added phosphate recovered in the iron-bound fraction in the Pukepuke as distinct from the Foxton soil is doubtless a reflection of the higher 'free' iron oxide content of the former soil. The tendency for both the Foxton and Pukepuke soils to show an increase in the iron-bound phosphate fractions with increasing time after phosphate applications, agrees with the findings of Chang and Jackson (1958); Hsu (1960); Chang and Chu (1961); Smith (1965b, 1967, 1969) and Kaila (1967).

(iv) <u>Calcium-Bound Phosphate</u>: The fractionation procedure of Chang and Jackson (1957a) has been criticized on the basis that some of the reductant-soluble phosphate is extracted in the preceding calcium phosphate extraction, thus leading to overestimation of the latter fraction (Khin and Leeper, (1960). Preliminary investigations (Table 2.8) showed that the normality of HCl in the range of 0.01 to 1.0 had no significant effect on the amount of phosphate extracted from the Foxton soil when the phosphate in the acid extraction and the subsequent alkali extraction were summed. Therefore, in this particular soil, it would appear that the acid was not extracting reductant-soluble phosphate, for if this had been so, there would have been an increase in the amount of phosphate extracted as the normality of the HCl was increased. Further support for this conclusion is to be found in the work of Shah et al. (1968) who showed that, for the top horizon of the Foxton black soil, the sum of the acid-extractable calcium phosphate plus the non-occluded aluminium and iron phosphates was approximately equal to the phosphate extracted by 1N H_2SO_4, and the authors considered that these fractions may be approximately equated.

In contrast, the phosphate extracted by acid from the Pukepuke soil was dependent on the normality of the acid in the range of 0.01 to 1.0 (Table 2.9). If it could be shown that the increase in phosphate extracted with increasing normality of acid was accompanied by an increase in the amount of iron extracted, this would suggest that as the acid increased in strength, the reductant-soluble and/or occluded phosphate was being attacked. The results (Table 3.6) show that this was the case. Thus, as the acid strength was increased from 0.01N to 1.0N, each increase in the amount of phosphate extracted was accompanied by an increase in the amount of iron extracted (Table 3.6). Similar amounts of phosphate were extracted by 0.01N and 0.02N HCl, and although the amounts of iron appearing in these extracts were low, there was a five-fold increase between the 0.01 and 0.02N HCl extracts. As the normality of the HCl was increased from 0.04 to 0.1, the amount of phosphate extracted increased, and this was accompanied by an increase in the amount of iron extracted. The increase in the amount of phosphate extracted by 0.5N HCl was accompanied by an almost two-fold increase in the amount of iron extracted, and although 1.0N HCl extracted still more iron (representing approximately 60% of the iron extracted by citrate-dithionite-bicarbonate extractions) there was little increase in the amount of phosphate extracted. If the acid was extracting a certain fraction of phosphate at each normality, then the difference between the phosphate extracted from treated soils and that extracted from the control soils, would be expected to remain constant over the range of normalities, and approximately equal to the amount of applied phosphate. This occurred up to a strength of 0.1N (Table 3.7) but 0.5N HCl increased the difference between the amounts of phosphate extracted from the treated and control soils. The difference at 1.0N HCl was 11.3 mgP% higher than the mean difference over the range of 0.02 to 0.1N HCl. The fact that the difference of approximately 98 mgP% obtained over the range 0.01-0.1N HCl was higher than the mean value of the phosphate added and recovered in the fractionation, can be explained in terms of field variability of the soil. More importantly, the difference of 11.3 mgP% between the amounts of phosphate extracted by 1.0N and 0.1N HCl is slightly larger than the amount of added phosphate appearing in the residual phosphate fraction. When the reductant-soluble phosphate was determined on the treated and untreated Pukepuke soils, the phosphate applied which had not been recovered in the unoccluded phosphate fractions, was recovered in the reductant-soluble phosphate fraction.

Williams (1965) compared the method of Fife (similar to that used in the present study) for determination of calcium phosphate and a method modified by Williams (1965), over a range of six soils. He found good agreement in the amounts of calcium phosphate extracted by the two methods using two soils which apparently contained no calcium phosphate. However, appreciable differences between the two methods were found for the remaining samples. Williams (1965) considered that it was possible that the method of Fife overestimated calcium phosphate because of slight alteration of the sample during acid extraction. He added that visual observation showed considerably more organic matter to be extracted by NaOH from acid-treated samples than from the samples treated with alkali alone and he considered that this may have been due to partial break-down of iron oxide coatings or concretions by the acid treatment. Pretreatment with HCl has been shown to increase the amount of organic phosphate extracted from soils by NaOH solution (Mehta, et al. 1954), and Williams considered it reasonable to assume that this would apply to inorganic aluminium and iron phosphate. However, it has already been established that the acid used in this study (0.02N HCl) extracted very little iron. Furthermore, application of the fractionation procedure of Williams (1965) in the present study produced a calcium-bound phosphate value of 24.7 mgP% for the Pukepuke control soil which compares favourably with the value of 25.1 mgP% obtained by the method of Fife on the same series of samples.

It may be concluded therefore, that the method for determination of calcium-bound phosphate used in this study gave a good estimation of calcium-bound phosphate, but the procedure of Chang and Jackson (1957a) in which 0.5N H_2SO_4 is used to determine calcium-bound phosphate, may overestimate the calcium-bound phosphate at the expense of the reductant-soluble and/or occluded aluminium and iron phosphates in some soils, especially those high in iron oxide such as the Pukepuke soil of the present study.

On addition of phosphate, the Foxton and Pukepuke soils showed an increase in calcium-bound phosphate content. Saunders (1959b) found that application of phosphate in field trials to New Plymouth black loam over a number of years led to a small increase in the level of apatite phosphate. Because of the high sesquioxide content and the moderately acid reaction of the soil, Saunders considered that the build-up of calcium-bound phosphate was not due to retention of phosphate by calcium, but rather to the presence of residual water-insoluble apatite added in the phosphatic fertilizer. The increase in calcium-bound phosphate in the two soils of the present study may be due, at least in part, to unreacted apatite in the applied superphosphate. Of the 9.46%P in the superphosphate used in this experiment, 18% was not removed by two successive extractions of 1g superphosphate with 100ml of water.

The finding of Kaila (1967) that after incubation of soil with $CaCO_3$, the small amounts of fertilizer phosphate recovered in the acid soluble form did not depend on the rate of liming, even at pH 7, is supported by the small difference in the amounts of calcium-bound phosphate found in the two soils of the present study. However, calcium-bound phosphate may be expected to be more stable in the Pukepuke soil, because of its higher pH, than in the Foxton soil. This is supported by the finding that the calcium-bound phosphate fraction of the Foxton soil decreased with time at a faster rate than that of the Pukepuke soil.

(v) Residual Phosphate: An increase in the residual phosphate fraction of the Pukepuke soil six weeks after the application of superphosphate indicates that occlusion of phosphate added to soil may occur more rapidly than is generally believed. Increases in the reductant-soluble phosphate have been reported at eight weeks (Mandal and Das, 1970), three months (Kar and Chakravarti, 1969), and one hundred days (Chang and Chu, 1961) after phosphate application, but in all cases the soils were flooded. However, for the soils considered here, in the six weeks between application of superphosphate and the first sampling after application, rainfall was only 25.1mm (Table 3, Appendix 4) and no flooding occurred over this six week period. The explanation for this increase in residual phosphate over such a short time interval is most likely due to the high rate of phosphate application and the large content of iron in the soil. Examination of the coarse sand fraction of the A horizon of the Pukepuke soil revealed a number of roughly rounded reddish brown grains, with the superficial appearance of ironstone nodules. However, when these were broken open, they were found to be earthy and porous and lacking in any suggestion of concentric concretionary development. The majority of grains were earthy all the way through, but some appeared to contain remnants of the original, weathering, ferromagnesion minerals at their centres. The reddish brown earthy material was identified as consisting of the two phases goethite and β $Fe_2O_3.H_2O$

(Challis, pers. comm.), who suggested that the grains could possibly be pseudomorphs after biogenic iron pyrite, which is common in wet soils. However, the presence of what appeared to be original ferromagnesium minerals at the core of some of the grains would suggest that they could equally well be pseudomorphs after such weathering minerals (Pollok, pers. comm.). These pseudomorphs would provide a ready source of iron for the occlusion of phosphate.

The fact that the increased content of residual phosphate fraction resulting from the fertilizer additions was not extracted by NH_4F, NaOH or 0.5N HCl, indicates that it is not in a descrete form such as variscite, strengite or apatite. However, because it is solubilized by extraction with 1N HCl, which also removed a large amount of iron, it is suggested that this phosphate is simply occluded by an iron oxide coating, removal of which allows the phosphate to be extracted.

As previously stated, the term "residual phosphate" as used in this study includes the reductant-soluble phosphate, occluded aluminium and iron phosphate, and the residual phosphate of the Chang and Jackson (1957a) procedure. This latter fraction was believed to consist of secondary inorganic forms of phosphorus (Bauwin and Tyner, 1957). Syers, et al. (1967), studying four beach sands and Koputaroa sandy loam from the Manawatu sand country, found that apatite was present as inclusions in several of the volcanic derived minerals in beach sands, Since these apatite inclusions were partially resistant to attack by 1N HCl, it was concluded that residual or inert phosphate in soils may have both primary and secondary origins. Apatite inclusions have also been studied by Cescas, et al. (1970) who concluded that, in the beach sands of the Manawatu sand country, such inclusions are probably more significant than lattice phosphorus as contributions to total phosphate.

(vi) General Conclusions Concerning The Trends of Fixation And The Values Of The Fractionation Procedure:

The differences exhibited between the Foxton and Pukepuke soils in the percentage distribution of added phosphate within the phosphate fractions support the findings of Kaila (1963a) that fertilizer phosphorus accumulates in various fractions mainly according to the properties of the soils. Kaila (1964b) noted a greater accumulation of iron-bound phosphate as the phosphate sorption capacity of the soil increased, and this accords with the earlier work of Laverty and McLean (1961) and Volk and McLean (1963). The findings of the present study also fit this pattern, as the Pukepuke soil, with the higher phosphate sorption capacity, retained more of the added phosphate as iron-bound phosphate than did the Foxton soil with a lower phosphate sorption capacity.

The ratio of aluminium-bound phosphate:iron-bound phosphate (subsequently designated Al-P/Fe-P) shows a different behaviour for the two soils. In the Foxton soil, the Al-P/Fe-P ratio was 7.87 prior to phosphate addition, indicating the relative unimportance of the iron-bound phosphate fraction in this soil. Six weeks after application of superphosphate the ratio was 7.82, but by the end of the experimental period this ratio had decreased to 2.26. Application of superphosphate increased the Al-P/Fe-P ratio of the Pukepuke soil from 0.17 to 0.78, but by the end of the experimental period the ratio had fallen to 0.42, thus indicating a tendency to revert to its original value. These findings agree with those of Shelton and Coleman (1968) who showed that, with increasing time after application of phosphate, there was a decrease in aluminium-bound phosphate and an increase in iron-bound phosphate, a situation to be anticipated in view of solubility considerations.

Although it is fully recognized that sharp delineation of the forms of phosphate in soils is probably not realized under the conditions of the fractionation procedures employed in this study (nor for that matter by any other existing scheme of fractionation) it appears that, by the use of appropriate corrections, the relative importance of each phosphate fraction can be well established. However, it is essential to determine for each soil the optimum soil:extractant ratio and extraction time, and, for the determination of calcium-bound phosphate, the required initial normality of acid to produce the desired equilibrium pH value. One feature of the fractionation procedure of Fife is that it used a separate sub-sample in the determination of each phosphate fraction. This has the advantage over sequential extraction in that it obviates possible release of phosphate during acid extraction from CaF_2 formed during fluoride extraction of calcium carbonate-containing soils, Syers, et al. (1972).

* * * * * * *

B. SUMMARY

A study was made of the changes in availability and forms of phosphate binding over a twelve-month period following the application of commercial superphosphate under field conditions, in two contrasting soils of the Manawatu-Rangitikei sand country, using the reagents of Truog (1930), Olsen (1954) and Schofield (1955), and the fractionation procedure of Fife (pers. comm.). The two soils used for this study were the Foxton black sand, an excessively drained dune soil, and the Pukepuke brown sandy loam, a poorly drained sand plain soil. Fertilizer was applied in the autumn and the experimental period was designed to cover the approximate time interval between successive fertilizer applications in a farming situation.

The following conclusions were drawn from this study:-

(1) The Pukepuke soil possesses a higher phosphate sorption capacity than the Foxton soil; this is most likely due to the high iron oxide content of the Pukepuke soil and the amorphous nature of the clay fraction.

(2) Short term downward movement of applied phosphate from the top 5cm of soil was considerably greater in the Foxton soil than in the Pukepuke soil.

(3) Application of superphosphate to the Foxton and Pukepuke soils resulted in a large increase in the Truog, Olsen and Schofield phosphate levels. All three values fell rapidly with time, but whereas the Schofield values moved towards the value of the untreated plots, the Truog and Olsen values appeared to move towards an equilibrium level above that of the untreated soils.

(4) Olsen and Truog reagents extracted different fractions of phosphate. This was indicated by a different ratio of Olsen phosphate:Truog phosphate in the two soils coupled with a differing rate of decline of Olsen phosphate.

(5) Although the level of phosphate maintained in the soil solution was similar in the untreated Foxton and Pukepuke soils, the level of phosphate maintained in the soil solution was lower in the treated Pukepuke soil than in the treated Foxton soil. This was demonstrated by the amounts of phosphate in solution at equilibrium in $CaCl_2$ extracts.

(6) Sorption data obtained by the method of Ozanne and Shaw showed that to raise the phosphate level of the untreated soils to an adequate level required the addition of 4.5 times as much phosphate to the Pukepuke soil as to the Foxton soil.

(7) Addition of superphosphate to the two soils produced a temporary depression of pH, part of which may have been due to the salt effect.

(8) For both the Pukepuke and Foxton control soils, organic phosphorus accounted for much of the total phosphate in the top 5cm (43.6 and 52.8 percent respectively).

(9) The coefficient of variation for the estimation of the various phosphate fractions generally varied from 5-26% depending upon the soil and the fraction. The maximum variation was observed for the estimation of iron-bound phosphate.

(10) The order of importance, with respect to amount, of the inorganic phosphate fractions in the control soils was residual, calcium-bound, aluminium-bound and iron-bound phosphate in the Foxton soil and residual, iron-bound, calcium-

bound and aluminium-bound phosphate in the Pukepuke soil.

(11) Addition of superphosphate to the Foxton soil produced increases, in order of amount, in the aluminium-bound, easily-soluble, calcium-bound and iron-bound phosphate fractions, while increases, in order of amount, in the aluminium-bound, iron-bound, easily-soluble and calcium-bound phosphate fractions were found after addition of phosphate to the Pukepuke soil.

(12) Addition of superphosphate had no significant effect on the organic phosphorous levels in either soil over the twelve month experimental period.

(13) With increased time after application of superphosphate, both soils showed a decrease in the easily-soluble and aluminium-bound phosphate fractions and an increase in the iron-bound phosphate fraction. The Pukepuke soil showed a more rapid decline in the easily-soluble and aluminium-bound phosphate fractions than did the Foxton soil.

(14) The method for determination of calcium-bound phosphate used in the present study gave a good estimation of calcium-bound phosphate, but the procedure of Chang and Jackson (1957a) would overestimate the calcium-bound phosphate at the expense of the reductant-soluble and/or occluded aluminium and iron phosphates in the Pukepuke soil.

(15) The difference in pH between the two soils did not appear to affect the amount of added phosphate appearing in the calcium-bound phosphate fraction. It is suggested that the small increase in calcium-bound phosphate is at least partially due to the presence of unreacted apatite in the superphosphate applied to the soils. However, calcium-bound phosphate appeared to be more stable in the Pukepuke

soil where the pH was higher.

(16) An increase in the residual phosphate fraction of the Pukepuke soil was noted six weeks after the application of superphosphate. The fact that the increase in the residual phosphate fraction was not extracted by NH_4F, NaOH or 0.5N HCl indicates that it is not in a discrete form such as variscite, strengite or apatite. However, because it was solubilized by extraction with 1N HCl, which also removed a large amount of iron, it is suggested that this phosphate is occluded by an iron oxide coating, removal of which exposes the phosphate to the extracting reagent.

* * * * * * *

ACKNOWLEDGEMENTS

I wish to acknowledge gratefully the following people who have rendered assistance throughout the course of this study:

Dr. C.V. Fife for initiation of the project and helpful guidance and instruction throughout the course of study and in the preparation of this manuscript;

Mr J.A. Pollok for his assistance in the choice of field sites and guidance in pedological aspects of the study;

Dr. J.H. Kirkman for his valuable assistance with the X-ray analysis and in the preparation of this manuscript;

Professor J.K. Syers for constructive criticism of this manuscript;

Mrs Linda Morpeth for typing this thesis.

The author also expresses his thanks to the technicians of the Soil Science Department for their assistance, and to the Massey University Photographic Unit and Printery for the preparation of photographs and figures.

BIBLIOGRAPHY

AQUILERA, N.H. and JACKSON, M.L., 1953. Iron oxide removal from soils and clays. Proc. Soil Sci. Am. 17:359-364.

AHMAD, N. and JONES, R.L., 1967. Forms of occurrence of inorganic phosphorus and its chemical availability in the limestone soils of Barbados. Proc. Soil Sci. Soc. Am. 31:184-188.

AL-ABBAS, A.H.; SIRIWARDENE, P.P.; WEERASEKARA, D.A. et al. 1966. Isotopic exchange and availability studies on inorganic soil phosphorus fractions on some rice soils of Ceylon. Isotop. Pl. Nutr. Physiol., Proc. Symp. Vienna 13-25.

APPELT, H. and SCHALSCHA, E.B., 1970. Effect of added phosphate on the inorganic phosphate fractions of soils derived from volcanic ash. Proc. Soil Sci. Soc. Am. 34:599-602.

BALLARD, R., 1968. The phosphate status of the soils of Riverhead forest in relation to growth of Radiata pine. Thesis, Massey University, New Zealand.

BAPAT, M.V. and BEDEKAR, V.G., 1965. Fertilizer phosphorus in fractions of soil phosphorus. J. Indian Soc. Soil Sci. 13:273-279.

BAUWIN, G.R. and TYNER, F.H., 1957. The distribution of nonextractable phosphorus in some gray-brown podzolic, brunizem, and planosol soil profiles. Proc. Soil Sci. Soc. Am. 21:245-250.

BEZUGLAYA, YU.M., 1969. Forms of phosphorus compounds in sod-podzolic soils under long-term experiments. Soviet Soil Sci. 1:567-572.

BHANGOO, M.S. and SMITH, F.W., 1957. Fractionation of phosphorus in Kansas soils and its significance in response of wheat to phosphatic fertilizers. Agron. J. 49:354-358.

BLACK, C.A. and GORING, C.A.T., 1953. Organic phosphorus in soils. In Agronomy Monograph 4:123-152.

BLASCO, M.L. and BOHORQUEZ, N.A., 1968. Fractionation of phosphorus in tropical soils of Colombia. Agrochimica 12:173-178.

BORLAN, Z.; BORDEIASU, C.; HERA, C. et al. 1968. The use of soil chemical testing data in agriculture. Trans. 9th Int. Congr. Soil Sci. 4:733-741.

BRAY, R.H. and DICKMAN, S.R., 1942. Adsorbed phosphates in soils and their relation to crop responses. Proc. Soil Sci. Soc. Am. 6:312-320.

BRAY, R.H.; DICKMAN, S.R., and KURTZ, L.T., 1945. Determination of total organic and available forms of phosphorus in soils. Soil Sci. 59:39-45.

BROMFIELD, S.M., 1970. The inadequacy of corrections for resorption of phosphate during the extraction of aluminium bound soil phosphate. Soil Sci. 109:388-390.

CARNAHAN, J.A., 1957. Botany of the Manawatu Sand Country. Proc. N.Z. Ecol. Soc. 5:17-18.

CECCONI, S., 1960. Investigations on the phosphorus enrichment of soil. 1. Non-calcareous soils. Agrochimica 5:68-96.

CESCAS, M.P.; TYNER, E.H., and SYERS, J.K., 1970. Distribution of apatite and other mineral inclusions in a rhyolitic pumice ash and beach sands from New Zealand: an electron microprobe study. J. Soil Sci. 21:78-84.

CHAI, M.C. and CALDWELL, A.C., 1959. Forms of phosphorus and fixation in soils. Proc. Soil Sci. Soc. Am. 23:458-460.

CHANG, S.C. and CHU, W.K., 1961. The fate of soluble phosphate applied to soils. J. Soil Sci. 12:286-293.

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

CHANG, S.C. and JACKSON, M.L., 1957b. Solubility product of iron phosphate. Proc. Soil Sci. Soc. Am. 21:265-269.

CHANG, S.C. and JACKSON, M.L., 1958. Soil phosphorus fractions in some representative soils. J. Soil. Sci. 9:109-119.

CHANG, S.C. and JUO, S.R., 1963. Available phosphorus in relation to forms of phosphate in soils. Soil Sci. 95:91-96.

CHANG, S.C. and LIAW, F.H., 1962. Separation of aluminium phosphate from iron phosphate in soils. Science 136:386.

CHIRIKOV, F.V. and VOLKOVA, V.V., 1945. The availability to plants of the phosphoric acid of different forms of soil phosphate. Soils Fertil. 8:78-79.

CLARIDGE, G.G.C., 1961. Mineralogy and origin of the yellow-brown sands and related soils. N.Z. Geol. Geophys. 4:48-72.

COCKAYNE, L., 1911. Report on the dune areas of New Zealand, their geology, botany and reclamation. Government printer, Wellington.

COLWELL, J.D. and DONNELLY, J.D., 1971. Effects of soil composition on the relationships between soil test values for phosphorus fertilizer requirements. Aust. J. Soil Res. 9:43-54.

COWIE, J.D., 1957. The soils of the Manawatu sand country. Proc. N.Z. Ecol. Soc. 5:15-16.

COWIE, J.D., 1963. Dune-building phases in the Manawatu. N.Z. Jl. Geol. Geophys. 6:268-280.

COWIE, J.D., 1968. Pedology of soils from wind-blown sand in the Manawatu district. N.Z. Jl. Sci. 11:459-487.

COWIE, J.D.; FITZGERALD, P. and OWENS, W., 1967. Soils of the Manawatu-Rangitikei sand country. N.Z. Soil Bureau Bulletin 29.

COLE, C.V. and OLSEN, S.R. 1959. Phosphorus solubility in calcdreous soils, Proc. Soil Sci. Soc. Am. 21: 265-269.

COWIE, J.D. and HALL, G.D., 1965. Soils and agriculture of the Flock House, Bulls, Manawatu. N.Z. Soil Bureau Rep 1/1965.

COWIE, J.D. and SMITH, B.A.J., 1958. Soils and agriculture of the Oroua Downs, Glen Oroua and Taikorea Districts, Manawatu County. N.Z. Soil Bureau Bulletin 16.

DAHNKE, W.C.; MALCOLM, J.L. and MENENDEZ, M.E., 1964. Phosphorus fractions in selected soil profiles of El Salvador as related to their development. Soil Sci. 98:33-38.

DATTA, N.P. and KHERA, M.S., 1969. Phosphorus soil tests based upon correlations with inorganic phosphorus fractions and greenhouse tests. J. Indian Soc. Soil Sci. 17:191-196.

DEAN, L.A., 1938. An attempted fractionation of soil phosphorus. J. Agric. Sci. 28:234-246.

DEAN, L.A., 1949. Fixation of soil phosphorus. Adv. Agron. 1:391-411.

ENSMINGER, L.E. and COPE, J.T., 1947. Effect of soil reaction on the efficiency of various phosphates for cotton and on loss of phosphorus by fixation. J. Amer. Soc. Agron. 39:1-11.

EVANS, T.D. and SYERS, J.K., 1971. An application of autoradiography to study the spacial distribution of ^{32}P- labelled orthophosphate added to soil crumbs. Proc. Soil Sci. Soc. Am. 35:906-909.

FASSBENDER, H.W., 1968. Phosphate retention and its different chemical forms under laboratory conditions for 14 Costa Rica soils. Agrochimica 12:512-521.

FIFE, C.V., 1959a. An evaluation of ammonium fluoride as a selective extractant for aluminium soil phosphate: 1. Preliminary studies on non-soil systems. Soil Sci. 87:13-21.

FIFE, C.V., 1959b. An evaluation of ammonium fluoride as a selective extractant for aluminium-bound soil phosphate: 2. Preliminary studies on soils. Soil Sci. 87:83-88.

FIFE, C.V., 1962. An evaluation of ammonium fluoride as a selective extractant for aluminium-bound soil phosphate: 3. Detailed studies on selected soils (1). Soil Sci. 93:113-123.

FIFE, C.V., 1963. An evaluation of ammonium fluoride as a selective extractant for aluminium-bound soil phosphate: 4. Detailed studies on soils (2). Soil Sci. 96:112-120.

FISHER, R.A. and THOMAS, R.P., 1935. The determination of the forms of inorganic phosphorus in soils. J. Am. Soc. Agron. 27:863-873.

FISKELL, J.G.A. and SPENCER, W.F., 1964. Forms of phosphate in Lakeland fine sand after six years of heavy phosphate and lime applications. Soil Sci. 97:320-327.

FOLLETT, E.A.C.; MC HARDY, W.J.; MITCHELL, B.D. and SMITH, B.F.L., 1965. Chemical dissolution techniques in the study of soil clays. Part 1. Clay miner. 6:23-34.

FRAPS, G.S., 1906. Availability of phosphoric acid of the soil. J. Am. Chem. Soc. 28:823-834.

FRAPS, G.S. and FUDGE, J.F., 1945. The nature of the phosphates dissolved by various soil extractants. J. Am. Soc. Agron. 37:532-541.

GHANI, M.O., 1943. Fractionation of soil phosphorus. Indian J. Agric. Sci. 13:29-45.

GLENN, R.C.; HSU, P.H.; COREY, R.B. and JACKSON, M.L., 1959. Flow sheet for soil phosphate fractionation. Agron. Abstr. 9.

GRIGG, J.L., 1965a. Inorganic phosphorus in South Island soils and their solubility in commonly used extracting solutions. N.Z. Jl. Agric. Res. 8:313-326.

GRIGG, J.L., 1965b. Prediction of plant response to fertilizer by means of soil tests. 1. Correlation of yield of potatoes grown on recent and gley recent soils with results of various methods of assessing available soil phosphorus. N.Z. Jl. Agric. Res. 8:893-904.

GRIGG, J.L., 1966. Changes in forms of soil inorganic phosphorus in Lismore stony silt loam due to application of superphosphate to pasture. N.Z. Jl. Agric. Res. 9:182-190.

SEN GUPTA, M.B. and CORNFIELD, A.H., 1963. Phosphorus in calcareous soils. 4. Nature of, and factors influencing the fixation of added phosphate. J. Sci. Fd. Agric. 14:873-877.

HALSTEAD, R.L., 1967. Chemical availability of native and applied phosphorus in soils and their textural fractions. Proc. Soil Sci. Soc. Am. 31:414-419.

HANLEY, P.K.; MC DONNELL, P. and MURPHY, M.D., 1965. Phosphorus studies of Irish soils. 1. Soil description and analytical data for thirty representative soils selected for special cropping studies. Irish J. Agric. Res. 4:81-92.

HARTER, R.D., 1968. Adsorption of phosphorus by lake sediment. Proc. Soil Sci. Soc. Am. 32:514-518.

HARTER, R.D., 1969. Phosphorus adsorption sites in soils. Proc. Soil Sci. Soc. Am. 33:630-632.

HEMWALL, J.B., 1957. The fixation of phosphorus by soils. Adv. Agron. 9:95-112.

HIBBARD, P.L., 1935. Factors influencing phosphate fixation in soils. Soil Sci. 39:337-358.

HORTENSTINE, C.C., 1966. Phosphorus fixation and phosphorus fractions in sandy soils. Proc. Soil Crop Sci. Soc. Fla 26:136-142.

HUFFMAN, E.O., 1962. Reactions of phosphate in soils: recent research by T.V.A. Proc. Fertil. Soc. 71:5-35.

HUFFMAN, E.O., 1968. The reactions of fertilizer phosphate with soils. Outl. Agric. 5:202-207.

HUFFMAN, E.O. and TAYLOR, A.W., 1963. The behaviour of water-soluble phosphate in soils. J. Agric. Fd. Chem. 2:182-187.

HUMPHREYS, F.R. and PRITCHETT, W.L., 1971. Phosphorus adsorption and movement in some sandy forest soils. Proc. Soil Sci. Soc. Am. 35:495-500.

HSU, P.H., 1964. Adsorption of phosphate by aluminium and iron in soils. Proc. Soil Sci. Soc. Am. 28:474-478.

HSU, P.H. and JACKSON, M.L., 1960. Inorganic phosphate transformations by chemical weathering in soils as influenced by pH. Soil Sci. 90:16-24.

JACKSON, M.L., 1958. Soil chemical analysis. Prentice-Hall inc.

JOHN, M.K., 1970. Colorimetric determination of phosphorus in soil and plant materials with ascorbic acid. Soil Sci. 109:214-220.

JOHN, M.K. and GARDNER, E.H., 1971. Forms of phosphorus in a sequence of soils developed on Fraser river alluvium. Can. J. Soil Sci. 51:363-369.

JORDAN, J.; SIMKINS, C.; COREY, G.; KNIGHT, R. and BAKER, G.O., 1952. Uptake and movement of fertilizer phosphorus. Soil Sci. 73:305-313.

JUO, A.S.R. and ELLIS, B.G., 1968. Chemical and physical properties of iron and aluminium phosphates and their relation to phosphorus availability. Proc. Soil Sci. Soc. Am. 32:216-221.

KAILA, A., 1961a. Fertilizer phosphorus in some Finnish soils. Maataloust. Aikakausk. 33:131-139.

KAILA, A., 1961b. Effect of incubation and liming on the phosphorus fractions in soil Maataloust. Aikakausk. 33:185-193.

KAILA, A., 1963a. Fertilizer phosphorus in various fractions of soil phosphorus. Maataloust. Aikakausk. 35:36-46.

KAILA, A., 1963b. Dependence of the phosphate sorption capacity on the aluminium and iron in Finnish soils. Maataloust. Aikakausk. 35:165-177.

KAILA, A., 1964a. Fractions of inorganic phosphorus in Finnish mineral soils. Maataloust. Aikakausk. 36:1-13.

KAILA, A., 1964b. Forms of newly retained phosphorus in mineral soils. Maataloust. Aikakausk. 36:65-76.

KAILA, A., 1965a. The fate of water-soluble phosphate applied to some mineral soils. Maataloust. Aikakausk. 37:104-115.

KAILA, A., 1965b. Effect of liming on the mobilization of soil phosphorus. Maataloust. Aikakausk. 37:243-254.

KAILA, A., 1967. Effect of liming on the fate of applied superphosphate phosphorus in some mineral soils. Maataloust. Aikakausk. 39:5-13.

KAILA, A., 1969. Residual effect of rock phosphate and superphosphate. Maataloust. Aikakausk. 41:82-88.

KAR, A.K. and CHAKRAVARTI, S.N., 1969. Availability and fixation of applied phosphate in some Indian soils. J. Indian Soc. Soil Sci. 17:47-49.

KHANNA, P.K., 1967. Inorganic soil phosphate fractions as related to soil-test values by common methods. Pl. Soil 26:277-284.

KHANNA, P.K. and DATTA, N.P., 1968. Distribution of inorganic soil phosphorus in some Indian soils as affected by added phosphates. Indian J. Agric. Sci. 38:668-676.

KHANNA, S.S. and MAHAJAN, K.K., 1968. Study of the role of inorganic phosphorus added in a legume-wheat cropping sequence. Indian J. Agric. Sci. 38:757-765.

KHIN, A. and LEEPER, G.W., 1960. Modifications in Chang and Jackson's procedure for fractionating soil phosphorus. Agrochimica 4:246-254.

KURTZ., L.T., 1942. Elimination of fluoride interference in the molybdenum blue reaction. Ind. Engng. Chem. analyt. Edn. 14:855.

KURTZ, L.T. and QUIRK, J.P., 1965. Phosphate adsorption and phosphate fractions in field soils of varying histories of phosphate fertilization. Aust. J. Agric. Res. 16:403-412.

LARSEN, S.; GUNARY, D. and SUTTON, C.D., 1965. The rate of immobilization of applied phosphate in relation to soil properties. J. Soil Sci. 16:141-148.

LARSEN, S. and WIDDOWSON, A.E., 1968.
Chemical composition of soil solution. J. Sci. Fd. Agric. 19:693-695.

LAVERTY, J.C., and MC LEAN, E.O., 1961. Factors affecting yields and uptake of phosphorus by different crops. 3. Kinds of phosphate-native, applied and formed. Soil Sci. 91:166-171.

LEHR, J.R.; BROWN, W.E. and BROWN, E.H., 1959. Chemical behaviour of monocalcium phosphate monohydrate in soils. Proc. Soil Sci. Soc. Am. 23:3-7.

LINDSAY, W.L. and STEPHENSON, H.F., 1959. Nature of the reactions of monocalcium phosphate monohydrate in soils. 2. Dissolution and precipitation reactions involving iron, aluminium, manganese and calcium. Proc. Soil Sci. Soc. Am. 23:18-22.

LYNCH, P.B. and DAVIES, E.B., 1964. Top-dressing of grassland with phosphates and lime. 3. Residual effects. N.Z. Jl. Agric. Res. 7:299-338.

MC CONAGHY, S. and STEWART, J.W.B., 1963. Availability of soil and fertilizer phosphates to growing crops. J. Sci. Fd. Agric. 14:329-341.

MAC KENZIE, A.F., 1962. Inorganic soil phosphorus fractions of some Ontario soils as studied using isotopic exchange and solubility criteria. Can. J. Soil Sci. 42:150-156.

MAC KENZIE, A.F. and AMER, S.A., 1964. Reactions of iron, aluminium and calcium phosphates in six Ontario soils. Pl. Soil 21:17-25.

MAHAPATRA, I.C., 1969. Effect of liming on native and added inorganic phosphate fractions and their transformation and availability on flooding. J. Indian Soc. Soil Sci. 17:109-113.

MAHAPATRA, I.C. and PATRICK, W.H., 1969. Inorganic phosphate transformation in water-logged soils. Soil Sci. 107:281-288.

MANDAL, L.N. and DAS, R.K., 1970. Transformation of applied water soluble phosphate in acid lowland rice soils. Soil Sci. 110:263-267.

MANNING, P.B. and SALOMON, M., 1965. Forms of phosphorus in soil after long-continued fertilization. Proc. Soil. Sci. Soc. Am. 29:421-423.

MASSEY, D.L.; SHEARD, R.W. and MILLER, M.H., 1970. Availability of reaction products of fertilizer phosphorus to alfalfa and bromegrass seedlings. Can. J. Soil Sci. 50:141-149.

MATHAN, K.K. and DURAIRAJ, D.J., 1967. Phosphorus fixation in Nilgiri soils. Madras Agric. J. 54:421-427.

MATTINGLY, G.E.G., 1963. Residual value of superphosphate and rock phosphate on an acid soil. J. Agric. Sci. 60:409-414.

MATTINGLY, G.E.G. and TALIBUDEEN, O., 1967. Progress in the chemistry of fertilizer and soil phosphorus. In "Topics in phosphorus chemistry" part 4:157-290. Rothamsted Exp. Stn.

MEHRA, O.P. and JACKSON, M.L., 1960. Iron oxide removal from soils and clays by a dithionite-citrate system buffered with sodium bicarbonate. Proc. 7th Nat. Conf. Clays 1959, 5:317-327.

MEHTA, N.C.; LEGG, J.O.; GORING, C.A.I. and BLACK, C.A., 1954. Determination of organic phosphorus in soils. 1. Extraction methods. Proc. Soil Sci. Soc. Am. 18:443-449.

MITCHELL, J., 1932. The origin, nature, and importance of soil organic constituents having base exchange properties. J. Am. Soc. Agron. 24:256-275.

MITCHELL, W.A., 1966. Methods of mineralogical analysis of soil. Proc. Int. Study Group in Soils, Cambridge.

MITCHELL, B.D. and MACKENZIE, R.C., 1954. The removal of free iron oxides from soil clays. Soil Sci. 77:173-184.

MORILLO, M.R. and FASSBENDER, H.W., 1968. Forms and availability of phosphates in soils of the lower basin of the Choluteca River, Honduras. Turrialba 18:26-33.

MOSCHLER, W.W.; KREBS, R.D. and OBENSHAIN, S.S., 1957. Availability of residual phosphate and superphosphate applications to Groseclose silt loam. Proc. Soil Sci. Soc. Am. 21:293-295.

MOSER, F., 1941. Fixation and recovery of phosphate from some lateritic soils. Proc. Soil Sci. Soc. Am. 6:328-334.

MUIR, J.W., 1952. The determination of total phosphorus in soil. Analyst. 77:313-317.

MURPHY, J. and RILEY, J.P., 1962. A modified single solution method for the determination of phosphate in natural waters. Anal. Chim. Acta. 27:31-36.

MURRMANN, R.P. and PEECH, M. 1968. Reaction products of applied phosphate in limed soils. Proc. Soil Sci. Soc. Am 32: 493-496.

NYE, P.H., 1963. Soil analysis and the assessment of fertility in tropical soils. J. Sci. Fd. Agric. 14:277-280.

NYE, P.H., 1968. Processes in the root environment. J. Soil Sci. 19:205-215.

OLSEN, S.R.; COLE, C.V.; WATANABE, F.S. and DEAN, L.A., 1954. Estimation of available phosphorus in soils by extraction with sodium bicarbonate. Dep. Circ. U.S. Dept. Agric. 939.

OZANNE, P.G.; KIRTON, D.J. and SHAW, T.C., 1961. The loss of phosphorus from sandy soils. Aust. J. Agric. Res. 12:409-423.

OZANNE, P.G. and SHAW, T.C., 1967. Phosphate sorption by soils as a measure of the phosphate requirement for pasture growth. Aust. J. Agric. Res. 18:601-612.

PATEL, J.M. and MEHTA, B.V., 1961. Soil phosphorus fractionation studies. Proc. Soil Sci. Am. 25:190-192.

PETERSON, G.W. and COREY, R.B., 1966. A modified Chang and Jackson procedure for routine fractionation of inorganic soil phosphates. Proc. Soil. Sci. Soc. Am. 30:563-565.

PIPER, C.S., 1942. Soil and plant analysis. Hanssell press, Adelaide, Australia.

DU PLESSIS, S.F. and BURGER, R. dut. 1966. The availability of different phosphate fractions. S. Afr. J. Agric. Sci. 9:331-340.

PRATT, P.F., 1961. Phosphorus and aluminium interactions in the acidification of soils. Proc. Soil Sci. Soc. Am. 25:467-469.

PRATT, P.F. and GARBER, M.J., 1964. Correlations of phosphorus availability by chemical tests with inorganic phosphorus fractions. Proc. Soil Sci. Soc. Am. 28:23-26.

RAJENDRAN, N. and SUTTON, C.D., 1970. Re-sorption of soil phosphate during fractionation. J. Soil Sci. 21:199-202.

ROBERTSON, G., 1950. The colorimetric determination of aluminium in silicate materials. J. Sci. Fd. Agric. 1:59-63.

ROBERTSON, N.G., 1959. The climate of New Zealand. In "A descriptive atlas of New Zealand." Government printer, Wellington.

ROBERTSON, W.K. and HUTTON, C.E., 1960. Retention of fertilizer elements in Red Bay fine sandy loam. Proc. Soil Crop. Sci. Soc. Fla. 20:158-166.

ROBERTSON, W.K.; HUTTON, C.E. and THOMPSON, L.G., 1966. Availability and fractionation of residual phosphorus in soils high in aluminium and iron. Proc. Soil Sci. Soc. Am. 30:446-450.

RUSSELL, E.W., 1961. Soil conditions and plant growth. 9th ed. Longmans, Green and Co. Ltd., London.

SANDELL, E.B., 1944. Colorimetric determination of traces of metals. Interscience Publishers inc., New York.

SAUNDERS, W.M.H., 1958. The effect of different phosphate fertilizers on soil pH and the consequent effect on phosphate retention. N.Z. Jl. Agric. Res. 1:675-682.

SAUNDERS, W.M.H., 1959a. Effect of phosphate top-dressing on a soil from andesitic volcanic ash. 1. Forms of soil phosphorus and a method for their determination. N.Z. Jl. Agric. Res. 2:427-444.

SAUNDERS, W.M.H., 1959b. Effect of phosphate top-dressing on a soil from andesitic volcanic ash. 2. Effect on distribution of phosphorus and on related chemical properties. N.Z. Jl. Agric. Res. 2:445-462.

SAUNDERS, W.M.H., 1959c. Aluminium extracted by neutral citrate-dithionite reagent. Nature 184:2037.

SAUNDERS, W.M.H., 1968. Phosphorus. In "Soils of New Zealand." N.Z. Soil Bureau Bulletin 26, part 2.

SCARSETH, G.D. and TIDMORE, J.W., 1934. The fixation of phosphates by clay soils. J. Amer. Soc. Agron. 26:152-162.

SCHOFIELD, R.K., 1955. Can a precise meaning be given to "available" soil phosphorus? Soils Fertil. 18:373-375.

SELL, O.E. and OLSEN, L.C., 1946. The effect of surface-applied phosphate and limestone on soil nutrients and pH of permanent pasture. Proc. Soil Sci. Soc. Am. 11:238-245.

SHAH, R.; SYERS, J.K.; WILLIAMS, J.D.H. et al. 1968. The forms of inorganic phosphorus extracted from soils by N sulphuric acid. N.Z. Jl. Agric. Res. 11:184-191.

SHELTON, J.E. and COLEMAN, N.T., 1968. Inorganic phosphorus fractions and their relation to residual value of large applications of phosphorus on high phosphorus fixing soils. Proc. Soil Sci. Soc. Am. 32:91-94.

SHERRELL, C.G., 1970. Comparison of chemical extraction methods for the determination of "available" phosphate in soils. 1. Correlation between methods and yield and phosphorus uptake by white clover grown on 16 North Island soils in the glasshouse. N.Z. Jl. Agric. Res. 13:481-493.

SINGH, R.N.; MARTENS, D.C. and OBENSHAIN, S.S., 1966. Plant availability and form of residual phosphorus in Davidson clay loam. Proc. Soil Sci. Soc. Am. 30:617-620.

SMITH, A.N., 1965a. Aluminium and iron phosphates in soils. J. Aust. Inst. Agric. Sci. 31:110-126.

SMITH, A.N., 1965b. The supply of soluble phosphorus to the wheat plant from inorganic soil phosphorus. Pl. Soil 22:314-316.

SMITH, A.N., 1965c. Distinction between iron and aluminium phosphate in Chang and Jacksons procedure for fractionating inorganic soil phosphorus. Agrochimica 9:162-168.

SMITH, A.N., 1967. The role of inorganic soil phosphates in supplying phosphorus to the wheat plant. Agrochimica 11:79-91.

SMITH, A.N., 1968. The uptake of phosphorus by wheat and clover from four inorganic soil phosphate fractions after the addition of contrasting types of phosphate fertilizer. Pl. Soil 29:144-155.

SMITH, A.N., 1969a. Growth of wheat and changes in phosphorus availability in waterlogged soils. Agrochimica 13:235-242.

SMITH, A.N., 1969b. Fractionation of inorganic phosphorus in soils. The Chang and Jackson fractionation procedure: its limitations and uses. Agri. Digest No. 17:10-19.

SMITH, A.N., 1972. Corrections for resorption of phosphate during the extraction of aluminium-bound soil phosphate. Soil Sci. 113:55-56.

SMITH, A.N. and SIMPSON, K., 1950. Factors affecting the uptake of phosphorus by plants. J. Sci. Fd. Agric. 1:208-212.

SMITH, P.F., 1956. Effect of phosphatic fertilization on root growth, soil pH, and chemical constituents at different depths in an acid sandy Florida citrus soil. Proc. Fla. Hort. Soc. 69:25-29.

SRIVASTAVA, O.P. and PATHAK, A.N., 1969. A comparison of various laboratory methods for determining the phosphate availability in soils. Indian J. Sci. Ind. 34:77-82.

STEWARD, J.H. and OADES, J.M., 1972. The determination of organic phosphorus in soils. J. Soil Sci. 23:38-49.

SUSUKI, A.; LAWTON, K. and DOLL, E.C., 1963. Phosphorus uptake and soil tests as related to forms of phosphorus in some Michigan soils. Proc. Soil Sci. Soc. Am. 27:401-403.

SYERS, J.K.; ADAMS, J.A. and WALKER, T.W., 1970. Accumulation of organic matter in a chronosequence of soils developed on wind-blown sand in New Zealand. J. Soil Sci. 21:146-153.

SYERS, J.K.; CAMPBELL, A.S. and WALKER, T.W., 1970. Contribution of organic carbon and clay to cation exchange capacity in a chronosequence of sandy soils. Pl. Soil 33:104-112.

SYERS, J.K.; SHAH, R. and WALKER, T.W., 1969. Fractionation of phosphorus in two alluvial soils and particle size separates. Soil Sci. 108:283-289.

SYERS, J.K.; SMILLIE, G.W. and WILLIAMS, J.D.H., 1972. Calcium fluoride formation during extraction of calcareous soils with fluoride. 1. Implications to inorganic P fractionation schemes. Proc. Soil Sci. Soc. Am. 36:20-25.

SYERS, J.K. and WALKER, T.W., 1969a. Phosphorus transformations in a chronosequence of soils developed on wind-blown sand in New Zealand. 1. Total and organic phosphorus. J. Soil Sci. 20:57-64.

SYERS, J.K. and WALKER, T.W., 1969b. Phosphorus transformations in a chronosequence of soils developed on wind-blown sand in New Zealand. 2. Inorganic phosphorus. J. Soil Sci. 20:318-324.

SYERS, J.K.; WILLIAMS, J.D.H.; TYNER, E.H. and WALKER, T.W., 1969. Primary and secondary origin of "nonextractable" soil inorganic phosphorus. Proc. Soil Sci. Soc. Am. 33:635-636.

SYERS, J.K.; WILLIAMS, J.D.H. and WALKER, T.W., 1968. The determination of total phosphorus in soil and parent materials. N.Z. Jl. Agric. Res. 11:757-762.

TANDON, H.L.S., 1969. Fluoride extractable aluminium in soils. 1. Its relation to fluoride extractable phosphorus. Soil Sci. 108:397-401.

TAYLOR, A.W.; LINDSAY, W.L.; HUFFMAN, E.O. and GURNEY, E.L., 1963. Potassium and ammonium taranakites, amorphous aluminium phosphate, and variscite as sources of phosphate for plants. Proc. Soil Sci. Soc. Am. 27:148-151.

TERPUGOV, A.V. and YUZHAKOV, YU.I., 1969. Method of fractionating soil phosphorus. Soviet Soil Sci. 1:585-591.

TRIPATHI, B.R.; TANDON, H.L.S. and TYNER, E.H., 1970. Native inorganic phosphorus forms and their relation to some chemical indices of phosphorus availability for soils of Agra district, India. Soil Sci. 109:93-101.

TRUOG, E., 1930. The determination of readily available phosphorus in soils. J. Am. Soc. Agron. 22:874.

TRUOG, E. and DEAN, L.A., 1935. Determination of the phosphate and potash needs of soils by chemical analysis. Trans. 3rd Int. Congr. Soil Sci. 1:106-108.

VOLK, V.V. and MC LEAN, E.O., 1963. The fate of applied phosphorus in four Ohio soils. Proc. Soil Sci. Soc. Am. 27:53-58.

WATANABE, F.S. and OLSEN, S.R., 1965. Test of an ascorbic acid method for determining phosphorus in water and $NaHCO_3$ extracts from soil. Proc. Soil Sci. Soc. Am. 29:677-678.

WAY, J.T., 1850. On the power of soils to absorb manure. J. Royal Agric. Soc. 11:313-379.

WEIR, C.C. and SOPER, R.J., 1963. Solubility studies of phosphorus in some calcareous Manitoba soils. J. Soil Sci. 14:256-261.

WESTIN, F.C. and BUNTLEY, G.J., 1966. Soil phosphorus in South Dakota: 1. Inorganic phosphorus fractions in some soil series. Proc. Soil Sci. Soc. Am. 30:245-247.

WILD, A., 1950. The retention of phosphate by soil. A review. J. Soil Sci. 1:221-238.

WILD, A., 1964. Soluble phosphate in soil and uptake by plants. Nature 203:326-327.

WILLIAMS, C.H., 1950a. Studies on soil phosphorus: 1. A method for the partial fractionation of soil phosphorus. J. Agric. Sci. 40:233-242.

WILLIAMS, C.H., 1950b. Studies on soil phosphorus: 2. The nature of native and residual phosphorus in some South Australian soils. J. Agr. Sci. 40:243-256.

WILLIAMS, E.G. and SAUNDERS, W.M.H ., 1956. Distribution of phosphorus in profiles and particle-size fractions of some Scottish soils. J. Soil Sci. 7:90-108.

WILLIAMS, E.G. and STEWART, A.B., 1943. Studies on phosphate fixation in Scottish soils: 1. The recovery of added phosphate from a soil of the acid igneous group. J. Agric. Sci. 33:179-189.

WILLIAMS, J.D.H. Forms of soil phosphate in some genetically-related New Zealand soils. Phd. thesis, Lincoln College, N.Z.

WILLIAMS, J.D.H.; SYERS, J.K.; HARRIS, R.F. and ARMSTRONG, D.E., 1971. Fractionation of inorganic phosphate in calcareous lake sediments. Proc. Soil Sci. Am. 35:250-255.

WILLIAMS, J.D.H.; SYERS, J.K. and WALKER, T.W., 1967. Fractionation of soil inorganic phosphate by a modification of Chang and Jackson's procedure. Proc. Soil Sci. Soc. Am. 31:736-739.

WILLIAMS, J.D.H.; SYERS, J.K.; WALKER, T.W. and REX, R.W., 1970. A comparison of methods for the determination of soil organic phosphorus. Soil Sci. 110:13-18.

WILLIAMS, J.D.H. and WALKER, T.W., 1969. Fractionation of phosphate in a maturity sequence of New Zealand basaltic soil profiles. 1. Soil Sci. 107:22-30.

WILLIAMS, R., 1937. The solubility of soil phosphorus and other phosphorus compounds in sodium hydroxide solution. J. Agric. Sci. 27:260-270.

WOODS, J.T. and MELLON, M.G., 1941. The molybdenum blue reaction. Ind. Engng. Chem. analyt. Edn. 13:760-764.

YUAN, T.L. and FISKELL, J.G.A., 1959. Aluminium studies: 2. The extraction of aluminium from some Florida soils. Proc. Soil Sci. Soc. Am. 23:202-205.

YUAN, T.L.; ROBERTSON, W.K. and NELLER, J.R., 1960. Forms of newly fixed phosphorus in three acid sandy soils. Proc. Soil Sci. Am. 24:447-450.

*APPENDIX 1(a)

RAINFALL

(a) Mean monthly and annual rainfall (mm)
(b) Extreme monthly and annual rainfall (mm)
(c) Average annual number of raindays

Station		Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Year
Foxton	(a)	59.43	63.23	53.09	64.01	79.50	87.63	76.96	78.49	63.50	82.04	73.15	68.33	848.37
(1912–1954)	(b)	162.05	204.72	143.26	125.98	229.11	213.36	169.67	176.78	132.08	180.09	198.12	193.29	1128.78
	(c)													119
Waitarere	(a)	52.83	68.33	45.21	69.60	68.83	94.23	73.91	73.91	41.91	87.38	87.48	83.82	867.84
(1948–1954)	(b)	96.52	92.20	64.01	109.98	126.24	151.89	123.95	115.82	97.79	160.78	171.70	151.99	993.65
Glen Oroua	(a)	69.34	67.06	58.17	69.60	75.95	96.77	68.58	79.25	62.48	82.04	78.23	75.44	882.91
(1935–1954)	(b)	165.10	168.91	155.19	132.59	210.57	222.00	152.91	165.10	145.80	173.48	187.48	152.15	1004.57
Tangimoana	(a)	64.26	78.49	53.85	73.66	88.90	90.17	75.69	78.23	67.06	82.80	65.79	71.63	890.53
(1923–1949)	(b)	143.76	213.11	149.61	153.67	222.00	201.93	162.05	177.80	155.70	189.74	127.00	192.79	1049.53
	(c)													140
Flock House,	(a)	59.94	65.53	54.86	70.10	75.18	90.42	68.58	80.01	59.69	84.33	73.91	70.87	853.42
Bulls	(b)	159.51	164.34	113.54	130.05	197.36	194.31	149.10	184.66	153.92	174.24	232.16	180.59	1021.59
(1926–1954)	(c)													120
Waitatapia	(a)	64.80	68.58	59.69	78.74	84.58	86.87	78.99	74.17	68.07	91.19	77.72	69.85	904.80
(1895–1954)	(b)	196.93	196.60	192.02	198.12	232.16	224.03	163.32	191.26	162.56	179.32	172.47	192.79	1197.36
	(c)													143

*Adapted from Cowie, et al. (1967).

APPENDIX 1(b)

Temperatures (^{o}C) And Humidity At Flock House, Bulls (1948-1954)

	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Year
Mean Monthly Temperature	16.11	17.28	15.67	12.9	10.8	8.9	8.0	8.60	10.6	12.2	14.3	15.7	12.6
Mean Daily Maximum Temperature	20.6	21.8	20.2	17.3	15.6	13.0	12.3	13.1	14.9	16.4	18.3	19.8	16.9
Mean Daily Minimum Temperature	11.6	12.8	11.1	8.4	5.9	4.9	3.6	4.1	6.2	8.1	10.4	11.6	8.2
Absolute Maximum Temperature	28.3	30.0	27.2	23.6	25.0	19.9	18.1	19.2	21.9	21.6	23.7	30.6	30.6
Absolute Minimum Temperature	2.8	4.9	0.7	-1.6	-1.5	-4.4	-3.3	-2.6	-2.8	-1.1	2.5	3.1	4.4
Mean Number of Days of Ground Frost	0.2		0.2	2.7	6.3	9.2	14.2	9.7	5.8	2.3	0.1		50.7
Average Relative Humidity (%) at 9 a.m.	72	76	76	82	85	84	85	82	80	75	75	74	79
Mean 4" Earth Temperature at 9 a.m.	19.1	18.8	16.3	12.3	9.3	7.4	6.1	6.7	10.8	13.4	16.4	18.6	12.9
Mean 8" Earth Temperature at 9 a.m.	19.8	19.8	17.8	14.0	10.8	8.7	7.3	8.2	10.9	14.1	16.8	18.8	13.9

*Adapted from Cowie, et al. (1967).

APPENDIX 1(c)

*Sand Dune Vegetation In The Manawatu Sand Country

Situation	Type of Plant	Botanical Names	Common Names
Foredune	grass	Spinifex hirsutus	silvery sand grass
	"	Desmoschoenus spiralis	pingao
	"	Ammophila arenaria	marrum grass
Relatively stable inland slope of foredune	shrub	Cassinia leptophylla	cottonwood
	"	Coprosma acerosa	dune coprosma
	"	Pimelea arenaria	sand-pimelea
	"	Lupinus arboreus	tree lupin
Stable landward slope of foredune	herb	Gnaphalium luteoalbum	white cadweed
	"	Leontodon hispidus	
	"	Erigeron sp.	e.g. horseweed, plebrane
	grass	Deyecixia billardieri	
Further inland on more stable dunes	herb	Sonchus oleraceus	annual sowthistle
	grass	Holcus lanatus	Yorkshire fog
	"	Festuca arundinacea	tall fescue
	shrub	Olearia solundri	
	"	Leptaspermum scoparium	red tea-tree
	"	Ulex europaeus	gorse
	"	Cytisus scorparius	common broom
	"	Discaria toumatou	wild irishman
	grass	Arundo conspicua	toetoe
	"	Phormium tenax	flax
	tree	Cordyline australis	cabbage-tree
		Pteridium esculentum	bracken fern
		Muchlenbeckia complexa	

The original pre-European climax appears to have been stable shrubland. Today modified latter stages of the climax with principal species Pteridium escalentum and/or Lupinus arboreus occur with a varying admixture of the other shrubby species.

*Compiled from Cockayne (1911) and Carnahan (1957).

APPENDIX 1(d)

*Sand Plain Vegetation In The Manawatu Sand Country

Situation	Type of Plant	Botanical Name	Common Name
First colonists	grass-like herb	Carex pumila Selliera radicans Gunnera arenaria	dune sedge creeping-selliera sand gunnera
Second group of colonizers	herb	Scirpus nodosus	
		Leptocarpus simplex	red rush
		Mariscus ustulatus	mariscus
	grass	Holcus lanatus	Yorkshire fog
	herb	Trifolium sp.	
		Leontodon hispidus	
	herb	Ranunculus sp.	buttercup
Climax	shrub	Essentially the same shrubs and associated species as the latter enteries into the dune succession.	

In some sand-hollows, the pre-European succession appears to have proceeded to semi-swamp forest. Dominant species are Podocarpus dacrydioides and Laurelia novaezelandiae.

*Compiled from Cockayne (1911) and Carnahan (1957).

APPENDIX 2

PROFILE DESCRIPTIONS

Soil: Pukepuke brown sandy loam.

Location: Approximately 0.4 km north of Himatangi block road and Koputaroa road corner.

Grid Reference: N148/894291.

Slope: Flat.

Vegetation: Pasture. White clover (*Trifolium repens*), perennial rye (*Lolium perenne*), buttercup (*Ranunculus repens, L.*), narrow leaf plantain (*Plantago lanceolata, L.*), cocksfoot (*Dactylis glomerata*), Californian thistle (*Cirsium arvense*).

Horizon:

A_h 0-22cm. Dark brown (7.5YR3/2) sandy loam friable; weakly developed fine nutty structure; some reddish yellow and pale grey mottling; the latter occurring in pockets associated with surface gleying; abundant plant roots, many worms, moist; abrupt wavy boundary;

B1g 22-36cm. Grey (7.5YR5/0) sand, abundant large prominent strong brown mottles (7.5YR5/6); loose; single grained; some roots becoming fewer with depth; moist; diffuse boundary.

B2g 36-60cm. Dark grey (7.5YR4/0) sand; many large prominent strong brown mottles (7.5YR5/6); loose; single grained; some decaying tree

	roots; practically no living roots; wet; diffuse boundary;
Cgg 60cm.	Dark grey (7.5YR5/6) sand; loose; single grained; no plant roots; water table at 63cm.
Parent Material:	Wind-blown sand.
Classification:	Yellow brown sand.

Soil: Foxton black sand.

Location: Himatangi block road, 300 yards south of Paranui road.

Grid Reference: N148/883254.

Slope: 23°.

Aspect: N.N.E.

Vegetation: Browntop (*Agrostis tenuis*); sweet vernal (*Anthoxanthum odoratum*); white clover (*Trifolium repens*); flat weeds.

Horizon:

A_h 0-22cm. Black (10YR2/1) sand; very friable; moderately developed medium nutty structure; many roots; moist; abrupt boundary;

B 22-36cm. Dark brown (10YR4/3) sand; friable; weakly developed medium nutty structure in upper part of horizon grading to single grained beneath; some roots; moist; diffuse boundary;

C 36cm. Olive brown (2.5Y4/4) sand; loose; single grained; some roots but number decreasing with depth; moist.

Parent Material: Wind-blown sand.

Classification: Yellow brown sand.

APPENDIX 3

TABLE 1

Mean ($\bar{x}$) Standard Error (SE) And Coefficient Of Variation (CV) Of Total Phosphate Determined Prior To And At Intervals After The Addition Of Superphosphate To The Foxton And Pukepuke Phosphate Treated Soils, And For The Control Soils At The Commencement And End Of The Experimental Period

	Phosphate Treated Soils					Control Soils	
	Sampling Dates					Sampling Dates	
	Mar 5 1971	Apr 16 1971	Jul 14 1971	Nov 2 1971	Feb 23 1972	Apr 16 1971	Feb 23 1972
	Foxton Soils						
$\bar{x}$	62.11	102.77	94.17	94.53	87.56	61.13	62.61
SE	0.44	1.28	2.01	1.44	1.14	0.60	0.75
CV	2.26%	3.93%	6.76%	4.82%	4.14%	3.11%	3.80%
	Pukepuke Soils						
$\bar{x}$	167.83	258.99	254.76	246.88	238.30	162.24	153.79
SE	2.30	6.95	2.79	4.90	4.69	3.88	3.01
CV	4.33%	8.48%	3.47%	6.28%	6.23%	7.56%	6.19%

TABLE 2

Two-Tailed t Test Values Calculated As A Test For Significant Differences Between Total Phosphate Determined On Various Dates For The Foxton And Pukepuke Control And Phosphate Treated Soils

Test Between Samples Collected On	Foxton Soil		Pukepuke Soil	
	Control Soils	Phosphate Treated Soils	Control Soils	Phosphate Treated Soils
Apr 16 and Feb 23	1.370	11.280	4.922	3.439
Apr 16 and Jul 14	n.d.	4.078	n.d.	1.776
Jul 14 and Nov 2	n.d.	0.131	n.d.	1.425
Nov 2 and Feb 23	n.d.	2.353	n.d.	1.504

Figure required for significance at a particular probability.

5% 2.262

1% 3.250

n.d. not determined.

TABLE 3

Mean ($\bar{x}$) Standard Error (SE) And Coefficient Of Variation (CV). Of Schofield Extractable Phosphate Determined At Each Sampling For The Foxton And Pukepuke Control And Phosphate Treated Soils

	Sampling Dates						
	Apr 16 1971	May 19 1971	Jul 14 1971	Sep 8 1971	Nov 2 1971	Dec 24 1971	Feb 23 1972
	Foxton Control Soils Schofield Extractable Phosphate (mgP%)						
$\bar{x}$	0.018	0.012	0.027	0.024	0.018	0.025	0.025
SE	<0.001	0.001	0.001	0.001	0.001	<0.001	0.002
CV	5.50%	13.27%	16.99%	15.45%	10.99%	5.61%	26.70%
	Foxton Phosphate Treated Soils Schofield Extractable Phosphate (mgP%)						
$\bar{x}$	1.55	1.37	0.92	0.59	0.41	0.58	0.32
SE	0.06	0.08	0.08	0.03	0.02	0.03	0.03
CV	12.89%	19.36%	28.65%	16.37%	12.83%	14.21%	25.61%
	Pukepuke Control Soils Schofield Extractable Phosphate (mgP%)						
$\bar{x}$	0.027	0.047	0.022	0.021	0.019	0.023	0.025
SE	0.001	0.002	0.002	0.001	0.001	0.001	0.002
CV	14.52%	10.27%	22.57%	30.16%	10.69%	10.64%	26.70%
	Pukepuke Phosphate Treated Soils Schofield Extractable Phosphate (mgP%)						
$\bar{x}$	1.73	2.10	0.32	0.15	0.12	0.13	0.07
SE	0.16	0.13	0.04	0.01	0.01	0.01	<0.01
CV	29.17%	19.23%	34.97	22.67%	15.59%	13.78%	18.43%

TABLE 4

Mean ($\bar{x}$) Standard Error (SE) And Coefficient Of Variation (CV) Of Olsen And Truog Extractable Phosphate Determined At Each Sampling For The Foxton Control And Phosphate Treated Soils

	Sampling Dates						
	Apr 16 1971	May 19 1971	Jul 14 1971	Sep 8 1971	Nov 2 1971	Dec 24 1971	Feb 23 1972
	Foxton Control Soils Olsen Extractable Phosphate (mgP%)						
$\bar{x}$	1.02	0.64	0.37	0.71	0.68	0.68	0.63
SE	0.04	0.01	0.01	0.01	0.17	0.02	0.04
CV	11.67%	6.67%	11.37%	5.09%	8.17%	7.99%	21.62%
	Foxton Phosphate Treated Soils Olsen Extractable Phosphate (mgP%)						
$\bar{x}$	10.18	9.33	8.59	6.77	5.63	6.68	5.92
SE	1.46	0.33	0.44	0.22	0.24	0.23	0.36
CV	14.35%	11.25%	16.21%	10.20%	13.67%	10.93%	0.19%
	Foxton Control Soils Truog Extractable Phosphate (mgP%)						
$\bar{x}$	2.13	1.62	1.82	1.18	1.33	1.72	1.97
SE	0.21	0.03	0.06	0.04	0.02	0.04	0.11
CV	31.69%	6.21%	16.36%	10.51%	5.50%	7.80%	17.80%
	Foxton Phosphate Treated Soils Truog Extractable Phosphate (mgP%)						
$\bar{x}$	28.90	25.40	22.28	17.50	12.99	15.10	13.71
SE	1.16	1.68	0.97	0.49	0.58	0.41	0.66
CV	12.64%	20.94%	13.73%	8.70%	14.23%	8.65%	15.21%

TABLE 5

Mean ($\bar{x}$) Standard Error (SE) And Coefficient Of Variation (CV) Of Olsen And Truog Extractable Phosphate Determined At Each Sampling For The Pukepuke Control Soils And Phosphate Treated Soils

	Sampling Dates						
	Apr 16 1971	May 19 1971	Jul 14 1971	Sep 8 1971	Nov 2 1971	Dec 24 1971	Feb 23 1972
	Pukepuke Control Soils Olsen Extractable Phosphate (mgP%)						
$\bar{x}$ SE CV	2.11 0.07 9.89%	1.93 0.07 11.59%	1.49 0.05 10.23%	1.69 0.07 12.66%	1.27 0.03 7.82%	1.65 0.05 9.46%	1.69 0.07 13.46%
	Pukepuke Phosphate Treated Soils Olsen Extractable Phosphate (mgP%)						
$\bar{x}$ SE CV	21.48 0.71 10.41%	18.94 0.63 10.44%	16.80 1.03 19.42%	11.38 0.18 5.07%	7.52 0.33 13.85%	7.67 0.22 8.96%	7.91 0.23 9.37%
	Pukepuke Control Soils Truog Extractable Phosphate (mgP%)						
$\bar{x}$ SE CV	2.83 0.13 14.47%	4.25 0.19 14.10%	2.77 0.12 14.10%	3.87 0.17 13.56%	2.46 0.11 14.03%	3.40 0.16 15.15%	2.91 0.10 10.72%
	Pukepuke Phosphate Treated Soils Truog Extractable Phosphate (mgP%)						
$\bar{x}$ SE CV	37.30 1.92 16.28%	3.33 1.94 18.41%	33.50 1.56 14.71%	23.68 0.63 8.42%	16.24 0.61 11.94%	16.50 0.79 15.11%	16.29 0.52 10.18%

TABLE 6

Mean ($\bar{x}$) Standard Error (SE), And Coefficient Of Variation (CV) Of Four Inorganic Phosphate Fractions Determined For The Foxton Control And Phosphate Treated Soils

	Phosphate Treated Soils				Control Soils	
	Sampling Dates				Sampling Dates	
	Apr 16 1971	Jul 14 1971	Nov 2 1971	Feb 23 1972	Apr 16 1971	Feb 23 1972
	NH_4Cl-Soluble Phosphate (mgP%)					
$\bar{x}$	10.76	4.70	4.45	3.45	-	-
SE	0.64	0.35	0.26	0.22	-	-
CV	18.68%	23.32%	18.34%	20.19%	-	-
	Corrected Aluminium-Bound Phosphate (mgP%)					
$\bar{x}$	24.59	25.39	20.35	18.15	5.64	5.59
SE	0.81	1.03	0.81	0.88	0.11	0.12
CV	10.46%	12.80%	12.52%	15.28%	6.07%	7.04%
	Corrected Iron-Bound Phosphate (mgP%)					
$\bar{x}$	3.15	2.88	5.77	8.04	0.99	0.46
SE	0.56	0.34	0.48	0.56	0.22	0.08
CV	55.21%	37.44%	26.40%	22.03%	71.49%	57.26%
	Calcium-Bound Phosphate (mgP%)					
$\bar{x}$	17.47	13.43	11.19	10.41	8.49	8.24
SE	1.20	0.56	0.70	0.86	0.29	0.36
CV	21.79%	13.18%	19.88%	26.06%	10.99%	13.86%

TABLE 7

Mean ($\bar{x}$) Standard Error (SE), And Coefficient Of Variation (CV) Of Four Inorganic Phosphate Fractions Determined For The Pukepuke Control And Phosphate Treated Soils

	Phosphate Treated Soils				Control Soils	
	Sampling Dates				Sampling Dates	
	Apr 16 1971	Jul 14 1971	Nov 2 1971	Feb 23 1972	Apr 16 1971	Feb 23 1972
	NH_4Cl-Soluble Phosphate (mgP%)					
$\bar{x}$	17.61	9.90	5.34	3.67	-	-
SE	0.88	0.53	0.32	0.10	-	-
CV	15.83%	17.08%	18.50%	8.75%	-	-
	Corrected Aluminium-Bound Phosphate (mgP%)					
$\bar{x}$	36.74	34.52	27.91	23.88	6.70	2.87
SE	1.89	1.78	1.35	0.73	0.32	0.24
CV	16.26%	16.25%	15.33%	9.61%	14.91%	26.63%
	Corrected Iron-Bound Phosphate (mgP%)					
$\bar{x}$	46.78	53.07	55.42	57.20	26.83	21.84
SE	2.66	1.44	1.11	1.84	1.14	0.77
CV	17.97%	8.57%	6.36%	10.17%	13.40%	11.17%
	Calcium-Bound Phosphate (mgP%)					
$\bar{x}$	41.86	42.07	41.36	36.51	26.60	25.57
SE	3.51	1.28	1.84	1.25	0.66	0.48
CV	26.48%	9.61%	14.13%	10.86%	7.90%	5.48%

TABLE

Mean ($\bar{x}$) Standard Error (SE), And Coefficients Of Variation (CV) Of Organic Phosphate Fraction Determined For The Foxton And Pukepuke Control And Phosphate Treated Soils

	Phosphate Treated Soils Sampling Dates				Control Soils Sampling Dates	
	Apr 16 1971	Jul 14 1971	Nov 2 1971	Feb 23 1972	Apr 16 1971	Feb 23 1972
	Foxton Soils					
$\bar{x}$	32.30	32.81	33.56	32.29	32.30	33.61
SE	0.34	1.25	1.44	1.29	0.47	0.48
CV	3.28%	11.97%	13.62%	12.60%	4.60%	4.56%
	Pukepuke Soils					
$\bar{x}$	70.74	71.84	70.19	72.30	70.69	70.24
SE	1.38	1.97	1.60	1.92	1.39	1.57
CV	6.18%	8.69%	7.21%	8.40%	6.19%	7.08%

TABLE 9

Two-Tailed t Test Values Calculated As A Test For Significant Differences Between Particular Phosphate Fractions Determined On Various Dates For The Foxton Control And Phosphate Treated Soils

Test Between Samples Collected On	Phosphate Fractions					
	NH_4Cl-Soluble Phosphate	Corrected Aluminium-Bound Phosphate	Corrected Iron-Bound Phosphate	Calcium-Bound Phosphate	Organic Phosphate	Residual Phosphate
	Phosphate Treated Soils					
Apr 16 and Feb 23	11.116	5.418	7.097	6.282	0.008	0.256
Apr 16 and Jul 14	8.045	0.858	0.411	2.796	0.402	0.371
Jul 14 and Nov 2	1.677	4.399	4.617	2.544	0.337	0.021
Nov 2 and Feb 23	4.080	4.278	4.262	0.879	0.887	0.136
	Control Soils					
Apr 16 and Feb 23	-	0.602	1.933	0.638	1.722	0.944

Figure required for significance at a particular probability

5% 2.262

1% 3.250

TABLE 10

Two-Tailed t Test Values Calculated As A Test For Significant Differences Between Particular Phosphate Fractions Determined On Various Dates For The Pukepuke Control And Phosphate Treated Soils

Test Between Samples **Collected** On	NH_4Cl-Soluble Phosphate	Corrected Aluminium-Bound Phosphate	Corrected Iron-Bound Phosphate	Calcium-Bound Phosphate	Organic Phosphate	Residual Phosphate
	Phosphate Treated Soils					
Apr 16 and Feb 23	13.552	6.372	3.795	1.476	0.067	0.977
Apr 16 and Jul 14	4.809	0.747	2.646	0.055	0.419	1.811
Jul 14 and Nov 2	9.213	3.502	3.545	1.088	0.795	0.958
Nov 2 and Feb 23	5.816	2.967	1.005	2.144	0.682	0.644
	Control Soils					
Apr 16 and Feb 23	-	12.922	1.427	1.257	0.242	0.534

Figure required for significance at a particular probability

5% 2.262

1% 3.250

APPENDIX 4

TABLE 1

CLAY MINERALOGY

A. Pukepuke Brown Sandy Loam

Largely amorphous material (Al_2O_3, Fe_2O_3, SiO_2) with trace amounts of crystalline materials.

B. Foxton Black Sand

Major amounts of Chlorite, Kaolinite, Mica, Quartz and mixed layer 11-13Å material with minor amounts of Feldspars and mixed layer 18-28Å material.

TABLE 2

Particle - Size - Distribution For The Foxton Black And Pukepuke Brown Sandy Loam Soils

	Foxton Black Sand %	Pukepuke Brown Sandy Loam %
Clay <0.002 mm	4.0	11.0
Silt 0.02-0.002 mm	15.4	14.6
Fine sand 0.2-0.02 mm	63.8	51.1
Coarse sand 2-0.2 mm	16.8	24.3

TABLE 3

Rainfall (mm) Recorded At The Pukepuke Soil Site Over The Experimental Period

Date	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Jan	Feb
1				7.6		4.8	22.9					
2				7.4			1.0	3.3		5.3	1.5	4.6
3				6.6			6.4			24.1	20.3	
4			19.1				19.1	9.1				
5			31.8			4.1	2.0	18.5				
6				4.8	7.6		7.1	1.8				
7			29.7	5.1	0.5						21.3	
8								1.0		9.7	9.9	
9		0.5										7.4
10				1.5				5.8				
11		3.3		24.1								
12											2.0	
13			1.8					3.6			0.3	
14			1.3	28.7		7.6					1.5	
15			16.5	4.8			9.1		9.9			
16	0.5	1.0	1.8			6.4	2.5					
17	2.8					11.4		1.0	6.4			
18												
19				1.3			7.4	24.6				
20												
21		2.3						46.5				13.2
22		5.3		1.0		4.6				2.0	2.0	7.6
23				2.5			16.8		6.4			
24						5.1	6.6	2.5				19.8
25	0.5		1.3						8.6			2.0
26	4.6			9.1			4.6	1.0	11.4			
27	11.9				18.5	8.4				18.5		
28				16.0	6.6		4.6	3.0	6.4			
29				34.0								
30							7.6				20.3	
31					5.1	9.1	8.9	0.5			0.3	
Total	20.3	12.4	103.3	154.5	38.3	61.5	126.6	122.2	49.1	59.6	79.4	54.6

Total = 881.8 mm