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# Effect of added phosphorus on the availability and forms of phosphorus present in two soils of the Manawatu-Rangitikei sand country

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#### ABSTRACT

The changes in availability and forms of phosphorus over a 12-month period after the application of superphosphate to pasture on Foxton black sand and Pukepuke brown sandy loam were studied. Differences were large between the two soils in phosphorus sorption capacity, retention of applied phosphorus, and relative size of the inorganic phosphorus fractions. Decline in availability of phosphorus after application could largely be attributed to its removal from the upper 5 cm of the Foxton soil, but in the Pukepuke soil; conversion of applied phosphorus to sparingly soluble forms was the major factor involved.

# INTRODUCTION

An extensive complex of dunes, sand plains, and peaty swamps borders the west coast of the lower part of the North Island of New Zealand. 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).

Soils of the Manawatu–Rangitikei sand country have a naturally low available-phosphorus status and require annual applications of phosphorus for high pasture production. This need for regular application implies that the availability of the applied phosphorus in the rooting zone declines because of loss of phosphorus from this zone by leaching, a distinct possibility in such light-textured soils, conversion of phosphorus to sparingly soluble forms, inefficient return of dung and urine, build-up of organic phosphorus, removal in farm products, or a combination of these factors.

The object of the present study was to investigate changes in the availability and forms of phosphorus after the addition of superphosphate fertiliser to a sand dune and a sand plain soil.

# **MATERIALS AND METHODS**

# Soils

Two soils derived from wind-blown sand were

 Present address: Chemistry Department, University of Waikato, Hamilton, New Zealand. used. Pukepuke brown sandy loam is formed on low-lying sand plains where drainage is poor, the water table being at or near the surface for much of the winter and spring. Foxton black sand is formed on dunes where drainage is excessive, and consequently the soil is prone to drought. Some chemical and physical characteristics of the soils are presented in Table 1.

## Phosphorus treatment

Phosphorus, as superphosphate, was applied in a randomised block design trial (five replications) on each soil. The treatments were control, 250 g/m<sup>2</sup> of superphosphate on the Foxton black sand, and 500 g/m<sup>2</sup> of superphosphate on the Pukepuke brown sandy loam. These rates were chosen to ensure significant increases in the amounts of the phosphorus fractions above those already present in the soil. Soil samples (0-5 cm) were collected before, and 6 and 10 weeks after, the addition of superphosphate, and thereafter at 8-weekly intervals up to 50 weeks. Two samples of twelve 2.5 cm diameter cores were collected from each plot. The samples were air-dried and crushed to pass through a 2 mm sieve.

Laboratory procedures

Phosphorus in solution was determined by Watanabe & Olsen's (1965) modification of Murphy & Riley's (1962) method. Interference from fluoride was eliminated by the boric acid procedure of Kurtz (1942).

Total phosphorus was extracted by fusion with Na<sub>2</sub>CO<sub>3</sub> (Muir 1952) with the modification that

TABLE 1 — Some chemical and physical properties of the Foxton black sand and Pukepuke brown sandy loam (0-5 cm)

Property†	Unit	Foxton black sand	Pukepuke brown sandy loam
Clay Silt Fine sand Coarse sand pH Exchangeable Mg Exchangeable Ca A1 <sub>2</sub> O <sub>3</sub> Fe <sub>2</sub> O <sub>3</sub> Organic matter Bulk density	% % % mg/g mg/g mg/g mg/g g/g cc	4 15 64 17 5.7 0.13 1.1 20.1 6.2 9.9 1.16	11 15 51 24 7.4 0.34 8.8 16.6 67.3 21.7 0.78

<sup>†</sup> For method of determination refer to text

the melt was taken up in 10N H<sub>2</sub>SO<sub>4</sub>. Estimates of available phosphorus were determined using the procedures of Truog (1930), Olsen *et al.* (1954), and Schofield (1955). Phosphorus sorption was measured by the method of Ozanne & Shaw (1967).

Soil phosphorus was fractionated into "easilysoluble", "aluminium-bound", "iron-bound", "calcium-bound", "organic", and "residual" phosphorus by a fractionation procedure developed by Dr C. V. Fife (pers. comm.). This procedure differs from others in that a separate soil subsample is used for each fraction, and the "optimum" soil: extractant ratio and extraction time is determined for each extractant and soil. "Easily-soluble" phosphorus was extracted with 0.5M NH<sub>4</sub>Cl; "aluminium-bound" phosphorus with 0.5M NH<sub>4</sub>F at pH 8.5; "ironbound" phospherus with 1M NaOH after preleaching soil with 0.5M NaCl; and "calciumbound" phosphorus with 0.02N HCl. Organic phosphorus was determined by ignition of the sample at 550°c for 1 hour followed by extraction with 0.02N HCl and 1M NaOH. "Aluminiumbound" phosphorus was corrected for the resorption of phosphorus by iron oxide using the method of Williams et al. (1967).

There is some uncertainty on the form of soil phosphorus extracted at the various stages of the methods employed in the fractionation procedure, and it is recognised that the specified forms are not sharply delineated under the conditions of the extraction procedures employed.

"Free" iron oxide was extracted with dithionitecitrate-bicarbonate (Mehra & Jackson 1960) and iron in solution was measured by the thioglycollate method (Sandell 1944). Amorphous and

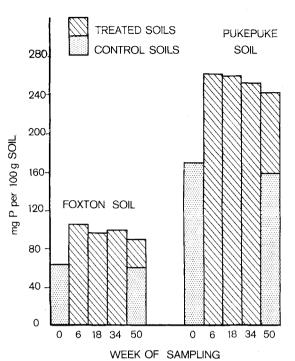


Fig. 1 — Total phosphorus in the Foxton and Pukepuke control and phosphorus-treated plots determined throughout the experimental period.

poorly-ordered alumino-silicate materials were extracted by the sodium carbonate method of Follett *et al.* (1965), and aluminium was determined by the aluminon method (Robertson 1950). Exchangeable calcium and magnesium were extracted with 1N NH<sub>4</sub>OA<sub>c</sub> and determined by atomic absorption. Organic matter was determined by combustion at 400°c for 8 hours (Mitchell 1932). Calcium carbonate was determined by the gravimetric method of Erikson & Gieseking (1947). Soil pH was measured electrometrically at a soil-water ratio of 1:2.5 after overnight standing.

Mechanical analyses were carried out according to the procedure outlined by Piper (1942). Clay fractions, after saturation with various cations and various heat treatments (Mitchell 1966), were subjected to X-ray diffraction.

#### RESULTS

The added phosphorus increased the total phosphorus by 41 mg P/100 g soil in the Foxton soil and by 99 mg P/100 g soil in the Pukepuke soil (Fig. 1). Of this added phosphorus 37% and 13% was lost from the upper 5 cm of the Foxton and Pukepuke soils, respectively, over the subsequent 12 months.

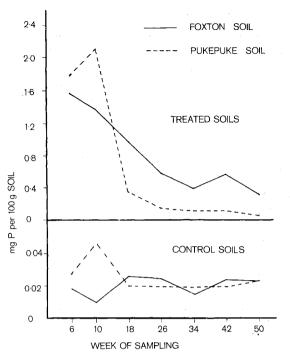


Fig. 2 -- Mean values for Schofield-extractable phosphorus determined at each sampling for the Foxton and Pukepuke control and phosphorus-treated soils.

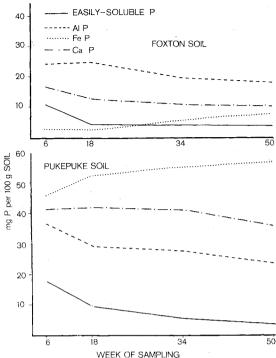


Fig. 3 — Inorganic phosphorus fractions in the Foxton and Pukepuke phosphorus-treated soils.

Values for phosphorus availability in treated plots of both soils fell rapidly with time (Fig. 2, Tables 4 and 5). Truog and Olsen values appeared to be moving towards a level above that of the untreated plots but Schofield's values tended to decline towards the values of the untreated plots.

For both the Foxton and Pukepuke control soils, organic phosphorus accounted for much of the total phosphorus in the top 5 cm (49.5% and 41.6% respectively). The inorganic phosphorus fractions showed large differences between the two soils in amount and relative proportion of each fraction (Table 2). In both soils, "resi-

TABLE 2 — Phosphorus fractions in the Foxton and Pukepuke control soils

	Foxton soil		Pukepuke soil	
Phosphorus fractions	mg P/100 g soil	% of total inorganic P	mg P/100 g soil	% of total inorganic P
"Easily-soluble" P	0		0	
"Aluminium-bound" P	5.6	18.2	6.7	7.0
"Iron-bound" P	0.9	2.9	26.8	28.3
"Calcium-bound" P	8.5	27.6	26.6	28.1
"Residual" P	15.8	51.3	34.5	36.6
	% of total P		% of total P	
Total inorganic P	30.8	50.4	94.6	58.4
Organic P	30.3	49.6	67.4	41.6
Total P	61.1		162.0	

TABLE 3—The percentage† of added phosphorus occurring in each phosphorus fraction at week 6 and week 50 in the Foxton and Pukepuke phosphorus-treated soils

	Foxton soil		Pukepuke soil	
-	Week 6	Week 50	Week 6	Week 50
"Easily-soluble" P "Aluminium-bound" P	26.3 46.4	13.0 50.0	19.0 32.4	4.5 25.7
"Iron-bound" P "Calcium-bound" P	5.3 22.0	29.5 7.5	21.5 16.4	43.3 11.0
"Residual" P	- <b>0</b>	0	10.7	15.5

<sup>\*</sup> Calculated from the difference between control and phosphorus-treated plots at sampling

TABLE 4 — Mean  $\pm$  standard error of Olsen-extractable phosphorus determined at each sampling for the Foxton and Pukepuke soils

Week of sampling		Olsen-extractat (mg		
	Foxton soil		Puker	ouke soil
	Control	Phosphorus- treated	Control	Phosphorus- treated
6 10 18 26 34 42 50	$\begin{array}{c} 1.02 \ \pm \ 0.04 \\ 0.64 \ \pm \ 0.01 \\ 0.37 \ \pm \ 0.01 \\ 0.71 \ \pm \ 0.01 \\ 0.68 \ \pm \ 0.17 \\ 0.68 \ \pm \ 0.02 \\ 0.63 \ \pm \ 0.04 \\ \end{array}$	$\begin{array}{c} 10.1 \;\; \pm \;\; 1.4 \\ 9.3 \;\; \pm \;\; 0.3 \\ 8.5 \;\; \pm \;\; 0.4 \\ 6.7 \;\; \pm \;\; 0.2 \\ 5.6 \;\; \pm \;\; 0.2 \\ 6.7 \;\; \pm \;\; 0.2 \\ 5.9 \;\; \pm \;\; 0.4 \\ \end{array}$	$\begin{array}{c} 2.11 \ \pm \ 0.07 \\ 1.93 \ \pm \ 0.07 \\ 1.49 \ \pm \ 0.05 \\ 1.69 \ \pm \ 0.07 \\ 1.27 \ \pm \ 0.03 \\ 1.65 \ \pm \ 0.05 \\ 1.69 \ \pm \ 0.07 \\ \end{array}$	$\begin{array}{c} 21.5 \ \pm \ 0.7 \\ 18.9 \ \pm \ 0.6 \\ 16.8 \ \pm \ 1.0 \\ 11.3 \ \pm \ 0.2 \\ 7.5 \ \pm \ 0.3 \\ 7.7 \ \pm \ 0.2 \\ 7.9 \ \pm \ 0.2 \\ \end{array}$

dual" phosphorus was the largest organic fraction, followed by "calcium-bound", "aluminium-bound", and "iron-bound" phosphorus in the Foxton soil; and by "iron-bound", calcium-bound", and "aluminium-bound" phosphorus in the Pukepuke soil.

In both soils the "aluminium-bound" phosphorus fraction increased to the greatest extent after addition of phosphorus (Table 3), followed

by "easily-soluble", "calcium-bound", and "iron-bound" phosphorus in the Foxton soil; and by "iron-bound", "easily-soluble", and "calcium-bound" phosphorus in the Pukepuke soil. The "residual" phosphorus fraction of the Pukepuke treated soil also showed a significant increase (0.01% level) at week 6, and showed a tendency to increase with time. This increased amount of the residual phosphorus fraction could be

TABLE 5 — Mean  $\pm$  standard error of Truog-extractable phosphorus determined at each sampling for the Foxton and Pukepuke soils

Week of sampling		Truog-extractab (mg	le phosphorus P%)	
	Foxton soil		Pukepuke soil	
	Control	Phosphorus- treated	Control	Phosphorus- treated
6 10 18 26 34 42 50	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$\begin{array}{c} 28.9 \; \pm \; 1.1 \\ 25.4 \; \pm \; 1.7 \\ 22.3 \; \pm \; 1.0 \\ 17.5 \; \pm \; 0.5 \\ 12.9 \; \pm \; 0.5 \\ 15.1 \; \pm \; 0.4 \\ 13.7 \; \pm \; 0.6 \end{array}$	$\begin{array}{c} 2.8 \; \pm \; 0.1 \\ 4.3 \; \pm \; 0.2 \\ 2.8 \; \pm \; 0.1 \\ 3.9 \; \pm \; 0.2 \\ 2.5 \; \pm \; 0.1 \\ 3.4 \; \pm \; 0.2 \\ 2.9 \; \pm \; 0.1 \end{array}$	$37.3 \pm 1.9$ $33.3 \pm 1.9$ $33.5 \pm 1.6$ $23.7 \pm 0.6$ $16.2 \pm 0.6$ $16.5 \pm 0.8$ $16.3 \pm 0.5$

TABLE 6 — Phosphorus sorbed by the Foxton and Pukepuke soils from solutions of varying concentration using a 1:20 soil:solution ratio with an 18-hour shaking period

Concentration of	% of added phosphorus sorbed		
phosphorus solution added μg/ml	Foxton soil	Pukepuke soil	
1.0	95	96	
2.5 5	94	98	
3 10	92 83	99 99	
15	74	99	
20	65	98	
40 100	44 21	94 78	
200	nd	60	
500	nd	48	

nd - not determined

extracted by 1N HCl. Large amounts of iron were extracted at the same time. The organic phosphorus was not increased by the phosphorus addition either in the Foxton or Pukepuke soils.

The two soils differed greatly in their ability to retain added phosphorus (Table 6), the Foxton soil showing lower phosphorus retention at a given equilibrium phosphorus concentration than the Pukepuke soil.

The clay fraction of the Pukepuke soil was largely amorphous material with trace amounts of crystalline constituents, but that of the Foxton soil consisted of major amounts of chlorite, kaolinite, mica, quartz, and mixed-layer 11–13 Å material, with minor amounts of feldspars and mixed-layer 18–28 Å material.

### DISCUSSION

The higher clay content of the Pukepuke soil than the Foxton soil (Table 1) agrees with Claridge (1961) who noted that clay content was higher in the wetter yellow-brown sands. The clay content of the Pukepuke soil is largely amorphous, but that of the Foxton soil contains mainly crystalline material. Because of this, and differences in the "free" iron-oxide content and moisture regimes of the two soils, large differences in the forms and amounts of phosphorus retained may be expected.

Both total phosphorus and phosphorus sorption data show that the Foxton soil retained less added phosphorus than the Pukepuke soil, and that shortterm movement of phosphorus may be appreciable in the former.

Although the Truog and Olsen values were higher for the treated Pukepuke soil than for the Foxton soil, the phosphorus concentration in CaCl<sub>2</sub> extracts was lower in the Pukepuke soil, suggesting a lower concentration in the soil solution also. The Truog value for each soil decreased at a similar rate after an initial rise because of phosphorus application. The Olsen value, however, decreased more rapidly in the Pukepuke than in the Foxton soil. reagent extracts predominantly "calcium phosphorus" (Chang & Juo 1963; Srivastava & Pathak 1969) and "aluminium phosphorus" (Susuki et al. 1963; Grigg 1965; Sherrell 1970), but Olsen's reagent extracts mainly "easily-soluble" "aluminium phosphorus" (Patel & Mehta 1961; Susuki et al. 1963; Datta & Kehra 1969), with less amounts of "iron phosphorus" (Datta & Kehra 1969). The more rapid decline of Olsen phosphorus in the Pukepuke soil may be due to the more rapid decline of "easily-soluble" and "aluminium-bound" fractions in this soil (Table 3), accompanied by a greater increase in the "iron-bound" fraction.

The major difference in distribution of phosphorus between the inorganic phosphorus fractions in the two soils is the amount of "aluminiumbound" and "iron-bound" phosphorus. A higher percentage of the inorganic phosphorus was found in the "iron-bound" fraction, and a lower percentage in the "aluminium-bound" fraction in the Pukepuke soil, probably because of the high "free" iron oxide content of that soil. After addition of phosphorus, the "easily-soluble" and "aluminium-bound" phosphorus fraction in both soils increased and then declined (Fig. 3). A higher proportion of the added phosphorus was found in these two fractions in the Foxton soil, but the rate of decline of these fractions was more rapid in the Pukepuke soil. The percentages of added phosphorus recovered in the "easilysoluble" phosphorus fraction in this study are considerably greater than those reported in the literature (Fassbender 1968; Yuan et al. 1960). This could be because of (i) the high rate of phosphorus application and (ii) the soil:extractant ratio used was considerably wider than that used by the authors reported above. may be expected to remove more phosphorus. The "iron-bound" phosphorus fraction of both soils increased with time (Fig. 4), and this would be anticipated from solubility considerations.

Kaila (1967) found that after incubation of soil with CaCO<sub>3</sub> the small amounts of fertiliser phosphorus recovered in the acid-soluble form did not depend on the rate of liming, even at pH 7, which agrees with the small difference in the amounts of "calcium-bound" phosphorus found in these two soils which differ widely in

pH. However, "calcium-bound" phosphorus may be expected to be more stable in the soil of higher pH. This is supported by the finding that the "calcium-bound" phosphorus fraction of the Foxton soil decreased with time at a faster rate than that of the Pukepuke soil (Fig. 3).

An increase in the residual phosphorus fraction of the Pukepuke soil 6 weeks after application of superphosphate indicates that occlusion of phosphorus added to soil occurred rapidly. increase in residual phosphorus over such a short time was most likely due to the high rate of application and the large content of iron in the soil. The increased content of residual phosphorus resulting from the fertiliser additions was not extracted by NH<sub>4</sub>F, NaOH, or 0.5N HCl, indicating that it is not in a discrete form such as variscite, strengite, or apatite. However, because it dissolved with 1N HCl, which also removed a large amount of iron, this phosphorus may be simply occluded by an iron oxide coating, and removal of this coating allowed the phosphorus to be extracted.

The differences between the Foxton and Pukepuke soils in the distribution of added phosphorus among the inorganic phosphorus fractions can be attributed to the differences in chemical and physical properties of the soils. In the 50 weeks after application of phosphorus, 55% and 64% of the applied phosphorus had either been removed from the upper 5 cm or converted to sparingly soluble forms ("iron-bound" and "residual-phosphorus") in the Foxton and Pukepuke soils respectively. In the Foxton soil the decline in the availability of applied phosphorus could be attributed largely to removal of phosphorus from the upper 5 cm, only a small percentage being converted to sparingly soluble forms, whereas in the Pukepuke soil, conversion of applied phosphorus to sparingly soluble forms was the major factor involved. This decrease in the availability of applied phosphorus necessitates regular application of phosphorus to maintain high levels of pasture production.

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