"THE FATE OF APPLIED PHOSPHATE IN A NEW ZEALAND YELLOW-GREY EARTH, AS INFLUENCED BY PHOSPHATE CARRIER AND SOIL REACTION."

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PART I

A. INTRODUCTION

A considerable amount of evidence has been accumulated in support of the presence in soils of iron, aluminium, and calcium bound phosphorus, as products of the phosphorus fixation process, but the quantitative evaluation of these forms has been continuously hampered by the lack of suitable procedures for their separate and selective determination.

Although the separate determination of calcium bound phosphorus has been successful (Fraps, 1906; Fisher and Thomas, 1935; Ghani, 1943a) a procedure for the separate determination of iron and aluminium bound phosphorus was not available until recently when Chang and Jackson (1957) included such a method in their proposed scheme for the fractionation of soil phosphorus. Theirs is a definite advance on previous procedures as it has been generally considered that, at least in acid soils, these two forms represent the dominant products of phosphorus fixation, while their relative abundance may be expected to vary considerably in different soils and under different soil conditions. Fife (1959-I, 1959-II) modified the procedure of Chang and Jackson for the separate estimation of Al-P, and (priv.comm.) developed procedures for the selective determination of iron, calcium, and organic P.

The object of the present study was to investigate what information these methods could provide concerning the trends of P. fixation in a New Zealand Yellow-Grey Earth from a long term field experiment, embodying three forms of phosphate fertiliser, applied with or without lime.

B. REVIEW OF THE LITERATURE

1. The fractionation of soil phosphorus

The use of selective chemical extracting solutions, which offer the opportunity to define discrete forms of soil phosphorus are an advance over those chemical extractants which determine that portion of soil phosphorus which may be available to plants, as these methods are empirical and hence must be calibrated against field experiments before useful information can be obtained. On the other hand the selective determination of soil phosphorus fractions appears to produce less empirical results since a knowledge of the nature of the various phosphate compounds in a soil, together with a knowledge of the conditions under which these different forms are available to the growing crop, gives a much more general means of assessing availability.

Fraps (1906), and Fisher and Thomas (1935) employed an acetic acid-Sodium acetate buffer at pH 5.0 for various extracting periods. Dilute H_2SO_4 at pH 3.0 was also used. These workers classified their results as:

1. Ca, Mg, and Mn phosphates;
2. Fe and Al phosphates;
3. Absorbed P and apatite.

Williams (1937) introduced NaOH as a selective extractant, and divided the forms of soil phosphorus into:

1. Alkali soluble P, said to include organic P, exchangeable P, and the more soluble inorganic forms such as water soluble -, dicalcium -, and sesquioxide-P;

2. Alkali insoluble P, consisting of apatites, possibly Titanium -, and crystal lattice-P.

Alkali and acid extractions were combined by Dean (1938), who suggested three soil phosphorus fractions;

1. Organic compounds, soluble in 0.25 n NaOH;
2. Inorganic compounds, dissolved by 0.25 n NaOH and 0.5 n H_2SO_4;
3. Insoluble compounds.

When it was found that soluble and exchangeable Ca and Mg interfered in the alkali extractions, Ghani (1943a) modified

Dean's procedure by making a pre-extraction with 0.2 n acetic acid, which was then followed by a succession of extractions with 0.25 n NaOH, and finally by an extraction with 2 n H_2SO_4. Five fractions were thus obtained:

1. Acetic acid soluble P; mono-, di-, and tricalcium phosphates
2. Alkali soluble inorganic P; Fe- and Al- phosphates;
3. Alkali soluble organic P;
4. Strong acid soluble P of the apatite type;
5. Insoluble P.

It was noticed that some P was being resorbed during the acetic acid extraction, which would subsequently be extracted by NaOH. Thus Ghani (1943C) modified his procedure by employing 8-hydroxy quinoline as a sorption blocking agent.

The use of 8-hydroxy quinoline was further explored by Williams (1950). He adapted Ghani's procedure and made successive extractions with 2.5% acetic acid and 1% 8-hydroxy quinoline, followed this with 0.1 n NaOH, and omitted the final extraction with H_2SO_4.

A different scheme for the fractionation of soil P was proposed by Bray and Kurtz (1945).

1. Total P was determined by the perchlorate digestion method of Sherman (1942).

2. Organic P was determined by essentially the method of Dickman and De Turk (1938).

3. Available P was determined by an extractant which consisted of 0.5 n Hcl and neutral 0.5 M.NH_4F. After the acid soluble forms of P had been dissolved, the subsequently added NH_4F would dissolve the remaining forms. The acid soluble forms could then be calculated by difference. Baewin and Tyner (1954) adopted this procedure and classified the soil P fraction as;

1. Total P; as suggested by Bray and Kurtz;
2. Extractable P; the sum of organic, acid soluble, and adsorbed forms;
3. Non extractable P - as the difference between (1) and (2).

Since Turner and Rice (1954) found that neutral NH_4F would

isolate Al - P, but not Fe - P, Chang and Jackson (1957) concluded that the method for "available P" of Bray and Kurtz would largely be a determination of Al - P.

Chang and Jackson (1957) adopted the use of neutral NH_4F for the discrete delineation of Al - P, and included the method in their proposed scheme of soil-P fractionation. Briefly their procedure is as follows; using a single sample of soil throughout, and washing the residue after each extraction twice with saturated NaCl solution to remove the reagents;

1. Pre-extract for 30 minutes with 1 n NH_4Cl to remove water soluble P and exchangeable Ca,

2. Extract Al - P at a 1:50 soil/solution ratio with neutral 0.5 M.NH_4F for 1 hour.

3. Extract Fe-P (1: 50 ratio) with 0.1 n NaOH for 17 hours.

4. Extract Ca-P (1: 50 ratio) with 0.5 n H_2SO_4 for 1 hour.

5. Extract "reductant soluble Fe-P" by the citrate-dithionite method of Aguilera and Jackson (1953). This time the washings are combined with the extract.

6. Extract "r.s. Al-P" with neutral 0.5 M.NH_4F, as under (2), or alternatively extract "r.s. Fe-Al-P" with 0.1 n NaOH, as under (3

7. Organic P is determined by the method of Bray and Kurtz (1945).

It has been suggested by Saunders (1959) and Yuan and Fiskell (1959) that the citrate-dithionite method is not specific for "reductant soluble Fe-P", but that appreciable amounts of 'r.s. Al-P" may be removed also.

Several modifications have been suggested by Aung Khin and Leeper (1960);

a. Extract Al-P with 0.5 M.NH_4F at pH 8.5 as proposed by Fife (1959-I).

b. Extract organic P after a more drastic treatment with H_2O_2 than employed by Bray and Kurtz.

c. Subject at least two separate samples to the procedure; one for the stages (1) to (4), the other for the stages (5) to (7), executing stage (7) first.

The modified procedure for the extraction of Al-P has been further refined by Fife (priv. comm.), and is included in a scheme for the fractionation of soil phosphorus developed by him (priv. comm.).

2. The fate of applied phosphate

From evidence in the literature it appears that the phosphate, liberated during the decomposition of fertiliser particles, is fixed in the top inch of an undisturbed soil, (Fiskell et al, 1953) and that the greatest proportion of fixed P may be accounted for in the clay fraction (Fine and Bartholomew, 1946; Moschler et al, 1957). Variations in the penetration of P down the soil profile are due to such factors as texture (Stephenson and Chapman, 1931; Pathak et al, 1950), drainage (McGregor, 1953; Lawton and Vomocil, 1954), the amount of P applied (Smith and Simpson, 1950; Heslep and Black, 1954) and its solubility in water (Haasjes and Sissingh, 1953, the sesquioxide content of the soil (Heck, 1934), and the pH, controlling cationactivity (Chang and Jackson, 1958); but the accumulation of P below the upper soil layer appears mainly due to biological activity distributing P in the organic form (Williams, 1950; Sandal and Garey, 1954; Jackman, 1955). The major inorganic complexes concerned with P fixation are calcium, aluminium, and iron (Dean, 1949; Wild, 1950; Williams, 1952).

From his studies on the fixation of applied P in an acid soil from Rothamsted, and a neutral soil from the Woburn plots, Dean (1938) concluded that, whereas in the acid soil P occurred mainly as Fe-P and Al-P, in the neutral soil P would be found mainly fixed as apatite or tri-Ca-P, and that many neutral and calcareous soils contained much P not fixed as apatite, while in acid soils P would also be present as apatite or tri-Ca-P.

For their studies on corn belt soils Bray and Kurtz (1945) found that both "adsorbed" and "acid soluble" P occurred. They showed that in soils of pH < 6 added soluble phosphates and acid soluble (rock-) phosphate tended to change into the relatively more

abundant adsorbed forms; an opposite trend was found to occur in soils of pH > 6 where adsorbed forms and added soluble phosphates changed into acid soluble forms while added acid soluble phosphates did not. They regarded pH 6 as the critical boundary between adsorbed and acid soluble forms of P in these soils. Williams (1950-I, 1950-II), in a study of some Australian pasture soils, also found that soil acidity had a considerable effect on the forms in which added P was fixed; at a high pH more P was retained in an acid soluble form (Ca-P) whereas at a low pH the alkali soluble forms were more abundant. (Fe-P and Al-P) Williams also found that phosphate topdressing would increase both organic and inorganic P forms in the soil, and also non extractable P. The accumulation of organic P was found to be disproportional to the amounts of P applied, and tended to approach a constant value irrespective of the amount and nature of the fertiliser applie Although the accumulation of inorganic P was directly proportional to the amounts applied, the use of Super, Basic Slag, or Rock phosph ate would lead to different distributions of inorganic P fractions. Where Super was applied the increase in inorganic P was equally divided between the acetic acid and alkali soluble fractions. Where Rock phosphate was applied most of the phosphorus was extracted in the acetic acid soluble fraction. The application of Basic Slag resulted in a greater increase in the acetic acid soluble fraction and a smaller increase in the alkali soluble fraction than in the soils to which Super had been applied.

Chang and Jackson (1958) subjected a number of samples, representing some widely different major soil groups, to their fractionation procedure. From this study they concluded that the formation of the various discrete chemical forms of phosphate in the soil apparently depended on such soil factors as pH, cation activity, solubility product of the various phosphates, degree of chemical weathering, and fertiliser practice. Immediately after the application of phosphate fertiliser Ca-P and Al-P were more likely to be formed than Fe-P due to the relatively higher activities in the soil of Ca and Al ions than Fe ions. Al-P at

first would increase more than Fe-P. As time elapsed, Ca-P and Al-P would change gradually into Fe-P, the least soluble form of these three. These three forms were found to occur not only in acid soils but also at neutral soil reactions, according to the principle of solubility product (Kittrick and Jackson, 1955 B, 1955 C, 1956; Chang and Jackson, 1957 C). Since Ca-P is more soluble than the other forms it would more easily be removed by crops, or shifted to the less soluble forms. However, an increase in the calcium activity and pH by liming would appear to favour the formation of Ca-P and the release, through repression of Fe and Al activity (Cole and Jackson, 1951), of P from the Al-P and Fe-P forms for plant use.

PART II - MATERIALS

A. "TRIAL I", MARTON

1. History

The experiment was laid down in 1932 at Marton by Mr A.W. Hudson, the then Crop Experimentalist of the Department of Agriculture.

The area chosen had been under new pasture since 1930, and had been grazed by sheep from the time of sowing to the laying down of the experiment.

The experiment was designed to evaluate the efficacy of three forms of phosphatic fertiliser with or without the addition of lime, using the "alternate mowing and grazing technique" devised by Hudson (1933).

Twelve replications of six treatments were divided into two equal sections, A and B. The plot arrangement is indicated on the accompanying plan (fig.1).

The treatments were;

1. Superphosphate, 4 cwt./ac./an.
2. Basic Slag, 612 lb. " "
3. "Gafsa" rock phosphate, 350 lb./ac./an.

1L. Super as for (1), + limestone.

2L. Basic Slag as for (2), + limestone.

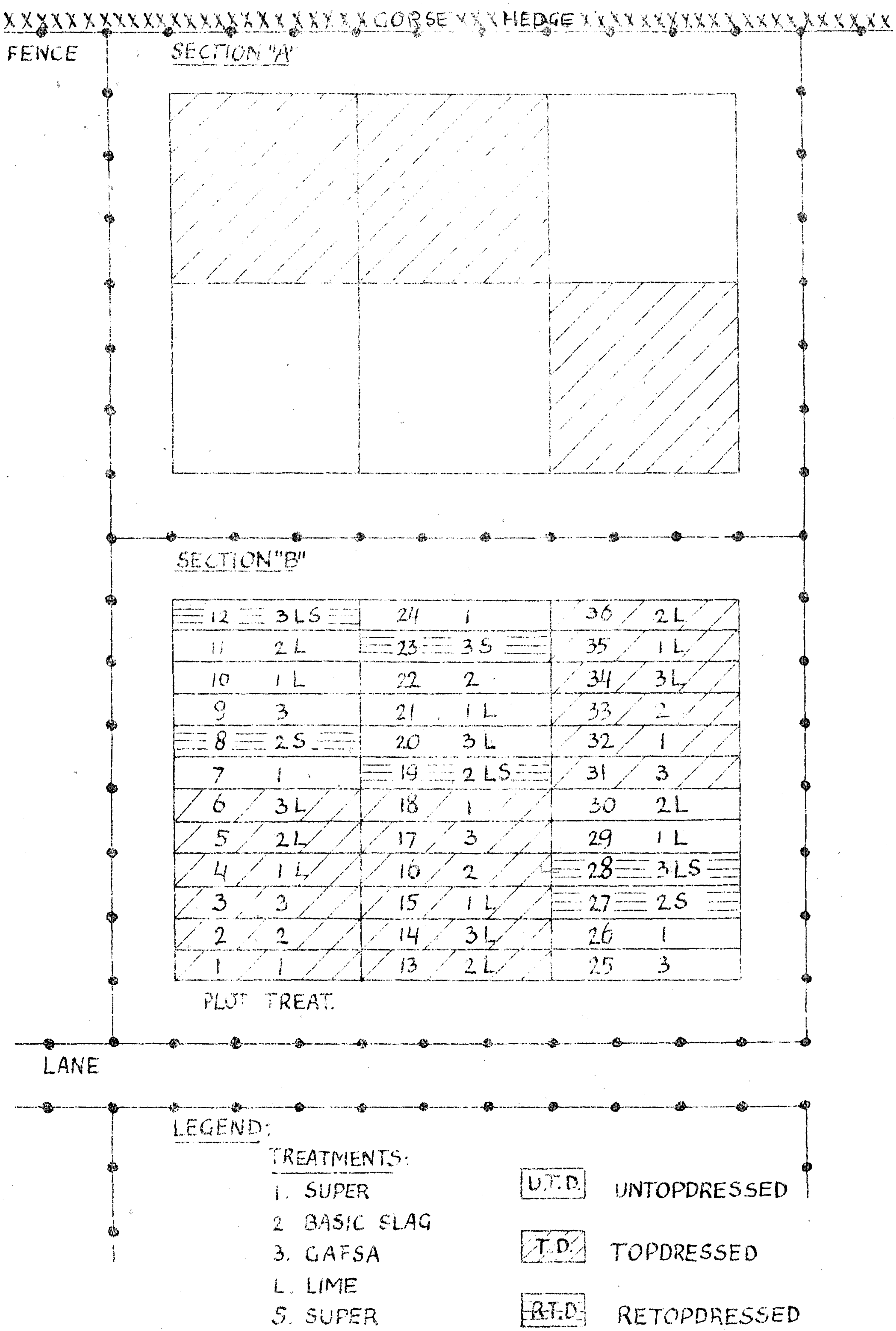
3L. Gafsa as for (3), + limestone.

Thus all treatments received the P_2O_5 equivalent of 4 cwt. of Super, applied in two equal dressings annually. Carbonate of lime was applied at 1 ton/ac. in the first year, and at 3 cwt/ac/an subsequently (Doak, 1942-II). The Marton Guide (1960) indicates an annual application of 5 cwt/ac/an. All treatments received regular applications of 30% Potash Salts, totalling 13 cwt./ac. over the first 8 years of the trial.

The technique of alternate mowing and grazing ensured that one section would be under sheep grazing while the other was cut for herbage yields. After two such cuts the section would be grazed while the production of the other was measured.

This technique enabled continuous production records to be

FIG. 1. PLAN OF "TRIAL I", AND LAY-OUT OF SAMPLED PLOTS.



secured under as near sheep grazing conditions as possible, without adversely affecting the sward. The mechanical analysis of the soil is given in Table I and indicates that the soil is a light silt loam (Doak, 1942-II).

Table I. Mechanical Analysis of Soil (% fractions), O.D. basis

	0"-2"	2"-4"	4"-6"	6"-10"
Clay	22.9	22.0	22.8	24.7
Silt	23.9	26.3	25.5	24.5
Fine sand	35.2	36.2	36.6	36.2
Coarse sand	4.9	5.1	5.2	7.2
Loss on ignition	10.7	9.8	9.0	7.7
Moisture loss	2.4	0.6	0.9	-
Total	100.0	100.0	100.0	100.3

According to the D.S.I.R. Soilbureau Bull.5 (1954) the soil is designated as;

"Marton loam from sandy mudstone, a Y.G. loam, classified as a transition to podzolic soils, pH approx. 5.9."

To date the experiment has undergone four stages, which are as follows (Marton Guide, 1960):

Stage 1 (1932-1940): 6 treatments, consisting of three forms of Phosphate, with and without Lime, applied regularly each year (treats.1-6, 12 reps.).

Stage 2 (1940-1951): Topdressing was discontinued, and the residual effects of previous fertiliser applications were studied (treats.1-6, 12 reps.).

Stage 3 (1951-1958): Topdressing resumed on half of the replicates, with the appropriate fertilisers, as for Stage 1. Potash (2 cwt/ac.) was applied to all plots in 1956 and 1957. The other half remained untopdressed. The change in topdressing policy will be referred to as T.D. for the re-topdressed plots, and U.T.D. for the untopdressed, residual plots (treats. 1-6 and 7-12 resp.: 6 reps.).

Stage 4 (1958 - present): The stage 3 programme was continued with the following modifications:

a) The "alternate mowing and grazing" technique was discontinued, and instead a "mowing with clippings returned" technique was instituted.

b) Section A was treated in 1958 with chemicals to kill the sward, followed by oversowing, to establish a new pasture sward.

c) Certain of the U.T.D. plots of Sections A and B were selected and topdressed with Super at 4 cwt./ac. annually from 1958 onwards, thus affording a comparison of responses to this fertiliser on residual plots now either carrying an old sward or a new sward, obtained by chemical turf-destruction followed by oversowing. The plots, pertaining to Section B, will be referred to as R.T.D. (treats. 8a and 9a, and 11a and 12a).

2. Final layout of treatments:

To facilitate the subsequent presentation of the results of analyses the treatments are listed in the following order:

Table 2 - Final layout of treatments

Stage	Old No.	New No.	Plot No.	Fertiliser applied	Code
T.D.	1	1	1-18-32	Super	S.
	2	2	2-16-33	Basic Slag	B.S.
	3	3	3-17-31	Gafsa	G.
	1L	4	4-15-35	Super + Lime	S. + L.
	2L	5	5-13-36	Basic Slag + Lime	B.S. + L.
	3L	6	6-14-34	Gafsa + Lime	G. + L.
U.T.D.	1	7	7-24-26	Super	S.
	2	8	-22-	Basic Slag	B.S.
	3	9	9 - 25	Gafsa	G.
	1L	10	10-21-29	Super + Lime	S. + L.
	2L	11	11 - 30	Basic Slag + Lime	B.S. + L.
	3L	12	-20-	Gafsa + Lime	G. + L.

R.T.D.	2S	8a	8 - 27	(Basic Slag) + Super(1958)	B.S. + S.
	3S	9a	-23-	(Gafsa) + Super (1958)	G. + S.
	2LS	11a	-19-	(Basic Slag + Lime) + Super (1958)	B.S.+L.+S
	3LS	12a	12 - 28	(Gafsa + Lime) + Super(1958)	G. + L.+S

3. Discussion of results of "Trial I" to date

Soil test data for pH, Lime, P_2O_5, and Dry Matter yields were compiled from the results presented by Doak (1942-II), and the official files of the experiment (by permission N.Z.Dept.Agric.1960)

A. pH:

The results are presented in table 3.

Table 3 pH results to date (0"-2" core)

Period	Year	1	2	3	1L	2L	3L
1.	1932	5.5	5.4	5.5	5.5	5.4	5.4
	33	5.5	5.6	5.6	6.1	6.2	6.1
	34	5.5	5.9	5.7	6.4	6.7	6.4
	35	5.6	6.1	5.7	6.3	6.7	6.4
	36	5.2	5.7	5.5	5.9	6.4	6.3
	37	5.1	5.5	5.3	5.6	6.1	5.8
	38	5.6	6.3	5.8	6.4	6.7	6.4
	39	5.6	6.2	5.7	6.2	6.8	6.4
	40	5.6	6.3	5.7	6.4	6.7	6.4
2.							
(1941-'50)		No data available					
3.	50	Untopdressed					
		1	2	3	1L	2L	3L
	51	5.5	5.8	5.7	5.3	5.9	5.7
	52	5.4	5.4	5.5	5.6	5.8	5.6
	53	5.4	5.5	5.4	5.5	5.6	5.3
	54	5.6	5.9	5.7	5.8	5.8	5.9

Topdressed					
1	2	3	1L	2L	3L
5.5	5.8	5.7	5.3	5.9	5.7
5.3	5.6	5.5	6.1	6.2	6.1
4.9	5.7	5.4	6.0	6.2	6.2
5.6	6.1	5.8	6.5	6.7	6.6

(Contd.)

	Untopdressed						Topdressed					
	1	2	3	1L	2L	3L	1	2	3	1L	2L	3L
55	5.5	5.6	5.7	5.6	5.8	5.7	5.6	5.9	5.8	6.4	6.5	6.5
56	5.6	5.7	5.7	5.8	6.0	5.8	5.8	6.2	5.9	6.5	6.7	6.6
57	5.6	5.6	5.5	5.6	5.8	5.6	5.6	6.1	5.8	6.2	6.5	6.4
58	5.4	5.3	5.4	5.8	5.6	5.6	5.4	5.9	5.7	6.1	6.4	6.2

The main treatment effects of decreasing the acidity of the soi may be shown in the following order; Super Gafsa Basic Slag, an No Lime Lime.

The effects of Basic Slag over the first 8 year period were most pronounced, and enhanced by liming. On the other hand, the addition of lime appeared to have effectively masked the individual effects of Super and Gafsa.

At the beginning of the third period the residual effects of Basic Slag and Gafsa could be noted, while those of Super and liming were no longer apparent. Subsequently, during the third period these residual effects seemed to disappear altogether, and the soil reverted to its apparent, original acidity of pH 5.3-5.5.

Where topdressing was resumed the original effects of the first period appeared to recur, but after approximately 6 years a general decline was noted. This was even evident in the T.D. plots which received lime.

The effects of Basic Slag, Gafsa, and Lime are thus appreciable but not of long duration.

B. Lime:

The data are shown in table 4, and expressed as % exchangeable CaO (O.D. basis) for the first period (Doak, 1942-II), and as parts Ca per 20,000 of soil extract, determined by the flame photometer, for the third period (Grimmett, 1953; priv. comm.).

Table 4 Lime results to date (0"-2" core; expressed as exch. CaO%, O.D. soil)

Period	Year	1	2	3	1L	2L	3L
1.	1932	.191	.192	.190	.194	.192	.192
	33	.200	.219	.198	.290	.299	.298
	34	.226	.257	.212	.367	.456	.363
	35	.227	.296	.218	.368	.424	.366
	36	.248	.300	.246	.383	.435	.374
	37	.261	.324	.246	.376	.431	.371
	38	.258	.349	.256	.396	.464	.387
	39	.266	.354	.254	.399	.473	.395
	40	.260	.356	.266	.419	.467	.403

2. 1941-'50; No data available.

(Results expressed as parts Ca per 20,000 in extract)

		Untopdressed						Topdressed					
		1	2	3	1L	2L	3L	1	2	3	1L	2L	3L
3	51	7	8	7	9	8	8	7	8	7	9	8	8
	52	7	8	5	7	7	8	7	8	6	9	9	8
	53	7	7	6	8	8	8	5	8	8	9	9	10
	54	6	6	6	7	8	7	6	8	8	11	13	11
	55	5	6	5	6	8	7	6	8	7	12	13	12
	56	5	6	5	7	8	7	7	9	8	11	13	12
	57	5	7	6	7	7	7	7	9	8	12	13	12
	58	5	6	5	7	7	7	6	9	7	11	13	11

A general increase in the lime status of the soils during the first period was evident, the approximate order being; Gafsa < Super < Basic Slag, and No Lime < Lime. This situation resembled that found for pH.

At the beginning of, and during the third period, the residual effects of liming had persisted slightly, but a further diminishing of the effects was apparent.

Where topdressing was resumed in the third period the only significant effect of raising the lime status was shown by Basic Slag. Liming itself apparently effectively masked individual

treatment effects. The general decline after the first 6 years of topdressing, as noted with the pH, was not evident here.

C. P_2O_5:

The data are presented in table 5, expressed as % P_2O_5 soluble in HCl for the first and second periods (Doak 1942-II), and as parts P per 50 million of soil extract (Truog test) for the third period (Grimmett, 1953; priv. comm.).

Some statistics for the P_2O_5 data were available (Doak, 1942-II)

Standard error : 0.0006.

Least significant difference: 0.002 (5%), 0.003 (1%).

Table 5 Phosphate results to date (0"-2" core)

(HCl Soluble P_2O_5%)

Period	Year	1	2	3	1L	2L	3L
1.	1932	.100	.102	.102	.099	.102	.103
	33	.117	.113	.115	.112	.114	.114
	34	.125	.122	.126	.121	.125	.126
	35	.130	.131	.131	.133	.127	.133
	36	.132	.129	.129	.131	.132	.132
	37	.147	.146	.150	.152	.145	.155
	38	.155	.153	.157	.156	.159	.163
	39	.163	.155	.165	.172	.158	.173
	40	.172	.169	.174	.185	.171	.184
		(Topdressing ceases)					
2.	1941	.175	.173	.168	.171	.176	.176
	42	.165	.158	.162	.162	.161	.170
	44	.170	.169	.160	.164	.159	.165
	45	.164	.157	.162	.152	.163	.169
	46	.178	.170	.178	.171	.163	.164
	49	.149	.137	.136	.128	.135	.129

(Parts P per 50 million (Truog test)

							Topdressing resumes					
		1	2	3	1L	2L	3L	1	2	3	1L	2L	3L
3	1951	2.5	2.8	3.1	2.0	2.6	3.3	2.5	2.8	3.1	2.0	2.6	3.3
	52	2.5	3.1	3.0	3.7	3.8	4.5	5.0	3.8	4.7	3.7	6.1	8.8
	53	4.5	9.5	3.0	4.0	4.0	7.0	3.0	2.5	7.0	6.0	7.5	13.0
	54	2.0	2.0	2.0	2.0	3.0	2.0	5.0	5.0	7.0	6.0	8.0	16.0
	55	4.3	5.0	4.6	4.0	4.3	3.6	10.3	11.3	15.3	15.0	15.3	29.6
	56	3.3	3.0	3.3	4.0	4.3	3.6	14.3	13.3	18.0	13.0	16.3	30.0
	57	3.0	3.3	2.6	3.3	4.6	3.6	15.5	14.3	28.2	17.7	17.0	33.2
	58	4.7	4.2	3.8	5.7	4.8	4.3	14.3	15.3	25.8	18.3	21.8	37.8

The treatments resulted in a gradual accumulation of acid soluble P during the first period. Individual treatment difference were generally significant, and of the order; Gafsa > Super > Basic Slag, which differences were increasingly accentuated by liming, insofar that the difference between Gafsa and Super diminished, while the difference between these treatments and Basic Slag became highly significant. During the second period a general decline in the levels of P was evident, the rate of decline, if taken over the entire period, being greater for Basic Slag and Gafsa than for Super. The rate of decline was also greater for the limed than for the unlimed treatments, excepting Basic Slag where it was equal.

During the third period treatment differences were inconsistent.

Where topdressing was resumed a rapid accumulation of P was evident, once again accentuated by liming. The effects of the Gafsa treatment were most notable, and appeared to be a function of the solubility of the phosphate in this fertiliser.

The solubility of the phosphates in the three fertilisers is shown in table 6.

Table 6 - Phosphate Solubility of Super, Basic Slag & Gafsa

	% Total P_2O_5	% Citric Acid Soluble P_2O_5	% Water soluble P_2O_5	Insoluble P_2O_5	Residue
Super	22.0		20.3	1.7	Unreacted rock phosphate
Basic Slag	16.1	13.1	-	3.0	Si-apatite (Collings, 1955)
Gafsa	28.2	9.5	-	18.7	Apatite.

It may be concluded that during the topdressing periods phosphate residues accumulated, the magnitude and the rate of the accumulations depending on the apatite content of the fertiliser, the pH, and the Ca ion activity, which would be enhanced by liming, and which would favour the formation of Ca-P. This confirms the findings of Chang and Jackson (1958).

D. Dry Matter Yields:

Table 7 has been adapted from the file data, which are presented in Appendix I, the object being to reduce the very wide annual fluctuations.

Table 7 - Dry Matter Yields

Period	Year	Yield of Super	Yields relative to Super=100					Control (headland)
			B.S.	G.	S + L.	B.S.+ L.	G +L	
1.	1932	7000	96	90	106	97	92	-
	33	7500	94	93	109	102	97	-
	34	9400	99	95	106	100	99	-
	35	11700	103	97	110	104	103	-
	36	12600	99	95	102	98	98	-
	37	8100	101	96	105	101	100	-
	38	8500	107	98	111	108	109	-
	39	9300	104	98	110	101	99	-
	40	8600	99	94	109	106	103	-

Topdressing ceases

(Contd.)

Per-Period	Year	Yield of Super	Yields, relative to Super = 100					Control (headland)	Topdressing resumes					
			BS	G	S+L	BS+L	G+L		S	BS	G	S+L	BS+L	G+L
2.	1941	10900	106	100	117	117	114	-						
	42	7000	103	101	114	109	113	-						
	43	7800	104	100	117	114	114	-						
	44	9700	101	99	111	109	111	-						
	45	6900	99	94	112	107	106	-						
	46	5400	107	106	111	117	117	-						
	47	3500	103	94	111	114	117	97						
	48	6600	103	102	105	106	108	94						
	49	5900	93	93	98	97	100	97						
	50	5400	94	96	100	107	111	89						
3.	51	5500	87	100	95	102	105	89	113	100	95	104	113	102
	52	6600	86	95	89	98	100	95	103	106	102	106	106	102
	53	5200	94	96	100	104	102	104	121	123	117	125	123	117
	54	5000	92	94	98	108	104	106	124	128	118	140	136	130
	55	5600	88	86	88	93	95	91	113	116	114	123	118	107
	56	6400	91	91	88	92	94	98	111	111	108	119	111	105
	57	6800	91	90	85	93	91	88	110	107	115	116	101	97
	58													

There is clear evidence of a general herbage production trend reflecting the effects of topdressing, liming, and the intervening period when no fertilisers were applied.

Individual treatment effects were of the order Super > Basic Slag > Gafsa, and Lime > No Lime, excepting Basic Slag plus Lime where no lime response occurred. During the second period the residual effect of Gafsa was apparent, although of short duration, after which the original order was approximately re-established.

Liming appeared to double the period of residual effects.

During the third period treatment differences tended to disappear altogether; Super, however, tended to remain superior throughout. It may be interesting to note the decline in production of the treatments other than Super, which tended to approach that

of the "headlands", which, from the latter half of the second period, had been cut to serve as "control plots". Where topdressing was resumed a rapid response became apparent in the sward, with a gradually increasing liming response also evident. The upward trend, however, appeared not to continue, which was attributed to a dominance of inferior herbage species which had invaded the sward during the second period.

This is supported by the trends observed for pH, Ca, and P; for on this basis a greater production than was obtained could be expected.

B. SAMPLE TAKING FOR THE PRESENT INVESTIGATION

On the assumption that soils from the sections A and B of the field experiment would differ considerably, due to the introduction on Section A of a period of chemical turf destruction, followed by oversowing, and on the observation of clearly apparent sward differences between sections A and B, it was decided to sample only section B. This would supposedly supply three replicates for each treatment, each replicate plot to be treated as a separate sample in the laboratory, for it was not known at the time that a fourth stage had been introduced in 1958. The data obtained from the laboratory analyses were rearranged to include the fourth stage when that information came to hand.

50 Cores of ¾" diameter were taken from the 0"-2" soil layer of each plot and bulked. Sampling was done at random, a zig-zag course being taken over the plot without estimating the sampling interval.

The plots had not yet received the first annual application of fertiliser, hence the samples would be representative of the treatment effects of 1959 and earlier. It was also fortunate that the routine soil test samples for 1960 had not been taken by the staff of the experimental area, hence there was little chance of this set having been affected by old core holes.

The samples were taken to the laboratory in double-wrapped, brown paper bags. On arrival they were spread out on sheets of paper to dry out at room temperature.

After approximately three days the samples were passed through a 2 mm. sieve, the coarser particles were broken up in a wooden mortar, and turf debris was discarded. The samples were found to be free of stones and gravel.

After a further two days drying the "air dry soil" samples were partitioned until approximately 50 gm. was obtained. These sub samples were ground in a porcelain mortar until the soils had been passed through a 0.2 mm. sieve in their entirety. The "fine soil" thus obtained was bottled and used for the subsequent analyse

The sampling and sample processing procedure has been verified (Jackson, 1958).

C. ADDITIONAL DATA

1. Soil Moisture Determinations

To express subsequent results of analyses on an ovendried soil basis moisture was determined on all the samples. The results are shown in Appendix II.

Procedure:

A duplicate sample of 10 gms. "fine soil" was placed in weighed aluminium containers provided with a lid. The containers with soil were placed in an oven, set at 105-110 degrees Centigrade and left to dry overnight. The samples were cooled in a desiccator and reweighed. Moisture loss was expressed as a percentage of the air dry soil.

2. pH determinations

To aid interpretation of the distribution of soil phosphorus fractions the pH was determined on all the samples.

a. Procedure:

A duplicate sample of 10 gms. "air dry soil" was mixed with 25 ml. water, and kept in suspension for 1 hour. The pH was determined on the suspension with the "Cambridge" pH meter, using a glass electrode. The instrument was calibrated against a standard buffer every time a series of samples was tested.

The results, expressed to the nearest 0.1 pH unit, are presented in table 8. Detailed test results are contained in Appendix III.

Table 8. pH results: Summarised Data

Treatment			Replication 1	2	3	Mean
T.D.	1	S.	5.4	5.4	5.4	5.4 ± 0.04
	2	B.S.	6.1	6.0	5.9	6.0 "
	3	G.	5.8	5.7	5.6	5.7 "
	4	S. + L.	6.2	6.1	6.0	6.1 "
	5	B.S. + L.	6.6	6.4	6.4	6.5 "
	6	G. + L.	6.3	6.3	6.3	6.3 "
U.T.D.	7	S.	5.4	5.3	5.4	5.4 "
	8	B.S.		5.5		5.5 ± 0.1
	9	G.	5.4		5.4	5.4 ± 0.1
	10	S. + L.	5.5	5.5	5.5	5.5 ± 0.04
	11	B.S. + L.	5.5		5.6	5.5 ± 0.1
	12	G. + L.		5.6		5.6 ± 0.1
R.T.D.	8a	B.S. + S.	5.6		5.4	5.5 ± 0.05
	9a	G. + S.		5.4		5.4 ± 0.08
	11a	B.S. + L + S		5.5		5.5 ± 0.08
	12a	G. + L + S	5.5		5.4	5.5 ± 0.05

Statistical treatment of the data gave evidence that treatment differences were not affected by plot variation. (App. XVI)

Analysis of Variance of pH results

Source	S.S.	d.f.	M.S.	F	Result
Treats.	4.37	11	0.397	66.2	**
Error	0.11	18	0.006		
Total	4.48	29			

Least sign. diff.

d	1%	5%
1 & 4	0.2	0.1
1 & 9	0.2	0.2
1 & 8	0.3	0.2
9 & 8	0.3	0.2

The least significant differences between treatments were computed according to the number of replicates available (Glenday, priv. comm.)

b. Discussion:

The effect of lime on raising the pH is highly significant in the T.D. series; it has persisted significantly in the Super and Gafsa plots of the U.T.D. series, but is not evident in the R.T.D. series.

The "liming effects" in the T.D. series of Basic Slag are evident, and to a lesser extent for Gafsa, when compared with Super. These effects are apparently not masked by the addition of lime. This trend is also reflected in the U.T.D. series although it is no longer significant.

The effects of Super alone are not significant, which is also evident in the R.T.D. series.

3. The determination of free Fe_2O_3 (Jackson, 1958 p.168)

a. Requirements:

1) Fresh Sodium dithionite: weigh out 0.5 gm. lots prior to each determination.
2) 0.3 M. Sodium citrate: dissolve 88 gm. tribasic Na Citrate per litre.
3) 1 M $NaHCO_3$: dissolve 84 gm. per litre.
4) Saturated NaCl solution: approx. 400 gms. per litre.
5) 30% H_2O_2.
6) 6 n HCl: dilute 60 ml. 10 n HCl to 100 ml.
7) 10% KCNS solution.

b. Procedure: Weigh out 0.5 gm. "fine soil" into a 50 ml. centrifuge tube, add 20 ml. Na citrate and 2½ ml. $NaHCO_3$, place on the waterbath set at 80 degrees Centigrade.

As soon as the tube contents have reached this temperature, add 0.5 gm. $Na_2S_2O_4$ and stir rapidly for 15 minutes. At the end of this period rinse the stirring rods with a little water, remove the tubes and clear the liquid by centrifuging. Decant the

supernatant liquid via a stirring rod into a 250 ml. volumetric flask through a filter funnel.

Wash the residue twice with 10 ml. portions of saturated NaCl solution, recentrifuge each time, and add the washings to the contents in the flask. Rinse rod and funnel with a little water and finally make the flasks up to volume. Mix contents well. From the extract in the flask take two aliquots of 10 ml. each and place one in a 50 ml. volumetric flask for Fe colour development, the other in a 50 ml. volumetric flask for the organic matter determination. Also run a reagent blank in this series using no soil.

c. Colour development:

To the 10 ml. aliquot in each of the flasks add water to obtain a volume of approximately 35 ml. Add 3 drops of H_2O_2 and 3 ml. of 6 n HCl. Then add to the flask on which the Fe colour is to be developed, 3 ml of 20% KCNS and make up to volume with water, mix contents well. The organic matter blank flask is made up to volume after the 6 n HCl has been added. Mix the contents well. Read the Fe colours 5 minutes after the addition of KCNS on the photometer at wavelength 490 mmu and slitwidth 0.02 mm. The organic matter blanks can be read afterwards, or at any convenient time.

The sum total of the reagent and organic matter blanks is subtracted from the Fe value to obtain a true value which is subsequently converted to % free Fe_2O_3. Prepare a standard curve, using a range of concentrations of Fe of 0.2-3.0 gamma per ml. from a standard stock solution of Fe containing 1 mg Fe/ml.

d. Conversion of photometer readings to % Fe_2O_3:

$$\% \, Fe_2O_3 = \frac{B.R. \times \text{curve factor} \times Fe_2O_3 \text{ factor} \times 200 \times 50 \times 5}{1000000}$$

where;

B.R. = Beckman photometer reading, blank adjusted.

Curve factor = Conversion of B.R. to gamma Fe/ml (log = 0.8508)

Fe_2O_3 factor = Conversion of Fe to Fe_2O_3 (log = 0.1549).

Division by 10^6 converts from mgm. to %.

Hence % Fe_2O_3 = B.R. x combined factor

= log B.R. + log 0.7047-1

(take antilog)

e. Laboratory hints:

The amount of Fe extracted has been shown to be dependent on temperature, the efficacy of the Na dithionite, and the amount of stirring applied (Fife, priv. comm.). Hence it is important that for comparable results a rigid routine be employed. Thus the dithionite is weighed out after the tubes have been placed on the waterbath, to allow these to come up to temperature. Once the dithionite is added no time is lost in commencing to stir the mixture, using a separate glass rod for each tube. Continue to stir for 15 minutes, starting at one end of the batch and working up to the other, etc. At the end of the stirring period rinse the rods with a little water. To reduce washing time use a number of testtubes equal to the number of samples being processed. Fill these tubes with 10 ml portions of sat. NaCl and mark the position of the meniscus with crayon. Every time the residue is washed the contents of the testtube are simply poured over, with a rod, the residue is again brought into suspension, the rod is rinsed with a little salt solution, and the tube is ready for centrifuging. While centrifugation is in progress, the testtubes are again filled with NaCl solution to their marks, and another batch of 10 ml portions is ready for use.

It is advisable to keep the extracts, from which the aliquots were taken, until the photometer readings have been made, as a check aliquot can be taken should a reading appear anomalous. It takes far longer to produce an extract than it takes to throw it away even though one may be tempted to do this due to shortages of glassware and time.

The need to use fresh Sodium dithionite must be stressed. For when this series of analyses had been completed it was found by Fife (priv. comm.) that a recently received batch of this chemical extracted an appreciably greater quantity of free iron oxide than the material used originally.

Hence the extractions were repeated for each treatment, and from the yield increment a factor was obtained to adjust the results for the remaining plots. In fact, the concentration of Fe_2O_3 in the extract was found to be so high that a five fold dilution was necessary, as prescribed in the procedure.

f. Discussion:

The tabulated results are contained in Appendix IV and IVa. The mean for all plots was calculated on an O.D. soil basis; 1.26%, range 1.00% - 1.69%.

There appeared to be no treatment differences, and the plots were simply regarded as a sample series; having plotted the results according to the trial lay-out (see below), there appeared to be as much variation over the field as was shown by the tabulate results contained in the appendix (plot numbers are bracketed, results are rounded off to nearest 0.1 unit).

(12)	1.3	(24)	1.3	(36)	1.6
(11)	1.4	(23)	1.2	(35)	1.3
(10)	1.2	(22)	1.3	(34)	1.5
(9)	1.1	(21)	1.0	(33)	1.7
(8)	1.3	(20)	1.1	(32)	1.7
(7)	1.2	(19)	1.2	(31)	1.3
(6)	1.2	(18)	1.3	(30)	1.3
(5)	1.3	(17)	1.1	(29)	1.0
(4)	1.2	(16)	1.2	(28)	1.0
(3)	1.2	(15)	1.1	(27)	1.3
(2)	1.4	(14)	1.1	(26)	1.2
(1)	1.4	(13)	1.4	(25)	1.2

D. LABORATORY EQUIPMENT:

For weighing a "Bunge" air dampened analytical balance was used.

Chemicals for bulk stock solutions were weighed out on the students' laboratory balance.

Extractions were carried out on an open box type rotary shaker at a speed of 40 r.p.m.

Centrifugations were made with a "Wiccig", inclined head centrifuge, with a capacity of 6 tubes, topspeed 4000 r.p.m.

Colorimetric determinations on the extracts were made with a "Beckman" quartz spectrophotometer.

In addition to a set of 50 ml. centrifuge tubes, and a set of 50 ml. volumetric flasks, the usual range of laboratory glassware was used for the measurement of solution quantities, the storing of extracts, and the preparation and storing of stock solutions.

A drying oven, set at 105-110 degrees Centigrade was used for the moisture determinations of the soil samples, and for the drying of glassware. In order to match the size of batches being processed with the capacity of the equipment in use, a series of tube racks was made, each rack having a capacity of 6.

When the determinations for total phosphorus were made, stands were required to accommodate the flasks with extract in the water bath. To this end a simple stand, consisting of rigid galvanised wire screen with No.8 galvanised wire legs and reinforcings was found quite suitable. The height of the stand is such that the extract volume is completely immersed. The weight of the flask itself then will keep it upright.

To keep the temperature of the water bath constant, and to avoid excessive steaming a lid was also made in the following manner

In a sheet of galvanised iron, of a size to fit the top of the waterbath, cut a series of holes of a diameter to give clearance to the necks of the flasks, and at a spacing determined by the diameter of the flasks and the size of the batch to be processed. Also cut a hole in some convenient position at the rear to accommodate a cork with a thermometer fitted.

Cut this sheet into strips, the cuts being made along the centre lines of the holes.

Fit a handle to each section which will give it rigidity as well.

Made in this manner it is possible to immerse the entire batch in sets, each set being located by the half holes of each lid section.

PART III - METHODS

A. INTRODUCTION

From a consideration of the solubility of chemical forms of P under alkaline and acid conditions, and by refining the alkaline NH_4F procedure (Fife, 1959-I, 1959-II) for the separate determination of Al-P, Fife (priv. comm.) developed a procedure for the fractionation of soil phosphorus, which is remarkable for its simplicity.

Briefly the scheme is as follows:

1. Total P is determined by the method of Bray and Kurtz (1945).
2. Fe-P and Al-P are determined together by extraction with 1 n NaOH of a sample from which exchangeable Ca has been removed by washing with NaCl solution.
3. Fe-P, Al-P, and Ca-P are determined together by making an extraction with 0.1 n HCl, followed by an extraction with 1 n NaOH, and combining the results.
4. Al-P is extracted with 0.5 M NH_4F at pH 8.5, corrections being applied for resorption of P and hydrolysis of Fe-P. The correction values are determined in separate experiments.
5. Organic P is obtained by subtracting (3) from (1).
6. Ca-P is calculated as the difference between (3) and (2).
7. Fe-P is represented by the difference between (2) and (4).

1. TOTAL P, AND ITS COLORIMETRIC DETERMINATION

A. REQUIREMENTS:

60% Perchloric acid; dilute 416.6 ml 72% to 500 ml with water.

2 n Sulphuric acid; dilute 55.6 ml. of 36 n Sulphuric acid to 1 litre with water, taking care to add the acid to the water and not vice versa!

1 n Sulphuric acid; dilute 50 ml. 2 n Sulphuric acid to 100 ml with water.

2 n Sodium carbonate; dissolve 106 gm. in 1 litre water.

Sodium bisulfite solution; dissolve 5.2 gm. in 100 ml 1 n H_2SO_4. This solution will keep for 1 week.

Or dissolve 4.75 gm. $Na_2S_2O_5$ in 100 ml 1 n H_2SO_4 (keeps for 1 week also).

Metol reagent: dissolve 0.42 gm metol and 6.3 gm Na-bisulfite with water to obtain 100 ml solution, which will keep for 3-4 days only.

Quinaldine red indicator: Make a 0.01% aqueous solution.

Standard phosphate solution: (par. 3d of this section).

Sulfomolybdic acid: ignite c.p. MoO_3 in a porcelain dish at dull red heat, but below the melting point, for 1 hour in the muffle oven. Cool, and weigh 7.2 gm into a 800 ml. Kjeldahl flask.

Add 250 ml. conc. Sulphuric acid, a few glass beads, and boil the mixture until solution is complete (a slight turbidity does not matter). Cool, and preserve in a glass stoppered bottle.

B. PROCEDURE:

1. Preparation of the phosphate extract by perchloric acid digestion:

Weigh out single lots of 0.4 gm. "fine soil", place in a 25 ml. Kjeldahl flask, add 7.5 ml. of 60% perchloric acid, and digest on the burner in the fume cupboard for 20 minutes after the dark organic matter colour has disappeared.

Allow the flasks to cool a little, dilute the contents with a small quantity of hot water and filter into a suitably sized volumetric flask - say 250 ml. Wash the residue in the flask and on the filter repeatedly with water. Finally bring the contents in the receiving flask to volume with water.

2. Development of colour on the extract:

Pipette a suitable duplicate aliquot - 10 ml. - into 50 ml. volumetric flasks, add one drop of quinaldine red, and rinse the necks with a little water. Adjust the pH with 2 n Na_2CO_3 or 2 n H_2SO_4 until the red colour has just disappeared. Add water to attain a volume of approximately 25 ml. (use a spare 50 ml. flask with 25 ml. water as a guide).

Add 5 ml. $NaHSO_3$ solution and place flasks on the waterbath set at 95 degrees Centigrade. Digest for 25 minutes after the flasks have attained this temperature. Carefully pipette 0.5 ml. of the sulfomolybdic reagent into the flasks by letting the reagent flow slowly down the neck and swirling the contents to avoid sputtering, and cracking of the glassware.

Next pipette 2 ml. of the metol reagent into the flasks and rinse the necks with a little hot water. Continue digestion for a further hour. Take out the flasks, cool, make volume up to the mark, mix contents and read the colours on the photometer at wave length 815 mmu, and slit width 0.02 mm. The colours last approximately 4 hours and there is a 4-5% fading in 24 hours, detectable only by the photometer.

The photometer readings are converted to mg P/100 gm. soil by the following calculation;

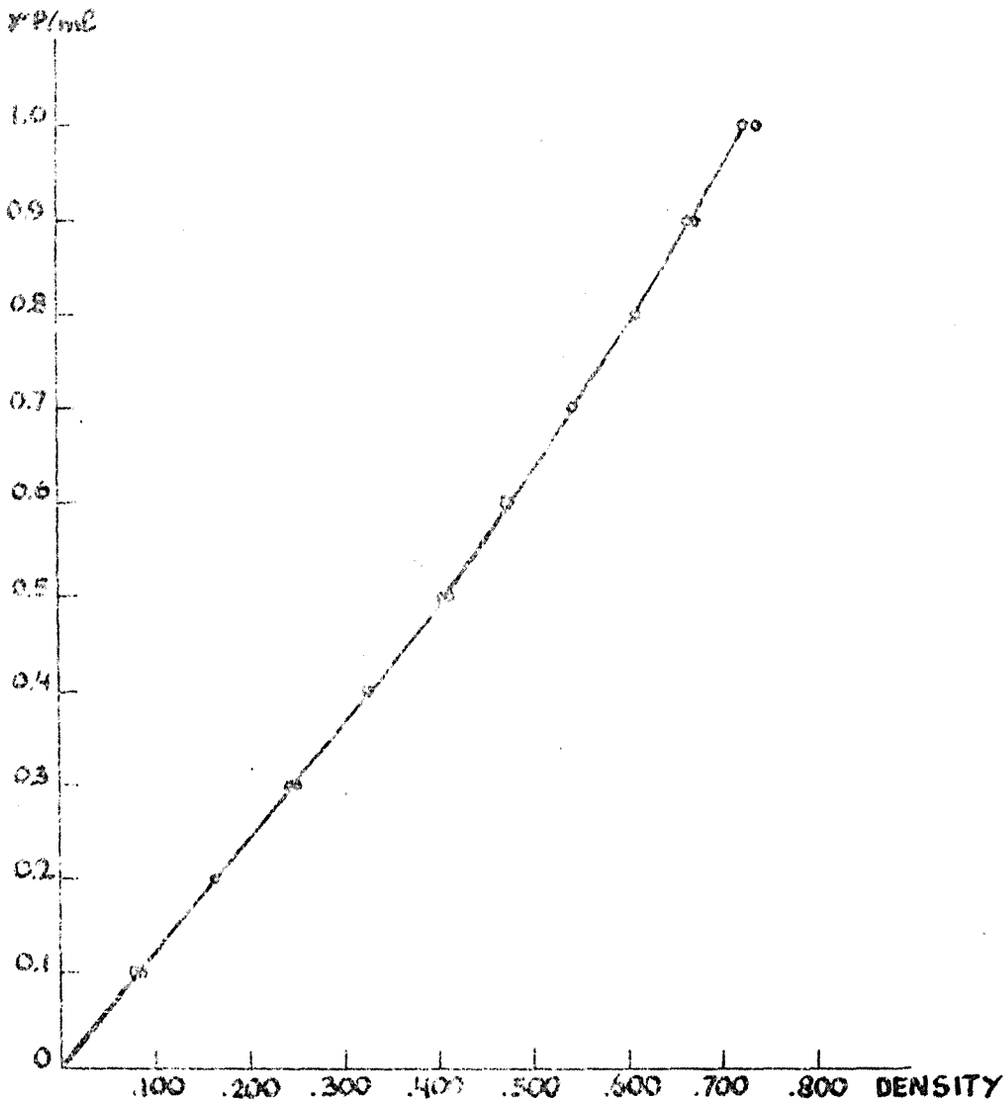
$$\text{mg P/100 gm soil} = \frac{\text{B.R.} \times \text{factor} \times 50 \times 25 \times 250}{1000}.$$

Adjust values finally to an O.D. basis.

The factor is obtained from the slope of the standard curve prepared from a range of phosphate concentrations of 0.1-1.0 gamma P/ml., using the standard P solution, and developing the colours similarly. In this concentration range Beer's law is applicable only up to 0.6 gamma P/ml.; hence it is undesirable to exceed this concentration in the unknown extract solutions, as well as from the standpoint of readability alone (Schricker and Dawson, 1939); this is confirmed in the present work (fig.2, Appendix Va).

When the samples were extracted strictly according to the procedure of Bray and Kurtz it was found that the colours, developed on a 10 ml aliquot and taken from a 50 ml. extract volume, were

FIG. 2. STANDARD P CURVE – PHOSPHOMOLYBDIC BLUE COLOUR IN AN H_2SO_4 SYSTEM.



BECKMAN READINGS MADE AT 815 mμ WAVELENGTH AND 0.02 mm SLITWIDTH.

DERIVED CONVERSION FACTOR = 1.25.

beyond readability. Accordingly the size of the aliquot was reduced, five fold in this case, in order to obtain concentrations within the range of 0.2-0.4 gamma P/ml. In order to avoid the inconvenience of pipetting such small aliquot quantities, the dilution of extracts, prepared in Fife's laboratory, was increased fivefold, as described in this procedure.

A short experiment was conducted with the photometer to determine whether, at a slit width of 0.02 mm, the wavelength of 815 mmu, normally used for molybdenum blue colour determinations, could also be employed here.

The results (table 9, fig. 3) indicate this to be possible without introducing a significant error.

Table 9. Relationship between colour density and wavelength ("Beckman" photometer)

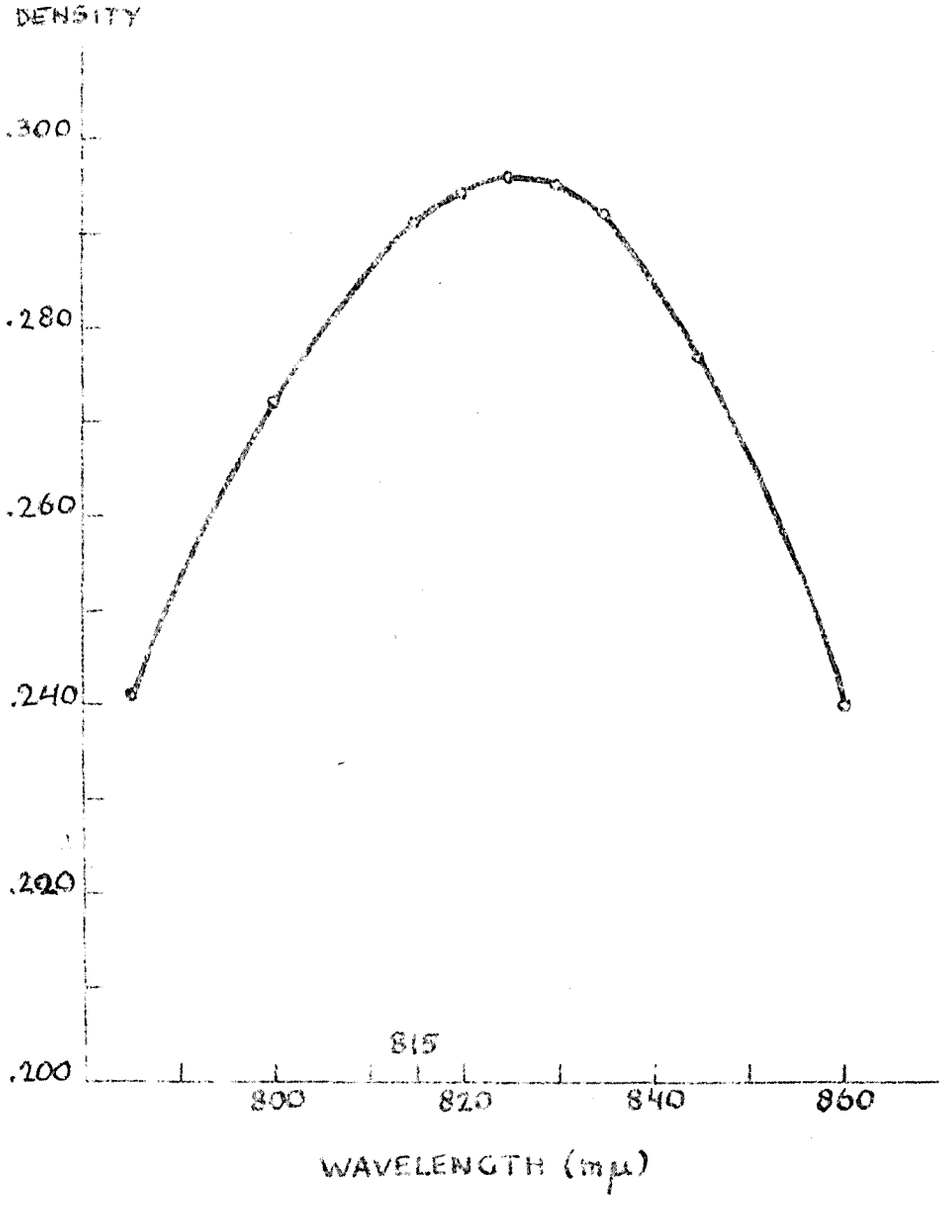
Wavelength	B. readings
785	.241
800	.272
815	.291
820	.294
825	.296
830	.295
835	.292
845	.277
860	.240

C. HINTS ON LABORATORY WORK;

When the Kjeldahl flasks have been installed - the set used in this laboratory has its own burner stand and vacuum exhausted glass fume trap - the flames of the burners are adjusted until the stage has been reached when all the flasks will commence boiling at the same time. The 20 minute digestion period is then taken from the moment the last flask changes colour.

It is also advisable to boil gently to avoid excessive spattering. During the digestion the flasks are occasionally

FIG. 3. RELATIONSHIP BETWEEN COLOUR DENSITY AND WAVELENGTH ("BECKMAN" PHOTOMETER).



rotated on their stand so that spatters are taken up in the bulk liquid.

The hot water, used during the washing process, will cause the filtration to proceed at a rapid pace, but too hot a washing liquid will disintegrate the filters.

Use a stirring rod - a short and thin rod that will stand in the filter funnel - to guide the washings on to the filters, and leave the rod resting in the funnels between operations, taking care when replacing it or the filter will be punctured.

Each washing is allowed to percolate completely before the next one is added. The waterbath, with a thermostat fitted, should have a sufficiently large heating capacity to bring the flasks up to temperature rapidly when the colours are to be developed.

2. ALKALI SOLUBLE P, AND ITS COLORIMETRIC DETERMINATION

A. INTRODUCTION

In this procedure the soil is extracted with 1 n NaOH at room-temperature for 40 hours. The efficiency of NaOH at this concentration appears far greater in the removal of Fe-P and Al-P than 0.1 n NaOH, which is supported by the following data (Fife, priv. comm.);

Table 10. Comparison of the efficiency of 0.1 n NaOH and 1n NaOH (1:10 ratio extractions)

P. bearing Mineral	% of total P_2O_5 dissolved	
	0.1 n NaOH	1 n NaOH
Variscite	45.40	95.24
Barrandite	56.84	93.81
Strengite	82.63	93.56
K-Taranakite	67.56	96.33
K-Fe-Taranakite	65.30	97.19
K-Fe-Phosphate	85.47	94.14

From evidence Fife (priv. comm.) concluded that the amount of P extracted was independent of the conventional soil/solution ratios employed, and that with time no increase in the amount of organic matter in the extract occurred. Resorption of P was also found not to take place, and the 40 hour extraction period was considered adequate.

B. REQUIREMENTS:

0.5 M NaCl: dissolve 29.23 gm. in 1 litre water.

Acetone: A.R. grade.

1 n NaOH: dissolve 40.0 gm. in 1 litre water.

Approx. 1 n HCl: dilute 100 ml. 10 n HCl to 1 litre with water.

To ensure correct neutralisation of NaOH by HCl a titration test is made with methyl red as indicator. It is desirable that a slight excess of HCl be present to cause the precipitation of organic matter in the extract. Therefore adjust the strength of the HCl so that, in a titration with 10 ml. portions of NaOH, 9.5 ml. of HCl is sufficient to create the end point (Fife, priv. comm.).

C. PROCEDURE:

Duplicate lots of 0.25 gm. of "fine soil" are placed on moistened filter papers, fitted into funnels. Suspend the filters over 50 ml. volumetric flasks. Leach the soil with portions of 0.5 M NaCl until nearly 50 ml. has been attained. The filters are allowed to drain completely before the next portion is added. Remove the flasks and make up to volume with water. Mix the contents. Withdraw 15 ml. with the pipette and discard this. The molybdenum blue colour is developed as described below (par. E.).

Also make a blank determination on a separate 35 ml. portion of NaCl.

The soil residue on the filters is washed twice with acetone, then put in a warm place to dry. Or alternatively - and better suited to the general procedure when working with batches - the washed filters with soil are placed on a tube rack and put aside to dry overnight, making certain that no dust or other matter can cause contamination.

When dried insert the papers with soil in 50 ml. centrifuge tubes, add 25 ml. 1 n NaOH, stopper, and shake vigorously by hand to reduce the paper to a pulp. Place the tubes in the shaker and shake for 40 hours. At the end of this period centrifuge well, take a 15 ml. aliquot and run this into a centrifuge tube containing 15 ml. of approximately 1 n HCl. Centrifuge again to remove the precipitated organic matter. Take a 20 ml. aliquot, which is equal to a 10 ml. aliquot of the original extract, and add this to 15 ml. water in a 50 ml. volumetric flask. Develop the colour as described below under par. E. Keep the remaining neutralized extracts. Colour is also developed on a blank, made up of 1 n NaOH and 1 n HCl in the same proportions as the unknown.

Prepare also an organic matter blank series of 5 ml. aliquots taken from the remainder of the neutralised extracts; dilute the aliquots to 25 ml. with water, after which the colour is read off

directly on the photometer.

It is necessary to recentrifuge the extract remainders to remove the cloudiness caused by the previous aliquot withdrawal. Subtraction of the blank values from the main readings produces the true values for subsequent calculation.

D. CALCULATIONS:

a. For leachate:

$$\text{Mg P/100 gm. soil} = \frac{\text{B.R. x factor x 50 x 400}}{1000}$$

b. For NaOH extraction:

$$\text{Mg P/100 gm. soil} = \frac{\text{B.R. x factor x 50 x 2.5 x 400}}{1000}$$

The factor is obtained from the standard P curve (par.E). Finally adjust values to O.D. basis.

E. THE DETERMINATION OF P BY THE PHOSPHO-MOLYBDIC BLUE COLOUR IN AN HCl SYSTEM

(Dickman and Bray, 1940, with slight modifications by Fife (1960, priv. comm.).

1. Requirements:

Ammonium molybdate solution: dissolve 7.5 gm. powdered Ammonium molybdate in 175 ml. water in a 500 ml. volumetric flask. While constantly swirling the contents, add slowly 175 ml. 10 n HCl, then make up to volume with water. This solution will keep for 2 months, date the flask for reference (Jackson, 1958).

10 n HCl: dilute 1500 ml. concentrated HCl by pouring it slowly into 200 ml. water.

Stannous chloride solution: dilute 0.6 ml. concentrated $SnCl_2$ solution to 100 ml. with water in a volumetric flask. This solution keeps for 1 day only and should be freshly prepared prior to each set of determinations.

Concentrated stannous chloride solution: dissolve 10 gm. $SnCl_2$ in 25 ml. concentrated HCl and store in darkness in a stoppered brown glass bottle. This solution keeps for about a fortnight, date the bottle for reference.

Standard P solution: to obtain a standard solution containing

50 gamma P per ml. dissolve 0.2194 gm. KH_2PO_4 in 1 litre water in a volumetric flask.

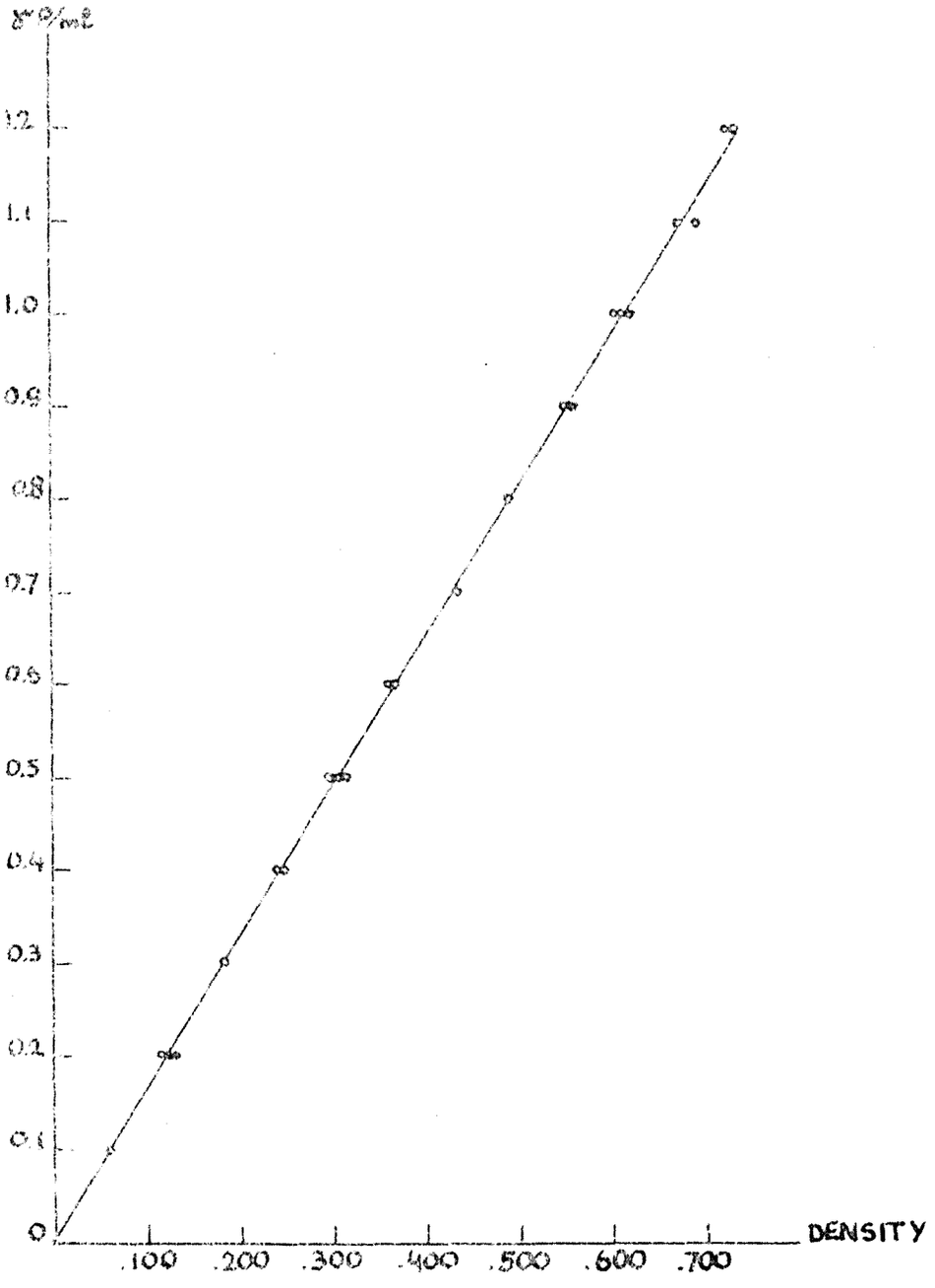
Preparation of the standard P curve: employing a range of 0.1-1.2 gamma P/ml. pipette into 50 ml. volumetric flasks - to which approx. 25 ml. water has been added - 0.1 up to 1.2 ml. of the standard P solution. Wash down the neck with water from the wash bottle until approx. 35 ml. is obtained. Add the molybdate and stannous chloride reagents (10 ml. and 5 ml. resp.), make flasks up to volume, and read colours on the photometer. Plot the results. The curve will obey Beer's law over this range. From the slope of this curve (fig. 4) obtain the factor required to convert the Beckman photometer readings of the test solutions t gamma P/ml.

A record of several standard P determinations is contained in the Appendix (V) and summarised in table 11, including checks which were made from time to time. There is no doubt that the performance of the photometer has been remarkably consistent for the period during which it was operated.

Table 11. Summary of standard P determinations

Gamma P/ml	Beckman true readings			
	20.4.60	4.5.60	12.11.60	Checks
0.1	.061	.063		
0.2	.123	.119		.126
0.3	.185	.184		
0.4	.240	.241		.248
0.5	.297	.314	.309	
0.6	.360	.368		
0.7	.435	.434		
0.8	-	.492		
0.9	.560	.551		
1.0	.620	.612	.609	.613
1.1	.694	.672		.697
1.2	.726	.729		

FIG. 4. STANDARD P CURVE – PHOSPHOMOLYBDIC BLUE COLOUR IN AN HCl SYSTEM.



BECKMAN READINGS MADE AT 815 mμ WAVELENGTH AND 0.02 mm SLITWIDTH.

DERIVED CONVERSION FACTOR = 1.625.

2. Procedure:

Pipette from the test extract a convenient aliquot - usually 10 ml. - into a 50 ml. volumetric flask to which approx. 25 ml. water has been added.

Add 10 ml. of the molybdate reagent, and mix with a swirling motion.

Then add 5 ml. of the stannous chloride reagent and mix again.

Make up to final volume with water, stopper, and mix contents thoroughly - three inversions will suffice.

Read the developed colour after 15 minutes on the ("Beckman") spectrophotometer, set at wavelength 815 mmu., and slit width 0.02 mm. The colours will keep for less than two hours.

3. Laboratory hints:

A batch of 18 extracts has been found very suitable for colour development, as by the time the reagents have been added, and the photometer is ready for use, the first sample will be 15 minutes old. Further-more, as each reading takes about 1 to 2 minutes this synchronizes very well with the speed of pipetting and mixing, and the colour on each sample will be fully developed when it is due for reading.

A sequence of operations for a batch of 18 samples would be as follows, assuming that the sample extract aliquots have been pipetted out into their flasks and the reagents have been prepared.

1. Switch on the photometer as it requires about 20 minutes to warm up.

2. Pipette out the molybdate reagent, mixing the flask which has received its quotum with one hand, while filling the pipette with the other.

3. Act likewise when adding the stannous chloride reagent. Set timer for 15 minutes as soon as the first quantity has been added.

4. Make the flasks up to volume and mix.

5. Take the cell from its cleaning bath and rinse it well with water.

6. Start the readings as soon as the timer rings.

7. Rinse the cell 3 to 4 times after each reading with the next solution.

8. Check each reading until it has become consistent.

9. After the readings have been made switch off the photometer, rinse cell and return it to its cleaning bath, wash and drain all glassware.

After having processed several batches, using the same pipettes for each particular operation, one may achieve sufficient confidence in the modus operandi to employ 100 ml. Erlenmeyer flasks, and pipette out every required quantity in the following order:

1. 25 ml. water.
2. 10 ml. extract.
3. 10 ml. molybdate reagent.
4. 5 ml. stannous chloride reagent.

50 ml. total volume.

Pipetting errors will be reduced to a minimum by one having achieved a certain pipetting rhythm, while it is assumed that this error will be no greater than that embodied in the volumetric flasks. A check, made with a 50 ml. pipette on these flasks showed considerable variation to exist. Moreover, duplication remained as accurate after a tentative switch-over had been made to Erlenmeyer flasks.

4. Calculations:

The values obtained are those of the test solution and the blanks.

Whenever a fresh stock solution is prepared the blank determinations are repeated.

The blank values are subtracted from the extract value to obtain a result free from interference by any impurities in the chemicals used. Make certain to note in the workbook the sign of the blank value which may be either positive or negative.

Assuming that a 0.5 gm. soil sample was extracted with

25 ml. extractant (1:50 ratio); that a 10 ml. aliquot of cleared extract was taken, diluted to 50 ml. with reagents, and that the readings were made on this solution; and assuming that a standard P curve has been prepared, from which has been obtained the required conversion factor. Then the following calculation steps apply:

1. Beckman reading x factor = gamma P/ml. in 50 ml. flask;
2. (1) x 50 = gamma P in flask = gamma P in 10 ml. aliquot;
3. (2) x 2.5 = gamma P in 25 ml. extract = gamma P in 0.5 gm.soil
4. (3) x 200 = gamma P in 100 gm. soil.
5. $\frac{(4)}{1000}$ = mg P per 100 gm. soil.

Summarised, the following formula applies;

$$\text{mg P/100 gm. soil} = \frac{\text{B.R. x factor x 50 x 2.5 x 200}}{1000}$$

$$= \underline{\text{B.R. x factor x 25}}.$$

Finally adjust the results to O.D. soil basis.

3. THE EXTRACTION OF ACID AND ALKALI SOLUBLE P

By this succession of extractions total inorganic P, consisting of Fe, Al, and Ca bound P, is determined.

A. REQUIREMENTS:

0.1 n HCl: dilute 10 ml., 10 n HCl to 1 litre with water.

0.5 M NaCl: dissolve 29.23 gm. in 1 litre water.

Acetone: A.R. grade.

1 n NaOH: dissolve 40 gm. in 1 litre water.

Approx. 1 n HCl: dilute 100 ml, 10 n HCl to 1 litre with water.

N.B. A test titration is made to ensure that at least 9.5 ml. of 1 n HCl will neutralize 10 ml. 1 n NaOH, with methyl red as indicator. The small excess of not more than 0.5 ml.HCl will acidify the solution sufficiently to precipitate extracted organic matter.

B. PROCEDURE:

1. Extraction with 0.1 n HCl:

Place duplicate lots of 0.25 gm. "fine soil" in 50 ml. centrifuge tubes; add 20 ml. 0.1 n HCl, stopper, and shake for 4 hours on the shaking machine. The extract is cleared by centrifugation. On a 10 ml. aliquot P is determined colorimetrically. Prepare a blank of the extractant using no soil.

Discard the remaining extract, wash the soil residue twice with 20 ml. portions of 0.5 M NaCl, centrifuging in between. Finally wash the residue with 10 ml. acetone. The tubes may be placed in the oven, or another warm site to drive off the remaining acetone. Take care not to heat the residues.

2. Extraction with 1 n NaOH:

Taking the washed and dried soil residues proceed as described in par. 2c., taking care not to omit the blanks.

C. CALCULATIONS:

1. HCl extraction:

$$\text{mg P/100 gm. soil} = \frac{\text{B.R. x factor x 50 x 2 x 400}}{1000}$$

2. NaOH extraction:

$$\text{mg P/100 gm. soil} = \frac{\text{B.R. x factor x 50 x 2.5 x 400}}{1000}$$

The factor is obtained from the standard P curve (par. 2E).

Adjust values finally to O.D. soil basis.

B. PROCEDURE FOR THE DETERMINATION OF Al-P

1. The extraction of Al-P by 0.5 M NH_4F at pH 8.5

a. Requirements:

0.5 M Ammonium fluoride solution: dissolve 18.5 gm. in 1 litre water. Adjust the pH to 8.5 with ammonia. Store in a stoppered "pyrex" bottle.

Boric Acid Solution: dissolve 50 gm. per litre water; heat the water to aid dissolution.

Ammonium molybdate and stannous chloride reagents

(par. 2E, Section A.)

b. Procedure:

Place duplicate lots of 0.5 gm. "fine soil" in 50 ml. centrifuge tubes, add 25 ml. NH_4F solution, stopper, shake for the experimentally determined period, centrifuge to clear the extract, and determine P colorimetrically on a suitable aliquot - say 10 ml.

To eliminate fluoride interference with the development of colour the boric acid procedure of Kurtz (1942) is employed, which has been slightly modified by Fife (priv. comm.). Instead of pipetting the quantities of 15 ml. boric acid solution and 10 ml. water separately, the boric acid solution is additionally diluted with water in similar proportions. The pipetting order is then;

25 ml. dilute boric acid solution
10 ml. extract
15 ml. colour reagents
50 ml. total test solution.

The colours are read as usual after 15 minutes on the photometer - wavelength 815 mmu., slitwidth 0.02 mm. A blank determination is made, using no soil.

FOOTNOTE: The correction factor is calculated as the fraction of P extracted by three days' shaking reduced by the amount of released Fe-P, according to the slope of the curve and the amount of P extracted in three days:

$$\frac{3.08}{3.20} = 0.960 \quad \text{(fig. 5)}.$$

c. Calculations:

mg P/100 gm. soil = $\frac{\text{B.R. x factor x 50 x 2.5 x 200}}{1000}$; the factor is obtained from the standard P curve.

d. Additional determinations

The amount of P released by this method is dependent on the time of extraction and the resorption of P according to the soil/ extractant ratio employed. Therefore a series of experiments was conducted to determine the extent of these two factors, by which subsequently the normal procedure, and the values obtained, were adjusted.

2. The influence of time on the release of P in 0.5 M NH_4F at pH 8.5.

Soil from treatment 1 (Super, T.D.: plot 1) was used for this experiment, carried out in triplicate.

0.4 gm. soil was shaken with 20 ml. extractant (1:50 ratio) for periods ranging from 12 hours to 7 days, by 12 hour intervals. The extracts were cleared by centrifugation, and P was determined colorimetrically on a 10 ml. aliquot.

The results are presented in graphical form (fig. 5), and tabulated in Appendix VI.

It is apparent that the release of the greater proportion of Al-P occurs during the first 36 hours. After 3 days the release of Al-P appears complete, and further increments in P concentration are due to the, at this stage constant hydrolysis of Fe-P (Fife, priv.comm.).

After about 4 days an apparent equilibrium between the release of P and its resorption on to the soil matrix is established. It would be quite difficult to estimate the release of Fe-P, but by extrapolation the 3 day extraction period is reduced to a zero order which eliminates this aspect.

An extrapolation factor of 0.960 was calculated for this soil, and an extraction period of 3 days was adopted for the complete release of Al-P.

FIG. 5. THE INFLUENCE OF TIME ON THE RELEASE OF P BY 0.5 M NH_4F AT pH 8.5.

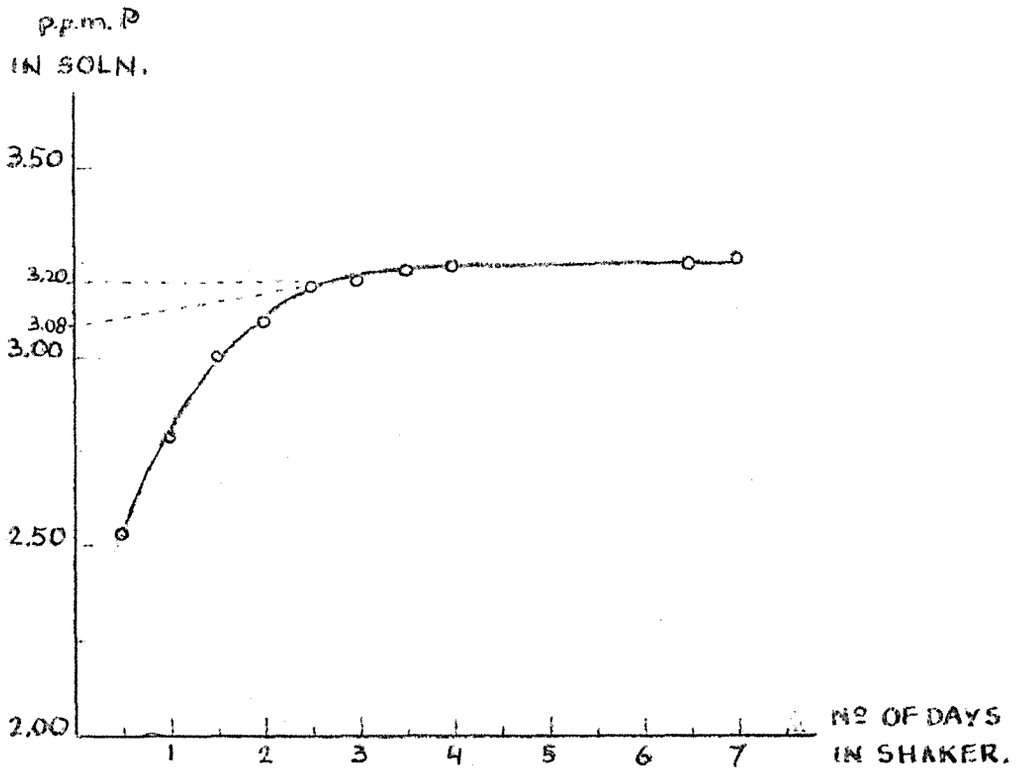
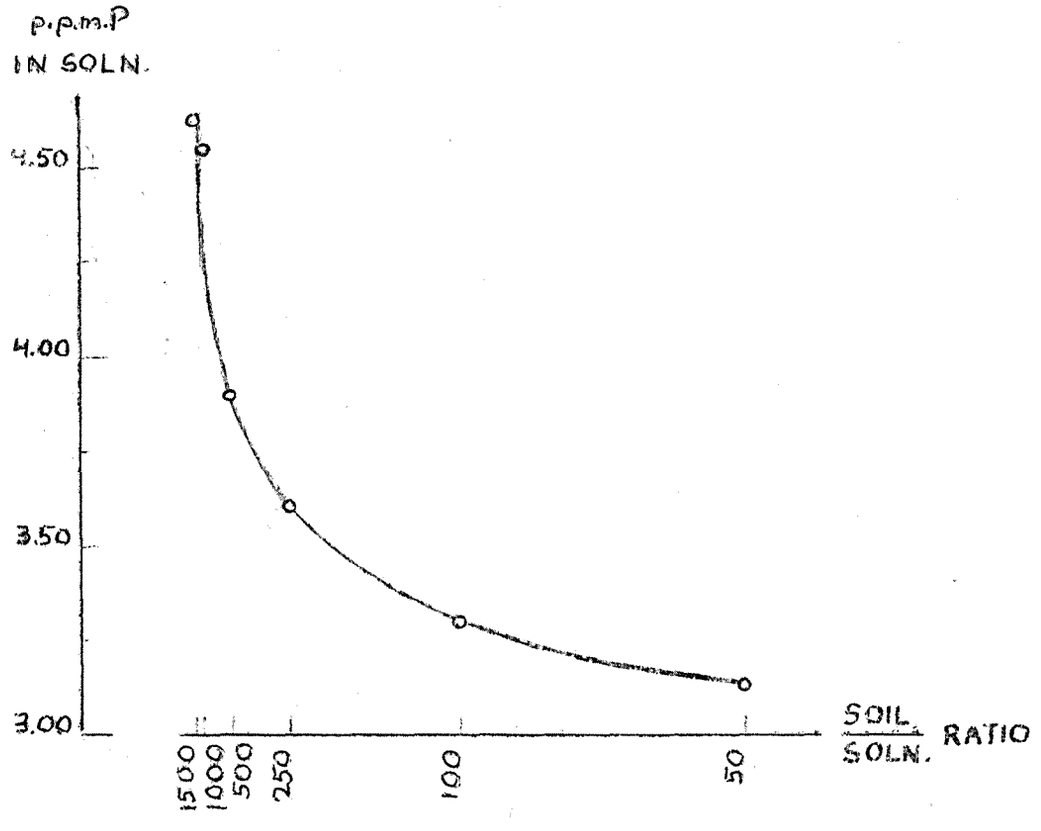


FIG. 6. THE INFLUENCE OF DILUTION ON THE RELEASE OF P BY 0.5 M NH_4F AT pH 8.5.



3. The influence of resorption on the extraction of Al-P by 0.5 M NH_4F at pH 8.5

Several methods may be employed to determine the extent of P resorption by which the values obtained from the normal procedure may be corrected.

a. The effect of soil/extractant ratio on the release of Al-P in 0.5 M NH_4F at pH 8.5

At increasing soil/extractant ratios over a 3 day shaking period, triplicate determinations on the release of P were made from the soil of treatment 1 (Super, T.D.: plot 1). The extracts were cleared by centrifugation and P was determined colorimetrically. The results (Appendix VII), adjusted to a common basis (1: 50 ratio), are shown graphically in fig. 6, which illustrates the added release of Al-P caused by widening the soil/extractant ratio.

Since hydrolysis of Fe-P is unaffected by increasing dilution, Fife (priv. comm.) concludes that the increased P concentration in the extract is due to a decrease in resorption of released P, which is complete at ratios in excess of 1: 1000.

The inconvenience of employing such dilutions in routine laboratory extractions is obvious, and accordingly a correction factor for the release of P at the normally used 1:50 ratio may be calculated on the basis of the increment of P, released at the sorption free dilution. In this case a calculated value of 1.061 was found (table 12).

b. The determination of sorption by the chemical recovery of added P.

Soils from each treatment were used in this experiment where, at a 1:50 soil/extractant ratio over a 3 day shaking period, quadruplicate determinations were made on the recovery of P, added to the extractant at a concentration of 2 gamma P/ml. (employing the standard P solution). A similar series employed extractant to which no P had been added. The extracts were cleared by centrifugation, and P was determined colorimetrically.

the percentage recovery of added P was calculated from the difference between the P concentrations in the extracts with and without added P. The results are presented in Appendix VIII, and summarised in table 12. Some treatment variation is evident.

c. The determination of sorption by the recovery of added P.-isotope.

Again soils from each treatment were shaken for a 3 day period at a 1:50 soil/extractant ratio in 0.5 M NH_4F at pH 8.5, to which had been added a "carrier free" amount of radio active P.

The extracts were cleared by centrifugation, and the amount of radiation was determined from a 0.3 ml. aliquot pipetted on to an aluminium sample pan and left to dry overnight. Counts were made over a 1 minute period and, with similarly prepared standards as reference, the percentage recovery was calculated (table 12, Appendix IX).

Several days later the experiment was repeated with soils from treatments 1 and 7 (Super T.D. and Super U.T.D., plots 1 and 7 resp.), but on this occasion 1 gamma/ml. of non radio active P was also included in the extractant, as it was suspected, from a comparison of the previous results with the results of the chemical recovery experiment, that isotopic exchange had occurred. However, the results obtained from this experiment appeared inconsistent and failed to confirm or refute this suspicion, as shown in table 12. Details of the result of this experiment are also tabulated in Appendix IX.

d. Comparison of the three methods

It is evident from table 12 that generally the recovery of P by chemical means is better than that for radio active P, indicating that isotopic exchange in this soil occurred. These sorption correction values were therefore disregarded in favour of the values obtained by chemical means.

Table 12. Percentage recovery, summary

No.	Treatment	Ratio Expt.	^{32}P	^{32}P + P	Chem. Recovery
1	S.	94.26	79.20	78.50	75.40
2	B.S.		78.72		79.37
3	G.		77.66		80.95
4	S. + L.		81.41		82.54
5	B.S. + L.		81.28		82.54
6	G. + L.		77.07		72.22
7	S.		70.78	74.16	73.81
8	B.S.		73.57		77.76
9	G.		68.82		73.02
10	S. + L.		69.39		73.81
11	B.S. + L.		69.31		73.02
12	G. + L.		76.86		78.56

Although the effect of adding P to the extractant in the chemical recovery experiment may tend to raise the recovery values slightly, Fife (priv.comm.) has shown for a number of soils that the percentage recovery is not seriously influenced by a range of additions of 0.5 - 3.0 gamma P/ml. In this work a higher recovery value was in fact obtained from the soil/extractant ratio experimen but it was disregarded in favour of those obtained from the chemica recovery experiment from which a correction value, appropriate to each treatment, was available (table 13).

Table 13. Sorption correction factors, summary

No.	Treatment	Ratio Expt.	^{32}P	^{32}P + P	Chem. Recovery
1	S.	1.061	1.263	1.274	1.326
2	B.S.		1.271		1.260
3	G.		1.290		1.235
4	S. + L.		1.229		1.211
5	B.S. + L.		1.233		1.211
6	G. + L.		1.300		1.385
7	S.		1.416	1.348	1.355
8	B.S.		1.362		1.286

(Contd.)

No.	Treatment	Ratio Expt.	^{32}P	$^{32}P + P$	Chem. Recovery
9	G.		1.453		1.379
10	S. + L.		1.445		1.355
11	B.S. + L.		1.443		1.370
12	G. + L.		1.303		1.273

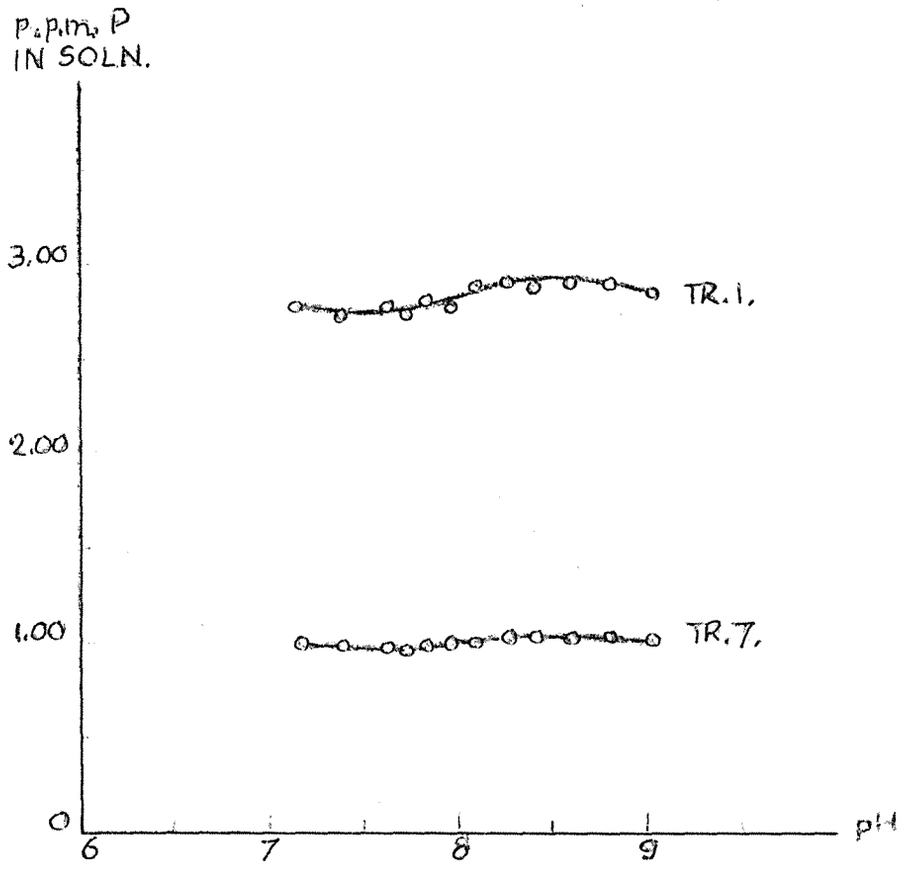
4. The solubility of Soil P in 0.5 M NH_4F over a range of pH.

Soils from treatments 1 and 7 (Super T.D. and Super U.T.D.: plot 32 and 26 resp.) were shaken for 4½ days with 0.5 M NH_4F, on which the pH was adjusted with either HCl or NH_4OH, at a 1:50 soil/extractant ratio. Although it was intended to shake for 3 days only, unforeseen circumstances prevented this. P was determined colorimetrically on the extracts, which were cleared by centrifugation. The pH at equilibrium was determined with the glass electrode on the remaining suspension. The results are presented in table 14, details of which are tabulated in Appendix X.

Table 14. Solubility of P in 0.5 M NH_4F

pH		p.p.m. P in solution	
Initial	At eqm.	treat. 1.	treat. 7.
5.35	7.16	2.77	0.99
5.60	7.39	2.73	0.97
6.38	7.61	2.77	0.98
7.10	7.71	2.72	0.96
7.45	7.81	2.79	0.97
7.78	7.96	2.77	0.99
8.00	8.07	2.87	0.99
8.24	8.26	2.90	1.03
8.40	8.40	2.87	1.03
8.62	8.60	2.90	1.02
8.82	8.80	2.90	1.04
9.06	9.03	2.85	1.01

FIG. 7. THE INFLUENCE OF pH ON THE SOLUBILITY OF P IN 0.5 M NH_4F.



It is apparent from fig. 7 that the solubility of P in 0.5 M NH_4F is little affected by topdressing treatment, suggesting that the greatest proportion is Al-P although some may be Fe-P released by hydrolysis as indicated by the release of P over time.

A comparison of these curves with those presented by Fife (1959-II) shows that the Marton Loam resembles the Manawatu silt loam. The increase in P solubility with increasing pH in the alkaline range, shown by the curves of these soils is not due to increasing hydrolysis of Fe-P but rather to a decrease in P resorption by free iron oxides. The conclusion may be reached that for the Marton Loam the use of 0.5 M NH_4F for the extraction of Al-P at pH 8.5 ensures maximum solubility of Al-P coincident with minimum Al-P resorption, while the release of Fe-P by hydrolysis may be discounted by extrapolation.

PART IV. RESULTS.

1. TOTAL PHOSPHORUS.

A summary of the data is shown in Table 15. Details of the analyses are tabulated in Appendix XI.

TABLE 15

TOTAL PHOSPHORUS. SUMMARISED DATA.
(Results expressed as mg/100 gm soil on O.D. basis).

Treatments			Replicates 1	2	3	Mean
T.D.	1	S.	114.56	110.40	112.61	112.5 ± 1.8
	2	B.S.	107.99	108.20	108.45	108.2 "
	3	G.	113.20	116.29	106.13	111.9 "
	4	S. + L.	113.08	106.57	107.46	109.0 "
	5	B.S. + L.	108.61	104.65	99.05	104.1 "
	6	G. + L.	113.49	108.20	108.09	109.9 "
L.T.D.	7	S.	85.42	84.20	80.86	83.5 "
	8	B.S.		82.66		82.7 ± 3.1
	9	G.	83.30		83.36	83.3 ± 2.2
	10	S. + L.	84.29	80.37	83.27	82.6 ± 1.8
	11	B.S. + L.	82.58		84.43	83.5 ± 2.2
	12	G. + L.		80.22		80.2 ± 3.1
R.T.D	2	B.S. + S.	95.18		90.86	93.0 ± 2.2
	3	G. + S.		87.59		87.6 ± 3.1
	2	B.S. + L. + S		89.36		89.4 ± 3.1
	3	G. + L. + S.	95.38		89.62	92.5 ± 2.2

From the analysis of variance, it is concluded that plot variation is not significant.

ANALYSIS OF VARIANCE

Source	S.S.	d.f.	E.M.S.	F.	Result
Treats.	5151.85	11	468.35	48.38	**
Error	174.23	18	9.68		
Total	5326.08	29			

To facilitate interpretation of the data , the least significant differences, according to the number of replications, were computed. These are presented in the table below.

Treats	1%	5%
1 and 4	7.3	5.3
1 " 9	8.2	6.0
1 " 8	10.3	7.6
9 " 8	11.0	8.0

The possible influence of liming, resulting in lower total P levels, was investigated statistically according to the following calculations; difference between means "no lime" and "lime"; 110.87 - 107.69 = 3.18.

L.S.D. at 1%	4.23
at 5%	3.00
Result	*

This effect of lime appears similar to the "liming effect" shown by Basic Slag, and it will be shown subsequently that it is almost entirely due to changes in the organic P fraction, caused by an increase in biological activity accelerating the mineralisation of organic P.

Individual treatment differences are not significant.

The lower levels of total P in the U.T.D. series are not significant but may be traced to the inorganic P fraction. The increase in total P, shown in the R.T.D. series, may be traced to the Al-P fraction, and indicates its significance in reflecting the changes in topdressing practice.

2. TOTAL INORGANIC PHOSPHORUS.

A summary of the results is presented in Table 16 which demonstrates the degree of plot variation; detailed results of the analyses are contained in appendix XII.

TABLE 16

TOTAL INORGANIC P. SUMMARISED DATA.

(Results expressed as mg P/100 gm. soil on O.D. basis).

Treatments			Replicates 1	2	3
T.D.	1	S.	37.69	35.53	36.09
	2	B.S.	34.96	36.02	34.49
	3	G.	39.52	39.99	31.42
	4	S. + L.	38.51	35.45	38.68
	5	B.S.+ L.	36.58	34.44	33.96
	6	G. + L.	40.52	39.25	37.30
U.T.D.	7	S.	16.25	14.57	14.71
	8	B.S.		15.03	
	9	G.	14.10		14.80
	10	S. + L.	16.70	13.92	14.16
	11	B.S. + L.	16.17		14.62
	12	G. + L.		13.88	
R.T.D.	2	B.S. + S.	24.14		19.51
	3	G. + S.		19.62	
	2	B.S.+ L.+ S.		19.49	
	3	G.+ L.+ S.	25.51		18.65

Since Ca-P is calculated as the difference between this fraction and alkali soluble P, it was considered necessary to separately assess the degree of variation due to plot and analysis duplication. (Glenday, priv. comm.)(App. XVI)

ANALYSIS OF VARIANCE

Source	S.S.	d.f.	E.M.S.	F.	Result
Treatments	6318.22	11	574.38	3039.04	**
Plots (residual)	127.63	18	7.09	37.51	**
Duplicates	5.66	30	0.189		
Total	6451.51	59			

It may be concluded that neither variation is significant. The degree of accuracy in the analytical work was determined by the "coefficient of repeatability", calculated as follows:-

$$s_d^2 = 0.189 \quad \text{(duplicates)}$$

and $$s_d^2 + 2s_p^2 = 7.09 \quad \text{(residual)}$$

hence $$s_p^2 = \frac{7.09 - 0.189}{2} = 3.451 \quad \text{(plots)}$$

therefore $$\frac{s_p^2}{s_d^2 + s_p^2} = \frac{3.451}{3.451 + 0.189} \times 100\% = 94.8\%$$

The combined lab. error, embodied in the plot variation for Ca-P equals:-

$$s^2_{d(aa)} + s^2_{d(la)} = 0.276$$

and where $s^2_{p(ca)} = \frac{1.974 - 0.276}{2} = 1.698$

this transferred lab. error will be of the order of:-

$$\frac{0.276}{1.698} \times 100\% = 4\% \text{ of the plot variance.}$$

($s^2_{d(aa)}$ - duplication variance acid-alkali extraction)
($s^2_{d(la)}$ - duplication variance leach-alkali extraction)

Hence, although the group extractions pose the problem of errors in the analytical work being transferred to the subsequent results, the repeatability of these extractions is of such a high order that this error may be disregarded.

3. ORGANIC PHOSPHORUS.

Subtraction of the acid-alkali soluble P values from those for total P is assumed to represent the values for organic P, presented in table 17.

TABLE 17

ORGANIC P.

(Results expressed as mg/100 gm. soil (O.D. basis).

Treatments			Replicates			Mean
			1	2	3	
T.D.	1	S.	76.87	74.87	76.52	76.1 ± 1.2
	2	B.S.	73.03	72.18	73.96	73.1 "
	3	G.	73.68	76.30	74.71	74.9 "
	4	S. + L.	74.57	71.12	68.78	71.5 "
	5	B.S. + L.	72.03	70.21	65.09	69.1 "
	6	G. + L.	72.97	68.95	70.79	70.9 "
U.T.D.	7	S.	69.17	69.63	66.15	68.3 "
	8	B.S.		67.63		67.6 ± 2.0
	9	G.	69.20		68.56	68.9 ± 1.4
	10	S.+ L.	67.59	66.45	69.11	67.7 ± 1.2
	11	B.S. + L.	66.41		69.81	68.1 ± 1.4
	12	G. + L.		66.34		66.2 ± 2.0
R.T.D.	2	B.S. + S.	71.04		71.35	71.2
	3	G. + S.		67.97		68.0
	2	B.S. + L. + S.		69.87		69.9
	3	G.+ L.+ S.	69.87		70.97	70.4

From the analysis of variance, it was concluded that plot variation was insignificant.

ANALYSIS OF VARIANCE.

Source	S.S.	d.f.	E.M.S.	F.	Result
Treatments	258.253	11	23.478	5.634	**
Error	75.012	18	4.167		
Total	333.265	29			

The degree of variance due to analytical error was considered negligible as the duplicate determinations of P on the total P extracts showed close agreement while the insignificant duplication error for total inorganic P was shown to be negligible. The least significant differences between treatments, depending on the number of available replicates, were computed.

TABLE OF L.S.D.

Treatments	1%	5%
1 and 4	4.8	3.5
1 " 9	5.4	3.9
1 " 8	6.8	5.0
9 " 8	7.2	5.3

The decrease in organic P levels, due to liming, was investigated statistically, and was shown to be highly significant, according to the following calculations:-

Difference means "no lime" and "lime": 74.68 - 70.50 = 4.18.

L.S.D.	at 1%	1.74
	at 5%	2.00
Result:		**

The conclusion is that liming has raised the pH to a level where increased biological activity caused increased mineralisation of P, and thus favoured a greater uptake of P by the plant (Mattson, et al, 1950). This effect was no

longer apparent in the U.T.D. series. The highly significant difference between the T.D. and U.T.D. series is apparently due to a general decrease in P availability, with the result that biological activity was depressed and contracted.

The effects due to individual treatments are not significant, as are the effects due to the resumption of topdressing, shown by the R.T.D. series.

It is concluded that significant changes in the levels of organic P are only caused over long periods of time by drastic changes in management practice, and that organic activity is affected more by soil reaction than by kind of phosphate carrier.

4. ALKALI SOLUBLE PHOSPHORUS.

Table 18 indicates the degree of plot and treatment variation, as shown by the summarised data, details of which are contained in appendix XIII.

TABLE 18

ALKALI SOLUBLE P. SUMMARISED DATA.
(Results expressed as mg /100 gm soil (O.D. basis)

Treatments			Replicates 1	2	3
T.D.	1	S.	32.42	30.57	30.25
	2	B.S.	31.14	31.18	27.38
	3	G.	27.52	27.90	23.54
	4	S. + L.	30.50	28.42	29.70
	5	B.S. + L.	29.67	26.81	24.84
	6	G. + L.	21.29	21.23	22.12
U.T.D.	7	S.	16.42	14.16	13.69
	8	B.S.		14.17	
	9	G.	14.90		13.59
	10	S. + L.	15.28	13.68	14.21
	11	B.S. + L.	14.22		14.21
	12	G. + L.		13.23	
R.T.D.	2	B.S. + S.	22.29		17.15
	3	G. + S.		18.76	
	2	B.S. + L. + S.		18.38	
	3	G. + L. + S.	21.51		16.54

The statistical analysis of the variance, caused by plot variation and analytical error, proved that neither influenced treatment variation significantly.

ANALYSIS OF VARIANCE

Source	S.S.	d.f.	E.M.S.	F.	Result
Treatments	2672.60	11	242.96	2802.31	**
Plots(residual)	48.13	18	2.6738	30.84	**
Duplicates	2.60	30	0.0867		
Total	2723.33	59			

The confidence that may be placed on the analytical work is shown by the magnitude of the "coefficient of repeatability", which was calculated as follows:-

$$s_d^2 = 0.0867 \quad \text{(duplicates)}$$

$$s_d^2 + 2 s_p^2 = 2.6738 \quad \text{(residual)}$$

$$\text{and} \quad s_p^2 = \frac{2.6738 - 0.0867}{2} = 1.2936 \text{ (plots)}$$

$$\text{therefore coeff. rep.} = \frac{1.2936}{0.0867 + 1.2936} \times 100\% = 93.8\%$$

Where Fe-P is calculated as the difference between alkali soluble P and P soluble in NH_4F, and where duplication in the latter analyses was excellent, it is evident that the accumulated analytical error, embodied in the plot variation of Fe-P, may be neglected.

5. CALCIUM BOUND PHOSPHORUS.

Subtraction of the combined values for Fe-P and Al-P (alkali soluble) from the values for Fe-P, Al-P, and Ca-P (acid-alkali soluble), represents the values for Ca-P, which are shown in Table 19.

TABLE 19

CALCIUM BOUND P.

(Results in mg/100 gm soil (O.D. Basis)

Treatments			Replicates 1	2	3	Mean
T.D.	1	S.	5.27	4.96	5.84	5.36 ± 0.81
	2	B.S.	3.82	4.84	7.11	5.26 "
	3	G.	12.00	12.09	7.88	10.66 "
	4	S. + L.	8.01	7.03	8.98	8.01 "
	5	B.S. + L.	6.91	7.63	9.12	7.89 "
	6	G. + L.	19.23	18.02	15.18	17.48 "
U.T.D.	7	S.	-0.17	0.41	1.02	0.42 "
	8	B.S.		0.86		0.86 ± 1.4
	9	G.	-0.80		1.21	0.21 ± 0.99
	10	S. + L.	1.42	0.24	-0.05	0.54 ± 0.81
	11	B.S. + L.	1.95		0.41	1.18 ± 0.99
	12	G. + L.		0.65		0.65 ± 1.4
R.T.D.	2	B.S. + S.	1.85		2.36	2.11
	3	G. + S.		0.86		0.86
	2	B.S. + L. + S.		1.11		1.11
	3	G. + L. + S.4.00			2.11	3.06

Treatment differences were not significantly influenced by plot variation as shown by statistical treatment of the data.

ANALYSIS OF VARIANCE

Source	S.S.	d.f.	E.M.S.	F.	Result
Treatments	811.734	11	73.794	37.382	**
Error	35.533	18	1.974		
Total	847.268	29			

It has been shown that the combined analytical error, embodied in the variance due to plots, could be disregarded.

The least significant differences, based on the number of replicates available for each treatment, are shown below:-

TABLE OF L.S.D.

Treatments	1%	5%
1 and 4	3.30	2.41
1 " 9	3.69	2.70
1 " 8	4.67	3.41
9 " 8	4.95	3.61

It is evident from the results that the levels of Ca-P in this soil are low, and apparently calcium phosphate residues of the fertilisers applied. In the R.T.D. series the resumption of topdressing with Super has not resulted in significant increases in the levels of Ca-P, which is additional evidence for the residual nature of this fraction. The effects of the solubility of the calcium phosphates in the fertilisers applied, and the effects of lime on the levels of Ca-P, are also significant, and confirm the observations made by Scheffer, et al (1956) and Chang and Jackson (1958). In the U.T.D. series, apparently only the least soluble forms of Ca-P remain.

It is concluded that the contribution to the Ca-P fraction in this soil was mainly caused by insoluble calcium phosphate residues (ex Gafsa) and liming, and that only a small proportion of these residues is highly resistant to decomposition over long periods of time.

6. ALUMINIUM BOUND PHOSPHORUS.

A summary of the results is presented in table 20. The tabulated details of the values obtained are shown in appendix XIV.

TABLE 20

Aluminium bound P, summarised data.

(Results expressed as mg/100 gm soil on O.D. basis)

Treatments			Replicates 1	2	3	Mean
T.D.	1	S.	21.29	18.79	18.13	19.41 ± 1.01
	2	B.S.	17.78	18.59	13.08	16.48 "
	3	G.	13.10	12.79	10.90	12.26 "
	4	S.+ L.	18.91	17.14	16.33	17.46 "
	5	B.S. + L.	17.66	13.99	11.54	14.40 "
	6	G.+ L.	10.97	8.64	10.28	9.96 "
U.T.D.	7	S.	7.74	6.38	5.77	6.63 "
	8	B.S.		5.54		5.54 ± 1.75
	9	G.	6.45		5.79	6.12 ± 1.23
	10	S. + L.	5.87	5.68	5.93	5.83 ± 1.01
	11	B.S. + L.	5.79		5.83	5.81 ± 1.23
	12	G.+ L.		5.33		5.33 ± 1.75
R.T.D.	2	B.S.+ S.	12.85		8.72	10.79 ± 1.23
	3	G.+ S.		11.20		11.20 ± 1.75
	2	B.S.+ L. + S.		10.24		10.24 ± 1.75
	3	G.+ L.+ S.	11.82		8.40	10.11 ± 1.23

The data were treated statistically to examine the effects of plot variation on the treatment differences. No attempt was made to separately assess analytical error as duplication agreement was excellent. Plot variation was found to be not significant.

ANALYSIS OF VARIANCE.

Source	S.S.	d.f.	E.M.S.	F.	Result
Treatments	765.043	11	69.549	22.863	**
Error	54.763	18	3.042		
Total	819.806	29			

The least significant differences between the treatments, based on the number of available replicates per treatment, are presented in the table below:-

TABLE OF L.S.D.

Treatments	1%	5%
1 and 4	4.10	2.99
1 " 9	4.58	3.35
1 " 8	5.79	4.23
9 " 8	6.15	4.49

A statistically significant effect of liming, depressing the levels of the Al-P in the T.D. series was found, based on the following calculations:-

Difference between means "no lime" and "lime":

16.05 - 13.94 = 2.1

L.S.D.	at 1%	2.4
	at 5%	1.7
Result:		*

This effect appeared counteracted by the greater solubility of the calcium phosphates in Super, and the order of treatment effects may be shown thus:-

Super > Basic Slag > Gafsa, and no lime > lime.

These effects were no longer apparent in the U.T.D. series, but a significant increase in Al-P levels was evident in the

R.T.D. series, indicating the importance of this fraction in soil. This was already indicated by the differences noted in the total P fraction.

7. IRON BOUND PHOSPHORUS.

This fraction is represented by the difference between alkali soluble P and NH_4F soluble P. The results are presented in Table 21.

TABLE 21.

IRON BOUND P.

(Results expressed as mg/100 gm soil (O.D. basis).

Treatments			Replicates 1	2	3	Mean
T.D.	1	S.	11.13	11.78	12.12	11.68 ± 0.16
	2	B.S.	13.36	12.59	14.30	13.42 "
	3	G.	14.42	15.11	12.64	14.06 "
	4	S.+ L.	11.59	11.28	13.37	12.08 "
	5	B.S.+ L.	12.01	12.82	13.30	12.71 "
	6	G.+ L.	10.32	12.59	11.84	11.58 "
U.T.D.	7	S.	8.68	7.78	7.92	8.13 "
	8	B.S.		8.63		8.63 ± 0.27
	9	G.	8.45		7.80	8.13 ± 0.19
	10	S.+ L.	9.41	8.00	8.28	8.56 ± 0.16
	11	B.S.+ L.	8.43		8.38	8.41 ± 0.19
	12	G.+ L.		7.90		7.90 ± 0.27
R.T.D.	2	B.S.+ S.	9.44		8.43	8.94
	3	G.+ S.		7.56		7.56
	2	B.S.+ L.+ S.		8.14		8.14
	3	G.+ L.+ S.	9.69		8.14	8.92

Statistical treatment of the data gave evidence that plot variation did not significantly influence the differences due to treatment.

ANALYSIS OF VARIANCE

Source	S.S.	d.f.	E.M.S.	F.	Result
Treatments	147.550	11	14.755	20.30	**
Error	13.087	18	0.727		
Total	160.637	29			

The least significant differences are shown in the table below:-

TABLE OF L.S.D.

Treatments	1%	5%
1 and 4	0.63	0.46
1 " 9	0.71	0.52
1 " 8	0.90	0.65
9 " 8	0.95	0.69

Significantly lower levels of Fe-P, caused by liming were found, according to the following calculations:-

Difference between means "no lime" and "lime":
13.05 - 12.12 = 0.97

L.S.D. at 1% 1.16
at 5% 0.84
Result: *

This relationship between pH and Fe ion activity confirms the observations made by Chang and Jackson (1958).

The effects of liming are not significant in the U.T.D. and R.T.D. series, due no doubt to the increasingly lowered activity of the phosphate ions caused by the continued depletion of the phosphate pool through uptake by the sward and leaching, and in the latter case due to the resumption of topdressing having taken place only recently whereas the formation of Fe-P is a s low process Chang and Jackson (1958).

It is interesting to note the inverse relationship apparent between the levels of Fe-P and the solubility of the calcium phosphates of the fertilisers applied, which is of the order, Super < Basic Slag < Gafsa, and opposite to that found for the Al-P fraction.

PART V

A. DISCUSSION AND CONCLUSIONS

The effects of the application of three phosphatic fertilizers of varying phosphate solubility on the distribution of fixed phosphorus in the Marton Loam are mainly shown by the inorganic P fractions.

Table 22. Summary of Soil Phosphorus Fractions

(Results expressed as mg/100 gm.soil)(O.D.basis)

No.	Treat.	pH	Ca-P	Al-P	Fe-P	Inorg. P	Org. P	Total P
1 T.D.	S	5.4	5.36	19.41	11.68	36.44	76.09	112.52
2	B.S.	6.0	5.26	16.48	13.42	35.16	73.06	108.21
3	G.	5.7	10.66	12.26	14.06	36.98	74.90	111.87
4	S + L	6.1	8.01	17.46	12.08	37.55	71.49	109.04
5	BS+ L	6.5	7.89	14.40	12.71	34.99	69.11	104.10
6	G + L	6.3	17.48	9.96	11.58	39.02	70.90	109.93
7 U.T.D.	S	5.4	0.42	6.63	8.13	15.18	68.32	83.49
8	B.S.	5.5	0.86	5.54	8.63	15.03	67.63	82.66
9	G.	5.4	0.21	6.12	8.13	14.45	68.88	83.33
10	S + L	5.5	0.54	5.83	8.56	14.93	67.72	82.64
11	BS+ L	5.5	1.18	5.81	8.41	15.40	68.11	83.51
12	G + L	5.6	0.65	5.33	7.90	13.88	66.34	80.22
2^{S} R.T.D.	(BS)+S	5.5	2.11	10.79	8.94	21.83	71.20	93.02
3^{S}	(G)+S	5.4	0.86	11.20	7.56	19.62	67.97	87.59
2^{SL}	(BS)+L+S	5.5	1.11	10.24	8.14	19.49	69.87	89.36
3^{SL}	(G)+L+S	5.5	3.06	10.11	8.92	22.08	70.42	92.50

The greater solubility of the phosphate in Superphosphate and Basic Slag than Gafsa is shown by the greater amount fixed by Al than Fe, and less residual phosphorus remains as Ca-P.

On the other hand, the changes induced by the application of lime are markedly shown in a reduction of the organic P levels, apparently due to the increased decomposition of organic matter

caused by greater biological activity. The phosphorus thus mineralised is apparently not fixed in inorganic form since a decrease rather than an increase is evident in the inorganic P fractions, excepting Ca-P. Liming appears to have favoured the persistence of the fertilizer residues in the Ca-P fraction. The data do not give evidence for the formation of Ca-P claimed by Chang and Jackson (1958).

The significant reductions in the levels of Al-P, Fe-P, and organic P are apparently the result of a downward movement of P in the profile, as was shown by Doak (1942-II) in his studies on this experiment.

Movement of P down the profile is apparently also the cause of the lower levels of P in all the fractions of the U.T.D. series, which changes, due to the cessation of topdressing, are highly significant for Ca-P and Al-P, and significant for Fe-P and organic P. With the resumption of topdressing, shown by the R.T.D. series, a significant increase in the Al-P levels only is apparent, which clearly demonstrates the importance of this form in reflecting the changes in topdressing practice.

The relative importance of the soil phosphorus fractions is shown in table 23 which clearly demonstrates that, although organic P is the largest fraction by far, the changes in topdressin practice do not affect it as much as the inorganic P fraction which thus may be considered the more labile reserve of soil phosphorus, and within which Al-P is the most important fraction.

Table 23. Summary of P fractions, as a percentage of total P.

No.	Treat.	pH	Ca-P	Al-P	Fe-P	Inorg. P.	Org. P	Total P
1 T.D.	S.	5.4	4.76	17.23	10.38	32.38	67.62	100.00
2	B.S.	6.0	4.86	15.23	12.40	32.49	67.51	"
3	G.	5.7	9.47	10.95	12.55	32.97	67.03	"
4	S. + L.	6.1	7.35	16.00	11.09	34.43	65.57	"
5	B.S.+ L.	6.5	7.62	13.76	12.25	33.63	66.37	"
6	G. + L.	6.3	15.88	9.06	10.56	35.50	64.50	"
7 UT.D.	S.	5.4	0.51	7.93	9.73	18.17	81.83	"
8	B.S.	5.5	1.04	6.70	10.44	18.18	81.82	"
9	G.	5.4	0.25	7.35	9.75	17.34	82.66	"
10	S. + L.	5.5	0.65	7.05	10.35	18.04	81.96	"
11	B.S. + L.	5.5	1.28	6.96	10.07	18.45	81.55	"
12	G. + L.	5.6	0.81	6.64	9.85	17.30	82.70	"
2^{S}R.T.D.	(BS) + S.	5.5	2.27	11.55	9.60	23.42	76.58	"
3^{S}	(G) + S.	5.4	0.98	12.79	8.63	22.40	77.60	"
2^{SL}	(BS)+ L.+ S.	5.5	1.24	11.46	9.11	21.81	78.19	"
3^{SL}	(G) + L.+ S.	5.5	3.28	10.88	9.62	23.78	76.22	"

This confirms the observations made by Bray and Kurtz (1945) who found in their studies on corn belt soils that the determination of "adsorbed P", which Chang and Jackson (1957) considered to be largely Al-P, showed a high correlation with crop responses obtained in the field.

Fife (priv. comm.) found for a number of soils that the NH_4F extraction procedure for the determination of Al-P, largely removed isotopically exchangeable P, which suggests that this fraction contains a high proportion of P available to the plant.

The changes that have taken place in the Ca-P and Fe-P fractions as a result of the changes in topdressing practice are slight, and it is assumed that the nature of the phosphate involved

is one of surface precipitated Ca-P and Fe-P, which, according to Chang and Jackson (1957) are most available (labile).

The residual nature of the Ca-P fraction indicates it to be mainly apatite (McIntyre et al., 1937; Chang and Jackson, 1957), and although McIntyre and Hatcher (1942) claimed the formation of apatite in soil as the result of applying Superphosphate to a limed soil, Moschler et al. (1957) reported the presence of this mineral only in soil treated with rock phosphate and not in soil treated with Superphosphate. Nagelschmidt and Nixon (1944), and Aslyng (1954) showed in addition that the actual formation of apatite would occur only under conditions of heavy phosphate fertilizer and lime applications over long periods of time.

The changes in the levels of Fe-P, Al-P and Ca-P, according to the changes in topdressing practice are a clear indication of the time involved in their formation.

Hence the "lability" of the various inorganic P fractions may be shown in the order Ca-P $>$ Al-P $>$ Fe-P which is in accord with the observations of Chang and Jackson (1958) on topdressing practice, based on the principle of solubility product.

It is evident from table 22 that the determination of total P, organic P, and inorganic P alone is an unreliable guide to the phosphate status in soil, and that only a complete fractionation of the forms in which fixed P occurs in a soil can give an indication of the changes in its distribution as a result of the changes in topdressing practice; this is particularly evident in the Al-P fraction in this soil. For it will no doubt depend on the relative abundance and surface activity of Ca, Al, and Fe in a soil to determine their individual importance in the problem of phosphate fixation (Chang and Jackson, 1958; Collwell, 1959).

B. SUMMARY

The effects of three phosphatic fertilizers of varying phosphate solubility, applied with or without lime, on a New Zealand Yellow-grey earth were traced from the distribution of the forms of soil phosphorus by the procedure for their separate determination, developed by Fife (1960, priv. comm.).

The fractionation procedure was discussed, and its simplicity and reliability was demonstrated.

A preliminary study was made of the changes in soil reaction, phosphate and lime status, and herbage production, according to the changes in topdressing practice, from data supplied by Doak (1942-II) and the New Zealand Department of Agriculture (priv. comm.).

The changes in topdressing practice were shown to cause marked changes in the levels and distribution of inorganic phosphorus, notably Aluminium bound phosphorus, and less in the organic phosphorus fraction.

Changes in the levels of organic phosphorus were shown to depend more on soil reaction affecting biological activity than on kind of fertilizer applied.

The effects of phosphate carrier were shown to be a function of the solubility of the phosphates in the fertilizer. The "liming effects" of Basic Slag increasing the pH, and the effects of Gafsa on the levels of calcium bound phosphorus were found to be significant.

The effects of soil reaction on the distribution of the phosphorus in the soil were shown to be in accord with the principle of solubility product (Kittrick and Jackson, 1956).

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APPENDIX

APPENDIX "I":

TRIAL "I" MARTON (Dept. of Agriculture file)

D.M. YIELDS TO DATE (annual totals in lbs/ac.)

Year	TREATMENTS						Control (headland)
	S	B.S.	G.	S+L	B.S. + L	G + L	
Stage 1							
1932	7000	6700	6300	7400	6800	6400	-
33	7500	7000	6900	8100	7600	7200	-
34	9400	9300	8900	10,000	9400	9300	-
35	11,700	12,100	11,400	12,900	12,200	1200	-
36	12,600	12,500	12,000	12,800	12,300	12,300	-
37	8100	8200	7800	8500	8200	8100	-
38	8500	9100	8300	9400	9200	9300	-
39	9300	9700	9100	10,200	9400	9200	-
40	8600	8500	8100	9400	9100	8900	-
	Topdressing Ceases						
Stage 2							
1941	10,900	11,600	10,900	12,700	12,700	12,400	-
42	7000	7200	7100	8000	7600	7900	-
43	7800	8100	7800	9100	8900	8900	-
44	9700	9800	9600	10,800	10,600	10,800	-
45	6900	6800	6500	7700	7400	7300	-
46	5400	5800	5700	6000	6300	6300	-
47	3500	3600	3300	3900	4000	4100	3400
48	6600	6800	6700	6700	7000	7100	6200
49	5900	5500	5500	5800	5700	5900	5700
50	5400	5100	5200	5400	5800	6000	4800
Stage 3							
1951	5500	4800	5500	5200	5600	5800	4900
52	6600	5700	6300	5900	6500	6600	6300
53	5200	4900	5000	5200	5400	5300	5400
54	5000	4600	4700	4900	5400	5200	5300
55	5600	4900	4800	4900	5200	5300	5100
56	6400	5800	5800	5600	5900	6000	6300
57	6800	6200	6100	5800	6300	6200	6000

Topdressing Results						
S	B.S.	G.	S+L	B.S. + L.	G + L	
6200	5500	5200	5700	6200	5600	
6800	7000	6700	7000	7000	6700	
6300	6400	6100	6500	6400	6100	
6200	6400	5900	7000	6800	6500	
6300	6500	6400	6900	6600	6000	
7100	7100	6900	7600	7100	6700	
7500	7300	7800	7900	6900	6600	

APPENDIX VII

TABLE SHOWING SOIL MOISTURE DETERMINATIONS

Treat	Plot	Moisture loss %			% O.D. Soil
		1	2	Mean	
1	1	4.9	4.9	4.9	95.1
	18	4.5	4.4	4.5	95.5
	32	3.4	3.7	3.6	96.4
2	2	4.9	4.9	4.9	95.1
	16	4.1	3.8	4.0	96.0
	33	3.3	3.6	3.5	96.5
3	3	4.1	4.0	4.1	95.9
	17	4.5	4.1	4.3	95.7
	31	3.5	3.7	3.6	96.4
4	4	4.0	4.0	4.0	96.0
	15	4.1	3.9	4.0	96.0
	35	3.7	3.6	3.7	96.3
5	5	4.1	3.9	4.0	96.0
	13	3.9	4.2	4.1	95.9
	36	3.7	3.9	3.8	96.2
6	6	4.1	3.9	4.0	96.0
	14	3.9	4.1	4.0	96.0
	34	3.8	4.0	3.9	96.1
7	7	4.0	3.9	4.0	96.0
	24	3.8	4.1	4.0	96.0
	26	3.8	4.0	3.9	96.1
8	22	4.2	4.0	4.1	95.9
9	9	3.9	3.9	3.9	96.1
	25	3.5	3.4	3.5	96.5
10	10	4.2	3.9	4.1	95.9
	21	3.9	3.7	3.8	96.2
	29	3.2	3.6	3.4	96.6
11	11	4.0	3.9	4.0	96.0
	30	3.7	3.9	3.8	96.2
12	20	4.2	4.0	4.1	95.9
8a	8	3.9	4.0	4.0	96.0
	27	3.2	3.4	3.3	96.7
9a	23	3.8	3.5	3.7	96.3
11a	19	4.2	4.4	4.3	95.7
12a	12	4.2	4.2	4.2	95.8
	28	3.6	3.7	3.7	96.3

APPENDIX VIII - Table of pH results

Treatment			Plot	pH			treat. mean
				1	2	Mean	
T.D.	1	S.	1	5.4	5.4	5.4	
			18	5.4	5.4	5.4	
			32	5.4	5.3	5.4	5.4
	2	B.S.	2	6.2	6.1	6.1	
			16	6.0	6.0	6.0	
			33	6.0	5.8	5.9	6.0
	3	G.	3	5.8	5.8	5.8	
			17	5.7	5.7	5.7	
			31	5.6	5.6	5.6	5.7
	4	S.+ L.	4	6.2	6.2	6.2	
			15	6.1	6.1	6.1	
			35	6.1	6.0	6.0	6.1
	5	B.S. + L.	5	6.6	6.5	6.6	
			13	6.4	6.4	6.4	
			36	6.5	6.3	6.4	6.5
	6	B. + L.	6	6.3	6.2	6.3	
			14	6.2	6.3	6.3	
			34	6.4	6.2	6.3	6.3
U.T.D.	7	S.	7	5.5	5.4	5.4	
			24	5.3	5.3	5.3	
			26	5.4	5.3	5.4	5.4
	8	B.S.	22	5.6	5.4	5.5	5.5
	9	G.	9	5.4	5.4	5.4	
			25	5.5	5.4	5.4	5.4
	10	S. + L.	10	5.6	5.5	5.5	
			21	5.5	5.4	5.5	
			29	5.5	5.4	5.5	5.5
	11	B.S. + L.	11	5.4	5.5	5.5	
			30	5.6	5.6	5.6	5.5
	12	G. + L.	20	5.7	5.5	5.6	5.6
R.T.D.	8a	B.S. + S.	8	5.6	5.5	5.6	
			27	5.4	5.4	5.4	5.5
	9a	G. + S.	23	5.5	5.4	5.4	5.4
	11a	B.S.+ L.+ S.	19	5.6	5.4	5.5	5.5
	12a	G. + L. + S.	12	5.5	5.5	5.5	
			28	5.5	5.4	5.4	5.5

APPENDIX IX

FREE Fe_2O_3 EXTRACTION

Treat No.	Plot	Beckman Readings Fe_2O_3	O.M.	Blank	Final	$\%Fe_2O_3$ (x.5066)	$\%Fe_2O_3$ (O.D. Basis)	Extra Yield Factor	Correct $Fe_2O_3\%$
1	1	449	046	020	383	.1940	.204	6.71	1.37
	18	442	053	015	374	.1895	.198	"	1.33
	32	549	061	015	473	.2396	.249	"	1.67
2	2	425	035	020	370	.1875	.197	7.05	1.39
	16	378	050	015	313	.1586	.165	"	1.16
	33	521	048	015	458	.2320	.240	"	1.69
3	3	450	052	020	378	.1872	.195	5.91	1.15
	17	409	054	015	340	.1719	.180	"	1.06
	31	498	053	015	430	.2178	.226	"	1.34
4	4	428	055	020	353	.1788	.186	6.30	1.17
	15	400	046	017	337	.1707	.178	"	1.12
	35	458	045	015	398	.2016	.209	"	1.32
5	5	415	063	020	332	.1682	.175	7.65	.134
	13	392	041	017	334	.1692	.176	"	1.35
	36	450	045	015	390	.1976	.205	"	1.57
6	6	415	060	020	335	.1697	.177	6.93	1.23
	14	365	041	017	307	.1555	.162	"	1.12
	34	460	047	015	398	.2016	.210	"	1.46
7	7	446	058	020	368	.1864	.194	6.41	1.24
	24	433	046	015	372	.1885	.196	"	1.26
	26	415	048	015	352	.1783	.186	"	1.19
8a	8	421	056	015	350	.1773	.185	6.91	1.28
8	22	414	046	015	353	.1788	.186	"	1.29
8a	27	420	050	015	355	.1799	.186	"	1.29
9	9	434	069	015	350	.1773	.184	6.13	1.13
9a	23	426	047	015	364	.1844	.191	"	1.17
9	25	448	051	015	384	.1945	.202	"	1.24
10	10	481	066	020	395	.1956	.204	5.76	1.18
	21	397	057	015	331	.1677	.174	"	1.00
	29	402	054	015	333	.1687	.175	"	1.01
11	11	458	062	020	376	.1905	.198	6.97	1.38
11a	19	380	052	015	313	.1586	.166	"	1.16
11	30	409	052	015	342	.1733	.180	"	1.25
12a	12	481	064	020	397	.2011	.210	6.40	1.34
12	20	377	047	015	315	.1596	.166	"	1.06
12a	28	374	049	015	310	.1570	.163	"	1.04

Mean 1.26%, range 1.00% - 1.69%

APPENDIX IVa

REPEAT Fe_2O_3 EXTRACTION WITH FRESH DITHIONITE

Extract diluted 5x for colorimetric readings "Old"
Fe_2O_3 yields adjusted with extra yield factor

Treat	Beckman Readings						Extra Yield Factor
	Fe_2O_3	O.M.	Blank	Average	Final (x5)	Previous	
1	540	007	013				
"	530	009	"	514	2570	383	6.71
2	539	009	"				
"	550	010	"	522	2610	370	7.05
3	468	009	"				
"	470	010	"	447	2235	378	5.91
4	469	012	"				
"	470	012	"	445	2225	353	6.30
5	539	014	"				
"	530	013	"	508	2540	332	7.65
6	490	016	"				
"	495	016	"	464	2320	335	6.93
7	500	014	"				
"	500	016	"	472	2360	368	6.41
8	511	014	"				
"	511	014	"	484	2420	350	6.91
9	460	020	"				
"	463	020	"	429	2145	350	6.13
10	500	016	"				
"	470	018	"	455	2275	395	5.76
11	570	015	"				
"	540	020	"	524	2620	376	6.97
12	560	017	"				
"	520	020	"	508	2540	397	6.40

APPENDIX V - TABLE OF P. STANDARDS

(Phosphomolybdic-blue in H.Cl system. Values expressed in Beckman photometer transmission readings.)

Gamma P/ml.	(20.4.60)			(4.5.60)			(12.11.60)			(Checks)		
	1	2	True mean	1	2	True mean	1	2	True Mean	1	2	Tru Mea
0.1	057	055	061	060	061	063						
0.2		118	123		116	119				121	121	126
0.3		180	185		181	184				(-003)	(-003)	(-003
0.4		235	240		237	241				238	234	248
0.5		292	297		311	314	310	310	309	(-012)	(-012)	(-012
0.6		355	360	359	359	368						
0.7		430	435		431	434						
0.8			-		489	492						
0.9		555	560		548	551				(-003)	(-003)	(-003
1.0		615	620		609	612	600	620	609	609	611	613
1.1	695	683	694		669	672				700	688	697
1.2		721	726	722	730	729				(-003)	(-003)	(-003
Blanks	-004	-006	-005	-003	-003	-003	+001	+001	+001			

Va TABLE OF P-STANDARDS

(Phosphomolybdic blue in Sulphuric acid system. Values are expressed as Beckman photometer transmission readings.)

Gamma P/ml.	B.rdngs.		true rdngs.	
	1	2	1	2
0.1	094	085	086	077
0.2	170	168	162	160
0.3		250		242
0.4		335		327
0.5	412	412		404
0.6	488	482	480	474
0.7		552		544
0.8		620		612
0.9	675	679	667	671
1.0	750	734	742	726
Blanks	+009	+007	(+008)	

Comments:

The limit of applicability of Beer's law lies at 0.6 gamma P/ml. test-solution. This is confirmed by Schricker & Dawson (1939).

APPENDIX VI

THE RELATIONSHIP BETWEEN TIME AND THE RELEASE OF P in 0.5M. NH_4F (pH 8.5)

(Soil/extractant ratio 1:50, results expressed as p.p.m. P in solution).

Time (Days)	BECKMAN READINGS					p.p.m. P (X 8.125)
	1	2	3	Mean	True	
½	315	320	320	318	312	2.54
1	352	347	347	349	343	2.79
1½	376	376	376	376	370	3.01
2	388	388	388	388	382	3.10
2½	394	398	398	397	391	3.18
3	400	400	400	400	394	3.20
3½	405	402	402	403	397	3.23
4	406	405	403	405	399	3.24
4½	433	440	436	436	430	3.49
5	440	440	440	440	434	3.53
5½	400	443	443	400	394	3.20
6	450	400	450	400	394	3.20
6½	406	460	460	406	400	3.25
7	423	460	408	408	402	3.27

BLANKS:

				Mean:
1. Reagent	+004	+001	-002	+001
2. Org.m.	+005	+005	+005	+005
			TOTAL	+006

CALCULATIONS: B.R. x factor x $\frac{50}{10}$ = gamma P/ml in extract

or B.R. x 8.125 = p.p.m. P in extract solution.

APPENDIX VII

THE INFLUENCE OF SOIL/EXTRACTANT RATIO ON THE CONCENTRATION OF P IN THE EXTRACT.

(Extractant used 0.5M NH_4F; results expressed as p.p.m. P).

Wt. soil (gm)	Vol. Ext. (ml)	Ratio	BECKMAN READINGS						p.p.m. P (x 8.12
			Soil Extr.	Org. m. Blank	Reagent Blank	Total Blank	True Mean	On 1:50 Basis	
0.5	25	1:50	388 388 388	+007	-004	+003	385	385	3.1
0.25	25	1:100	200 203 202	+003	-004	-001	203	406	3.3
0.10	25	1:250	087 087 086	+001	-004	-003	090	450	3.6
0.05	25	1:500	048 040 045	-	-004	-004	048	480	3.9
0.05	50	1:1000	025 024 024	-	-004	-004	028	560	4.5
0.03	50	1:1500	015 015 015	-	-004	-004	019	570	4.6

BLANK READINGS: Reagents: -004 -004 -004, mean -004

Org. matter: +005 +007 +009, " +007

CALCULATIONS: B.R. x factor x $\frac{50}{10}$ = gamma P/ml. in extract

or B.R. x 8.125 = p.p.m. P in extract solution.

THE CHEMICAL RECOVERY OF P

(.4 grm soil in 20 ml 0.5 M NH_4F (pH8.5), plus or minus added P, at the final conc. of 1 gamma/ml)

Plot & Treat	Extract Treat.	Beckman Readings 1	2	3	4	Mean	Diff	%rec[y]	Factor
1	+P	458	458	460	462	460			
(S)	-P	365	365	365	366	365	95	75.40	1.326
2	+P	420	420	420	420	420			
(B.S.)	-P	318	320	320	320	320	100	79.37	1.260
3	+P	342	342	342	342	342			
(G)	-P	240	241	240	240	240	102	80.95	1.235
4	+P	458	458	458	458	458			
(S+L)	-P	354	354	354	360	354	104	82.54	1.211
5	+P	438	440	442	440	440			
(B.S+L)	-P	335	335	337	337	336	104	82.54	1.211
6	+P	270	270	270	270	270			
(G+L)	-P	180	179	178	174	179	91	72.22	1.385
7	+P	224	224	224	225	224			
(S)	-P	129	130	133	133	131	93	73.81	1.355
8	+P	338	338	339	338	338			
(B.S)	-P	236	242	240	242	240	98	77.76	1.286
9	+P	204	209	208	207	207			
(G)	-P	117	117	115	112	115	92	73.02	1.370
10	+P	204	204	204	204	204			
(S+L)	-P	109	113	109	113	111	93	73.81	1.355
11	+P	200	200	201	204	201			
(B.S+L)	-P	109	111	107	110	109	92	73.02	1.370
12	+P	330	333	336	334	333			
(G+L)	-P	231	234	235	234	234	99	78.56	1.273

For treats 1-6:

Fluoride + P std:	123	123	125	125	124	true mean: 126
Reagent blank:	-003	-001	-002	-002	-002	

For treats 7-12:

Fluoride + P std:	121	121	121	121	121	true mean: 126
Reagent blank:	-006	-005	-005	-004	-005	

APPENDIX IX Recovery of P. isotope

(Radiation Counts made for 1 minute period)

Treatment	No.		Count	percent recovery	Corr. factor		Standards Count
T.D.	1	S.	22366	79.20	1.263		27980
	2	B.S.	22244	78.72	1.271		28678
	3	G.	21944	77.66	1.290		28679
	4	S.+ L.	23001	81.41	1.229		28306
	5	B.S. + L.	22960	81.28	1.233		27914
	6	G. + L.	21770	77.07	1.300		27960
U.T.D.	7	S.	19988	70.78	1.416	Mean	28250
	8	B.S.	20784	73.57	1.362		
	9	G.	19438	68.82	1.453		
	10	S. + L.	19595	69.39	1.445		
	11	B.S. + L.	19582	69.31	1.443		
	12	G. + L.	21706	76.86	1.303		

Recovery of P. isotope + added P.(1 gamma/ml)

(Radiation Counts made for 2 minute period)

T.D.	1	S.	31715	78.50	1.274		
U.T.D.	7	S.	29963	74.16	1.348		40400

APPENDIX X

SOLUBILITY OF P IN 0.5M AMMONIUM FLUORIDE

(1:50 ratio suspension shaken for 4½ days).

TREATMENT 1

pH		B.R.	True B.R.	p.p.m.P (X8.125)
Before	After			
5.35	7.16	329	340	2.77
5.60	7.39	325	336	2.73
6.38	7.61	329	340	2.77
7.10	7.71	323	334	2.72
7.45	7.81	332	343	2.79
7.78	7.96	329	340	2.77
8.00	8.07	342	353	2.87
8.24	8.26	345	356	2.90
8.40	8.40	342	353	2.87
8.62	8.80	345	356	2.90
9.06	9.03	340	351	2.85

TREATMENT 7

pH		B.R.	True B.R.	p.p.m.P (X8.125)
Before	After			
5.35	7.16	111	122	0.99
5.60	7.39	108	119	0.97
6.38	7.61	109	120	0.98
7.10	7.71	107	118	0.96
7.45	7.81	108	119	0.97
7.78	7.96	111	122	0.99
8.00	8.07	111	122	0.99
8.24	8.26	115	126	1.03
8.40	8.40	115	126	1.03
8.62	8.60	114	125	1.02
8.82	8.80	117	128	1.04
9.06	9.03	113	124	1.01

BLANKS: Reagents: -005 -003 -004 Mean -004

Org.matter: -007 -007 -007 Mean -007

Total -011

CALCULATIONS:

B.R. x factor x $\frac{50}{10}$ = gamma P/ml in extract

or B.R. x 8.125 = p.p.m. P in extract solution.

APPENDIX XI - Total Phosphorus ~~digested~~

(.4 gm soil with 7.5 ml perchl.ac.)

Treat.	Plot	B.Readings A	B	Mean	True Rdng.	Mg P 100 gm soil (x 390.5)	On oven dried basis	Treat. Means
1	1	290	290	290	.279	108.950	114.56	
	18	279	284	281	.270	105.435	110.40	
	32	288	290	289	.278	108.559	112.61	112.52
2	2	274	274	274	.263	102.702	107.99	
	16	278	276	277	.266	103.873	108.20	
	33	279	279	279	.268	104.654	108.45	108.21
3	3	288	290	289	.278	108.559	113.20	
	17	300	292	296	.285	111.293	116.29	
	31	273	273	273	.262	102.311	106.13	111.87
4	4	290	288	289	.278	108.559	113.08	
	15	275	270+	273	.262	102.311	106.57	
	35	278	274	276	.265	103.483	107.46	109.04
5	5	280	276	278	.267	104.264	108.61	
	13	269	269	268	.257	100.359	104.65	
	36	255	256	255	.244	95.282	99.05	104.10
6	6	287+	292	290	.279	108.950	113.49	
	14	277	277	277	.266	103.873	108.20	
	34	279	275	277	.266	103.873	108.09	109.93
7	7	222	220	221	.210	82.005	85.42	
	24	220	216	218	.207	80.834	84.20	
	26	210	210	210	.199	77.710	80.86	83.49
8	-	-	-	-	-	-	-	-
	22	214	214	214	.203	79.272	82.66	
	-	-	-	-	-	-	-	82.66
9	9	215	217	216	.205	80.053	83.30	
	-	-	-	-	-	-	-	
	25	215	218	217	.206	80.443	83.36	83.33
10	10	218	218	218	.207	80.834	84.29	
	21	208	210	209	.198	77.319	80.37	
	29	220	215	217	.206	80.443	83.27	82.64
11	11	215	213	214	.203	79.272	82.58	
	-	-	-	-	-	-	-	
	30	219	219	219	.208	81.224	84.43	83.51
12	-	-	-	-	-	-	-	
	20	208	208	208	.197	76.929	80.22	
	-	-	-	-	-	-	-	80.22

Blanks: + 011) + 011) + 011) Mean + 011

APPENDIX XII

H.Cl. and NaOH EXTRACTION (Fe, Al and Ca-P).

(0.25 gm soil extracted with 0.1 m.H.Cl, washed, extracted with 1 m. NaOH, results expressed as mg P/100 gm soil).

Treat/Plot		BECKMAN READINGS 1	2	Mean	Mg.P per 100gm soil (X65.0)	BECKMAN RDGS. 1	2	Mean	Mg.P per 100gm soil (81.25)	Total Mg P.	Total O.P. Basis
1	1	234	245	.2395	15.568	249	250	.2495	20.272	35.84	37.69
	18	195	204	.1995	12.968	260	256	.258	20.963	33.93	35.53
	32	214	214	.214	13.910	257	257	.257	20.881	34.79	36.09
2	2	205	218	.2115	13.748	240	240	.240	19.500	33.25	34.96
	16	214	210	.212	13.780	256	256	.256	20.800	34.58	36.02
	33	180	184	.182	11.830	271	267	.264	21.450	33.28	34.49
3	3	273	273	.273	17.745	248	248	.248	20.150	37.90	39.52
	17	276	274	.275	17.875	256	246	.251	20.397	38.27	39.99
	31	187	195	.191	12.415	222	218	.220	17.875	30.29	31.42
4	4	280	285	.2825	18.363	229	229	.229	18.606	36.97	38.51
	15	225	212	.2185	14.203	246	242	.244	19.825	34.03	35.49
	35	258	245	.258	16.770	254	250	.252	20.475	37.25	38.68
5	5	262	251	.2565	16.673	224	230	.227	18.444	35.12	36.58
	13	207	218	.2125	13.813	233	240	.2365	19.216	33.03	34.44
	36	206	198	.202	13.130	240	241	.2405	19.541	32.67	33.96
6.	6	337	325	.331	21.515	212	216	.214	17.388	38.90	40.52
	14	307	295	.301	19.565	214	232	.223	18.119	37.68	39.25
	34	259	269	.264	17.160	230	230	.230	18.688	35.85	37.30
7	7	050	050	050	3.250	150	154	152	12.350	15.60	16.25
	24	030	033	0315	2.048	147	147	147	11.944	13.99	14.57
	26	031	034	0325	2.113	146	150	148	12.025	14.14	14.71
8	22	043	043	043	2.795	143	143	143	11.619	14.41	15.03
	-	-	-	-	-	-	-	-	-	-	-
9	9	041	046	0435	2.828	132	132	132	10.725	13.55	14.10
	-	-	-	-	-	-	-	-	-	-	-
	25	035	032	0335	2.178	148	150	149	12.106	14.28	14.86
10	10	045	043	044	2.860	161	163	162	13.163	16.02	16.70
	21	036	036	036	2.340	136	136	136	11.050	13.39	13.92
	29	033	035	034	2.210	140	142	141	11.456	13.68	14.16
11	11	043	047	045	2.925	152	158	155	12.594	15.52	16.17
	-	-	-	-	-	-	-	-	-	-	-
	30	028	032	030	1.950	145	154	149	12.106	14.06	14.62
12	-	-	-	-	-	-	-	-	-	-	-
	20	036	036	036	2.340	135	135	135	10.969	13.31	13.81
	-	-	-	-	-	-	-	-	-	-	-

BLANKS: H.Cl. + reagents -005, -005 → -005

NaOH + H.Cl + reagents -005, -005 → -005

O.M. mean of 18 readings -001

∴ Total blanks: For H.Cl. extr. -005
For NaOH " -006

For Procedure and Calculations see separate sheet (pp 44)

APPENDIX XIII - Preleach - NaOH Extraction (Fe & Al - P)

(0.25 gm. soil leached with 0.5 M NaCl, washed, extracted with 1 n NaOH: Results expressed as mg P/100 gm soil)

Treat	Plot	Beckm.Rdngs(NaCl) 1	2	Mean	Mg P 100 gm (32.5x)	Beckm.Rdngs(NaOH) 1	2	Mean	Mg P 100gm (81.25)	Total Mg P	Total Mg P O.D basis
1	1	031	031	031	1.008	362	372	367	29.819	30.827	32.42
	18	025	024	0245	0.796	348	351	3495	28.397	29.193	30.57
	32	026	026	026	0.845	350	347	3485	28.316	29.161	30.25
2	2	043	044	0435	1.413	338	348	347	28.194	29.607	31.14
	16	048	044	046	1.495	352	348	350	28.438	29.933	31.18
	33	028	028	028	0.910	314	314	314	25.513	26.423	27.38
3	3	039	035	037	1.203	308	312	310	25.188	26.391	27.52
	17	028	030	029	0.943	315	319	317	25.756	26.699	27.90
	31	018	018	018	0.585	272	272	272	22.100	22.685	23.54
4	4	056	056	056	1.820	341	335	338	27.463	29.283	30.50
	15	052	047	0495	1.609	312	320	316	25.675	27.284	28.42
	35	040	040	040	1.300	332	340	336	27.300	28.600	29.70
5	5	048	052	050	1.625	332	329	3305	26.853	28.478	29.67
	13	045	042	0435	1.414	302	296	299	24.294	25.708	26.81
	36	033	033	033	1.073	280	282	281	22.831	23.904	24.84
6	6	021	022	0215	0.700	247	239	243	19.744	20.444	21.29
	14	027	022	0245	0.796	240	242	241	19.581	20.377	21.23
	34	024	024	024	0.780	252	252	252	20.475	21.255	22.12
7	7	020	020	020	0.650	186	186	186	15.113	15.763	16.42
	24	006	008	007	0.228	163	166	1645	13.366	13.594	14.16
	26	007	008	0075	0.244	158	160	159	12.919	13.163	13.69
8	-	-	-	-	-	-	-	-	-	-	-
	22	012	014	013	0.423	161	163	162	13.163	13.586	14.17
	-	-	-	-	-	-	-	-	-	-	-
9	9	013	013	013	0.423	170	172	171	13.894	14.317	14.90
	-	-	-	-	-	-	-	-	-	-	-
	25	007	007	007	0.228	156	161	1585	12.878	13.106	13.59
10	10	018	011	0145	0.471	177	172	1745	14.178	14.649	15.28
	21	009	011	010	0.325	156	160	158	12.838	13.163	13.68
	29	009	011	010	0.325	164	166	165	13.406	13.731	14.21
11	11	011	011	011	0.358	167	160	1635	13.284	13.642	14.22
	-	-	-	-	-	-	-	-	-	-	-
	30	011	015	013	0.423	161	165	163	13.244	13.667	14.21
12	-	-	-	-	-	-	-	-	-	-	-
	20	013	013	013	0.423	151	151	151	12.269	12.692	13.23
	-	-	-	-	-	-	-	-	-	-	-

APPENDIX XIV

.5 NH_4F EXTRACTION (pH 8.5)

.5 grm soil in 25 ml extract - Shake 72 hrs (Zero hour correction .960)

Treat	Plot	Beckman Readings A	B	Mean	True Reading	MgP 100gm (x40. 625	Recovery Factor (chemical)	MgP 100 gm	Final (on O.D. basis)	Final corrected (x.96
1	1	387	390	.389	.392	15.905	1.326	21.090	22.18	21.2
	18	344	344	.344	.347	14.097	"	18.693	19.57	18.7
	32	.338	332	.335	.338	13.731	"	18.207	18.89	18.1
2	2	341	341	.341	.344	13.975	1.260	17.609	18.52	17.7
	16	360	360	.360	.363	14.747	"	18.581	19.36	18.5
	33	.254	254	.254	.257	10.441	"	13.156	13.63	13.0
3	3	258	258	.258	.261	10.603	1.235	13.095	13.65	13.1
	17	253	251	.252	.254	10.319	"	12.744	13.32	12.7
	31	.215	215	.215	.218	8.856	"	10.937	11.35	10.9
4	4	.379	385	.382	.385	15.620	1.211	18.916	19.70	18.9
	15	.341	339	.340	.343	13.934	"	16.874	17.58	17.1
	35	.326	334	.330	.333	13.528	"	16.382	17.01	16.3
5	5	.357	355	.356	.359	14.584	1.211	17.661	18.40	17.6
	13	.281	281	.281	.284	11.538	"	13.973	14.57	13.9
	36	.230	234	.232	.235	9.547	"	11.561	12.02	11.5
6	6	.192	192	.192	.195	7.922	1.385	10.972	11.43	10.9
	14	.159	143	.151	.154	6.236	"	8.637	9.00	8.6
	34	.180	180	.180	.183	7.434	"	10.296	10.71	10.2
7	7	135	146	141	.141	5.708	1.355	7.734	8.06	7.7
	24	114	118	116	.116	4.713	"	6.386	6.65	6.3
	26	105	105	105	.105	4.266	"	5.780	6.01	5.7
8	-	-	-	-	-	-	-	-	-	-
	22	107	105	106	.106	4.306	1.286	5.538	5.77	5.5
	-	-	-	-	-	-	-	-	-	-
9	9	116	116	116	.116	4.713	1.370	6.457	6.72	6.4
	-	-	-	-	-	-	-	-	-	-
	25	106	103	105	.105	4.245	"	5.816	6.03	5.7
10	10	105	108	107	.107	4.327	1.355	5.863	6.11	5.8
	21	104	103	104	.104	4.205	"	5.698	5.92	5.6
	29	110	107	109	.109	4.408	"	5.973	6.18	5.9
11	11	105	103	104	.104	4.225	1.370	5.788	6.03	5.7
	-	-	-	-	-	-	-	-	-	-
	30	106	104	105	.105	4.266	"	5.844	6.07	5.8
12	-	-	-	-	-	-	-	-	-	-
	20	102	104	103	.103	4.184	1.273	5.326	5.55	5.3
	-	-	-	-	-	-	-	-	-	-

Blanks:

Fluoride + B. acid and reagents		Mean
	+ 002	+ 002
	+ 002	
	+ 002	

O.M. blank:

T.D. series:

Treat		
1	-005	Mean -005
2	-005	
3	-005	
4	-005	
5	-005	
6	-005	

U.T.D. Series

7	000	Mean -002
8	-002	
9	-002	
10	-002	
11	-003	
12	-004	

Final blank:

T.D.: +002 -005 = -003

U.T.D.: +002 -002 = 000

APPENDIX XV.

TABULATED RESULTS OF R.T.D. SERIES.

A. TOTAL P (PERCHLORIC ACID DIGESTION) R.T.D. SERIES.

Treat/Plot		BECKMAN READINGS 1	2	Mean	Final	Mg.P/ 100gm (X390.5)	Final (on O.D basis)	Treat Means
8a	8	245	245	245	234	91.377	95.18	
	27	235	237	236	225	87.863	90.86	93.0
9a	23	226	228	227	216	84.348	87.59	87.5
11a	19	229	231	230	219	85.520	89.36	89.3
12a	12	245	245	245	234	91.377	95.38	
	28	232	231	232	221	86.301	89.62	92.5

B. H.Cl + NaOH - Extraction (Fe. Al. Ca - P) R.T.D.SERIES.

Treat/ Plot		BECKMAN RDGS(H.Cl) 1	2	Mean	Mg.P/ 100gm (X65.0)	BECKMAN READINGS 1	2	Mean	Mg.P/ 100gm (81.25)	Total Mg.P	Total (O.D basis)
8a	8	8137	132	1345	8.743	179	176	1775	14.422	23.17	24.
	27	073	075	074	4.810	174	172	173	14.056	18.87	19.
9a	23	085	085	085	5.525	163	166	1645	13.366	18.89	19.
11a	19	087	073	080	5.200	170	161	1655	13.447	18.65	19.
12a	12	127	125	126	8.190	206	194	200	16.250	24.44	25.

C. PRELEACH + NaOH EXTRACTION (Fe + Al - P) R.T.D. SERIES

Treat/ Plot		BECKMAN RDGS(NaCl.) 1	2	Mean	Mg.P/ 100gm (X32.5)	BECKMAN RDGS(NaOH) 1	2	Mean	Mg.P/ 100gm X81.25	Total Mg.P	Total (O.D. basis
8a	8	019	018	0185	0.601	266	246	256	20.800	21.401	22.
	27	013	012	0125	0.406	198	200	199	16.169	16.575	17.
9a	23	016	016	016	.520	219	213	216	17.550	18.070	18.7
11a	19	015	015	015	0.488	210	211	2105	17.103	17.591	18.
12a	12	017	021	019	0.618	246	246	246	19.988	20.606	21.5
	28	014	016	015	0.488	186	197	190	15.438	15.926	16.

D. 0.5 M. NH_4F EXTRACTION (Al - P) R.T.D. SERIES.

Treat/ Plot		BECKMAN READINGS 1	2	Mean	Final	Mg.P/ 100gm (X40.625)	Sorption Factor (Chem.X Recov.)	Final Mg.P/ 100gm	Final (onOD basis)	Final Corrected (X.960)	Treatment
8a	8	248	244	246	246	9.994	1.286	12.852	13.39	12.85	
	27	168	168	168	168	6.825	1.286	8.777	9.08	8.72	10.7
9a	23	203	201	202	202	8.206	1.370	11.242	11.67	11.20	
11a	19	185	182	1835	1835	7.455	1.370	10.213	10.67	10.24	
12a	12	228	228	228	228	9.263	1.273	11.792	12.31	11.82	10.2
	28	165	161	163	163	6.620	1.273	8.427	8.80	8.45	

APPENDIX XVI STATISTICAL TREATMENT MODELS (Glenday, priv.comm

A. Calculation of the variance due to plot and treatment.

The data obtained from each analysis were regarded as a population and treatment means were "weighted" according to the number of replicates available. The "missing plots" of the R.T.D. series were excluded from the caluation as advised by Glenday.

The analysis of variance:

Treat. S.S. = $\frac{T_1^2}{3} + \ldots + \frac{T_9^2}{2} + \ldots + \frac{T_8^2}{1} \ldots - \frac{G^2}{30}$

where T_1 equals the sum of 3, 2, or 1 replicates per treatment, and G equals the sum of 30 data.

Total S.S. = S.S. of 30 data $- \frac{G^2}{30}$

there being 30 plots in the population.

The results are tabulated:

Source	S.S.	d.f.	E.M.S.	F	Result
Treatments	Tr	11	$M_T = \frac{Tr}{11}$	$\frac{M_T}{ME}$	?
Error	T_G-Tr	18	$M_E = \frac{E}{18}$		
Total	T_G	29			

Calculation of standard errors; on the basis of number of replicates per treatment.

For treatment 1 (3 reps.) S.E. = $\sqrt{\frac{ME}{3}}$

" " 9 (2 reps.) = $\sqrt{\frac{ME}{2}}$

" " 8 (1 rep.) = $\sqrt{M_E}$

Calculation of least significant differences;

$d_{0.05} = t_{18 \text{ d.f.}} \sqrt{M_E\left(\frac{1}{n_1} + \frac{1}{n_2}\right)}$ where n_1 and n_2 equal the number of replicates in the treatments being compared.

B. Calculation of the variance due to laboratory analysis, plot, and treatment.

The relative importance of duplication error in the laboratory analysis was assessed on the basis of two data per plot.

The analysis of variance;

$$\text{Treat. S.S.} = \frac{T_1^2}{6} + \ldots + \frac{T_9^2}{4} + \ldots + \frac{T_8^2}{2} \ldots - \frac{G^2}{60}$$

where T_i equals the sum of 6, 4, or 2 data available per treatment, and G equals the sum of 60 data.

$$T_i \text{ S.S.} = \frac{X_1^2}{2} + \frac{X_2^2}{2} + \ldots\ldots + \frac{X_{30}^2}{2} - \frac{G^2}{60}$$

where X_s equals the sum of the duplicate data per plot.

$$\text{Total S.S.} = \text{S.S. of 60 data} - \frac{G^2}{60}$$

Tabulating the results gives the following analysis;

Source	S.S.	d.f.	E.M.S.	F	Result
Treatments	T_r	11	M_T	M_T/M_1	?
Plots	$T_1 - T_r$	18	M_1	M_1/M_2	?
Duplicates	$T_0 - T_1$	30	M_2		
Total	T_0	59			

Calculation of the standard errors and least significant differences proceeds as before, using M_1.