

Fractionation of Soil Inorganic Phosphate by a Modification of Chang and Jackson's Procedure¹

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ABSTRACT

A modified version of the phosphate fractionation procedure of Chang and Jackson (1957) included the determination of "residual inorg. P" and introduced a revised nomenclature for the other fractions. Added phosphate sorbed during the fluoride extraction was usually completely recovered in the succeeding sodium hydroxide extraction; this enabled mutually compensating corrections to be applied to $\text{NH}_4\text{F-P}$ and 1st NaOH-P values. A second acid treatment increased the amount of Ca-P extracted. Further modifications simplified the colorimetric determinations of inorganic phosphate in several of the extracts. A measure of the reproducibility of fractionation results was also obtained.

Additional Key Words for Indexing: revised nomenclature.

SINCE ITS INCEPTION the phosphate fractionation procedure of Chang and Jackson (1957) has been widely used for investigations into the forms of native phosphate and transformations of applied phosphate in soils. However, the procedure has been criticized in the light of subsequent findings

concerning the effects of various extractants on pure compounds and on soils (Fife, 1959a, 1959b, 1962, 1963; Saunders, 1959; Khin and Leeper, 1960; Smith, 1965). A modified version³ of the original scheme was used as the starting point in a further revision of the procedure.

MATERIALS

To date, the fractionation procedure has been tested on a range of New Zealand soils, including a sequence of basaltic soils varying widely in degree of weathering, a graywacke rock sequence also varying in degree of weathering, a precipitation sequence of graywacke soils, and a chronosequence of soils developed on wind-blown sand. The soils are all unfertilized and freely drained;

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Table 1—Procedure for the fractionation of soil inorganic phosphate and the nomenclature used

Stage no.	Treatment	Name of fraction
1	0.5M NH ₄ Cl for 30 min	easily-soluble P
2	0.5M NH ₄ F, pH 8.2, for 24 hr, with correction for resorption of phosphate from solution during extraction	NH ₄ F-P
3	0.1N NaOH + 1M NaCl for 17 hr	1st NaOH-P
4	extraction with dithionite-citrate-bicarbonate	reductant-soluble P
5	1M NaOH for 17 hr	2nd NaOH-P
6	0.5N HCl for 1 hr, followed by 1N HCl for 4 hr if 1st HCl-P > 20 ppm	1st HCl-P
	ignition at 550C for 1 hr, followed by 1N HCl for 16 hr	2nd HCl-P
		sum = acid-extractable Ca-P
7	Na ₂ CO ₃ fusion	residual org. P
		residual inorg. P

consequently, this paper does not discuss the difficulties encountered when vivianite and other secondary ferrous compounds or fertilizer residues such as di-calcium phosphate are present in the materials undergoing fractionation.

METHODS

The procedure finally adopted is outlined in Table 1. The revised scheme contains two stages, during which "residual org. P" is removed prior to the determination of "residual inorg. P," that do not appear in the modified version.³ A more non-committal nomenclature was preferred, for reasons which will be discussed in subsequent publications.

Duplicate 0.5-g or 1.0-g unground (< 2 mm) or < 250 μ samples were used. The residues were washed once only with saturated NaCl solution between stages 1 and 6 and with distilled water after the determination of "acid-extractable Ca-P" and residual org. P. All extractions, except in stages 4 and 7, were performed at 25 \pm 1C.

Phosphate in the extracts was determined by the method of Dickman and Bray (1940) as modified by Fife (1959a) except in stages 4 and 7.

RESULTS AND DISCUSSION

Determination of Easily-Soluble P

For most soils this fraction was negligible. However, the standard treatment with NH₄Cl solution removed over 100 ppm P from the F/H horizons of two very young soils. Eleven consecutive extractions with NH₄Cl solution with extraction time totalling 133 hours, removed 460 and 350 ppm P, respectively, from these two exceptional horizons.

Measurable amounts of easily-soluble P, not exceeding 10 ppm P, were occasionally found in other samples. In these cases the fraction was included in the estimate of NH₄F-P.

Determination of NH₄F-P

The work of Fife (1962, 1963) suggests that a 1-hour extraction with NH₄F solution does not remove all aluminum-bound phosphate from soils, and that a 24-hour extraction is preferable. The pH of the fluoride reagent was fixed at 8.2. Organic matter in 10-ml aliquots of the extracts was precipitated by the addition of 20 ml of 0.8 M H₃BO₃/0.5 N HCl solution, followed by centrifugation.

The determination of NH₄F-P is complicated by the fact that soil ferric compounds sorb a part of the phosphate which is solubilized from other soil compounds during the extraction (Khin and Leeper, 1960; Fife, 1962). To overcome this difficulty Smith (1965) suggested a method based on values for the recovery of phosphate added at different levels to the fluoride extractant. In the procedure being described, a second soil sample, also pretreated with NH₄Cl solution, was extracted with NH₄F solution of pH 8.2 and containing 1.25 μ g P/ml. NH₄F-P values were corrected on the basis of the recovery values for the added phosphate. This was calculated as follows: the proportion of added phosphate sorbed by the soil during extraction (denoted by S_a) was calculated from the phosphate levels of fluoride extracts, with and without added phosphate.

Therefore:

$$1 - \frac{\text{difference in phosphate levels } (\mu\text{g/ml})}{1.25} = S_a,$$

and

$$\text{corrected NH}_4\text{F-P} = \text{uncorrected NH}_4\text{F-P} \times \frac{1}{1 - S_a}.$$

If the relation between sorbed phosphate and phosphate in solution is non-linear, neither correction procedure is entirely adequate.⁴

In a series of phosphate fractionations on sixteen New Zealand basaltic soil profiles⁴ the recovery of added phosphate ranged from 80–90% for weakly weathered soils to less than 40% in the subsoil horizons of strongly weathered soils.

Determination of 1st NaOH-P

To facilitate centrifugation 1M NaCl was added to the NaOH reagent.

In the case of 25 soil horizons, samples which had been treated with fluoride reagent containing added phosphate were also extracted with the NaOH reagent. In all but two cases the added phosphate sorbed during the fluoride extraction was recovered in the NaOH extract, so that the total recovery of added phosphate in the two extracts averaged 97 \pm 5%. Consequently assuming that the native soil phosphate behaved in the same manner as the added phosphate:

$$\text{corrected 1st NaOH-P} = \text{uncorrected 1st NaOH-P} - (\text{corrected NH}_4\text{F-P} - \text{uncorrected NH}_4\text{F-P}).$$

This correction, however, when applied to the two exceptional horizons, gave rise to negative values of 1st NaOH-P, and it was found that the NaOH extraction recovered about a half only of the added phosphate which had been sorbed during the fluoride extraction. When a correction that allowed for the incomplete recovery was applied, low, but positive, values of 1st NaOH-P were obtained for these horizons. Increasing the strength of the NaOH extractant to 1M might overcome the problem of incomplete recovery.

In sixteen profiles of basaltic soils⁴ the ratio of uncorrected NH₄F-P to uncorrected 1st NaOH-P exceeded unity in only two cases. The number of cases increased to eight, however,

³ R. C. Glenn, P. H. Hsu, M. L. Jackson, and R. B. Corey, 1959. Flow sheet for soil phosphorus fractionation. Agronomy Abstracts, p. 9.

⁴ J. D. H. Williams, 1965. Forms of soil phosphate in some genetically-related New Zealand soils. Ph.D. Thesis. Lincoln College, University of Canterbury, New Zealand.

Table 2—Mean values of uncorrected and corrected NH₄F-P and 1st NaOH-P for 16 New Zealand basaltic soil profiles*

Soil	Uncorr. NH ₄ F-P (a)	Corr. NH ₄ F-P (b)	Uncorr. 1st NaOH-P (c)	corr. 1st NaOH-P (d)	a/c	b/d
	ppm					
Camphill	17	22	42	37	0.40	0.59
Evans	130	150	151	131	0.86	1.15
Highcliff	60	75	88	73	0.68	1.03
Stewart	684	900	681	464	1.00	1.94
Dasher	244	428	430	246	0.57	1.74
Miri	24	43	70	51	0.34	0.84
Waiareka	93	114	112	91	0.83	1.25
Ohaeawai	93	151	69	26	1.35	5.81
Papakauri	19	34	84	69	0.23	0.49
Kiripaka	90	157	211	144	0.43	1.09
Maunu	173	304	329	198	0.53	1.54
Apotu	16	28	51	39	0.31	0.72
Waiotu	31	78	175	128	0.18	0.61
Ruatangata	11	17	36	30	0.31	0.57
Atawhai	4	5	21	20	0.19	0.25
Okaihau	2	3	61	60	0.03	0.05

* Calculated using the volume-weight values of individual horizons.

Table 3—Proportion of added phosphate recovered in three stages of the fractionation procedure for individual horizons of several New Zealand basaltic soil profiles

Soil + horizon	NH ₄ F	NaOH	NH ₄ F + NaOH	Dithionite-citrate-bicarbonate	NH ₄ F + NaOH + dithionite-citrate-bicarbonate
Stewart 1	0.82	0.19	1.01		
2	0.74	0.35	1.09		
3	0.75	0.27	1.02		
Dasher 2	0.26	0.74	1.00		
3	0.53	0.43	1.06		
4	0.71	0.34	1.05		
Ohaeawai 3	0.51	0.30	0.81	0.11	0.92
4	0.47	0.31	0.78	0.19	0.97
Okaihau 1	0.58	0.40	0.98	0.03	1.01
2	0.43	0.52	0.95	0.02	0.97
4	0.46	0.47	0.93	0.03	0.96

if corrected values were compared (Table 2). The same ratios for the 62 individual horizons of the profiles exceeded unity in 8 and 37 cases, respectively. The proportion of added phosphate recovered in three stages of the fractionation procedure for individual horizons of several basaltic soil profiles is shown in Table 3.

In two samples of beach sands containing 0.7% and 2.4% CaCO₃ in the form of shells, 14.1% and 15.2%, respectively, of phosphate added with the fluoride reagent was recovered in the acid-extractable Ca-P fraction. This behavior reflects the ability of CaCO₃ to sorb and retain phosphate against extraction by neutral or alkaline reagents. A 0.5-g sample of "Analar" CaCO₃ sorbed over 98% of the phosphate present in 100 ml of 0.1N NaOH containing 5 μg P/ml. Consequently, the procedure, if applied to calcareous soils, may underestimate the NH₄F-P, 1st NaOH-P, reductant-soluble P and 2nd NaOH-P fractions, and overestimate acid-extractable Ca-P by a compensating amount.

Determination of Reductant-Soluble P

The dithionite-citrate-bicarbonate reagent of Mehra and Jackson (1960) has the advantage of being buffered against decrease in pH during reaction with the soil; consequently, dissolution of apatite is minimized. The effectiveness of the reagent in this respect was shown by the fractionation results for a sample of unweathered finely ground mica-schist, which

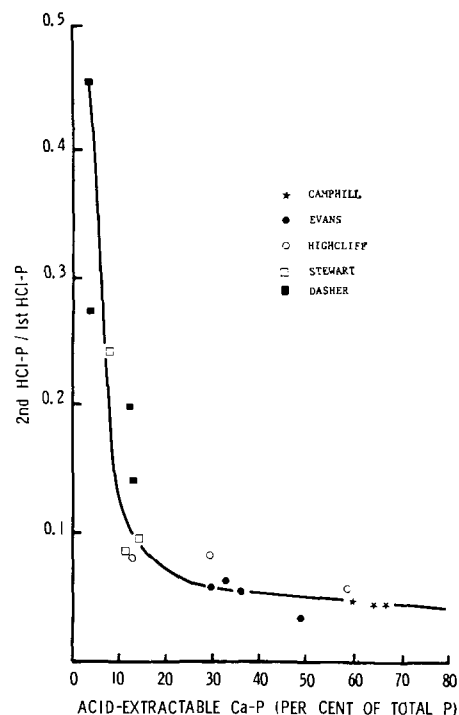


Fig. 1—2nd HCl-P/1st HCl-P and acid-extractable Ca-P for the horizons of five weakly weathered New Zealand soil profiles.

contained 750 ppm acid-extractable Ca-P but only 6 ppm reductant-soluble P.

The inorganic phosphate content of the extracts was determined by the method of Watanabe and Olsen (1962), after oxidation of dithionite by allowing the flasks to stand exposed to the atmosphere.

Determination of 2nd NaOH-P

Because of difficulties associated with the determination of residual org. P (see below) the strength of the NaOH extractant was increased to 1M and the extraction time increased to 17 hours.

Determination of Acid-Extractable Ca-P

In the determination of this fraction HCl was substituted for H₂SO₄. As a result, phosphate in the extract was determined by the colorimetric procedure of Dickman and Bray (1940), which tolerates ferric iron better than sulfomolybdic acid procedures (Jackson, 1958, p. 145) and which moreover was used for determining most of the other fractions.

Although a 1-hour extraction with 0.5N acid will completely dissolve samples of pure apatite (Chang and Jackson, 1957) it was found that a second extraction with acid removed additional amounts of phosphate from soils high in 1st HCl-P. The ratio of the quantities of phosphate in the first and second extracts was closely related to their sum when expressed as a percentage of total P (Fig. 1) suggesting that the phosphate in both HCl extracts originated from apatite. The presence of apatite inclusions within primary minerals in some of the samples is probably responsible for the discrepancy between these findings and those of Chang and Jack-

Table 4—Reproducibility of phosphate fractionation results for one sample included in each of five different batches

Batch no.	NH ₄ F-P	1st NaOH-P	Reductant-soluble P	2nd NaOH-P	Acid-extractable Ca-P	Residual inorg. P	Total inorg. P*	Residual org. P
					ppm			
1	340	192	493	143	0	70	1238	38
2	375	166	466	141	3	62	1213	52
3	379	204	466	132	3	64	1248	42
4	382	199	496	146	3	68	1294	53
5	339	198	464	132	0	78	1211	53
Mean	363	192	477	139	2	68	1241	48
	±22	±15	±16	±6	±2	±6	±37	±7

* Sum of inorganic P fractions.

son (1957). For this reason the sum of 1st HCl-P and 2nd HCl-P was denoted by the expression acid-extractable Ca-P.

Fractionation of a sample of unweathered mica-schist containing 790 ppm total P gave a value of 750 ppm for the acid-extractable Ca-P fraction while several moderately or strongly weathered basaltic soils apparently contained no acid-extractable Ca-P. These results agree with the postulated behavior of apatite during soil weathering (Chang and Jackson, 1958), suggesting that during fractionation no appreciable dissolution of apatite occurs prior to the determination of acid-extractable Ca-P and also that this fraction, as determined in this procedure, does not contain any aluminum- or iron-bound phosphate.

Determination of Residual Org. P

The determination of a fraction corresponding to acid-extractable Ca-P constitutes the last stage in the initial modification³ of the Chang and Jackson procedure. However, it was found that the procedure, if terminated at this point, did not extract all the phosphate present in any of the samples investigated. Khin and Leeper (1960) also found appreciable amounts of "residual" phosphate in a Krasnozern soil horizon.

In an attempt to distinguish between organic and inorganic forms of residual phosphate, residual org. P was removed and determined by a procedure based on the "ignition" method for total organic P of Walker and Adams (1958). In an attempt to minimize systematic errors associated with organic phosphate determination by ignition methods (Anderson, 1960; Williams and Walker, submitted for publication), as much phosphate as possible was removed from the sample prior to the determination of residual org. P, and it was for this reason that the severity of the second NaOH extraction was increased (see above). Regression analysis of the residual org. P and total organic P values for 16 basaltic soil profiles, both sets of values being expressed as a percentage of the total phosphate in the profile, gave a correlation coefficient of 0.73** (0.01), supporting the view that the residual org. P fraction of these soils was largely composed of organic phosphate.

Determination of Residual Inorg. P

This fraction was initially determined by HF digestion of the residue, but was subsequently determined by Na₂CO₃ fusion (Muir, 1952) [except that 9N H₂SO₄ was used for removal of the melt (Jackson, 1958)] after it was found

that the fusion procedure gave higher values in some instances, Phosphate was determined colorimetrically by the method of Fogg and Wilkinson (1958). In some of the soils examined this fraction consisted largely of included apatite not removed by the HCl treatments because of positional non-extractability. The significance of apatite inclusions in soil phosphorus studies will be discussed in a future publication.

To test the reproducibility of fractionation results, one sample was included in each of five different batches of samples undergoing fractionation. The results (Table 4) suggest that random errors as high as 20–30 ppm are possible in the determination of individual fractions, and random errors of 3% or more in the determination of "total inorg. P."

LITERATURE CITED

- Anderson, G. 1960. Factors affecting the estimation of phosphate esters in soil. *J. Sci. Food Agr.* 11:497–503.
- Chang, S. C., and M. L. Jackson. 1957. Fractionation of soil phosphorus. *Soil Sci.* 84:133–144.
- Chang, S. C., and M. L. Jackson. 1958. Soil phosphorus fractions in some representative soils. *J. Soil Sci.* 9:109–119.
- Dickman, S. R., and R. H. Bray. 1940. Colorimetric determination of phosphate. *Ind. Eng. Chem. Anal. Ed.* 12:665–668.
- Fife, C. V. 1959a, 1959b, 1962, 1963. An evaluation of ammonium fluoride as a selective extractant for aluminum-bound soil phosphate: I–IV. *Soil Sci.* 87:13–21, 83–88; 93:113–123; 96:112–120.
- Fogg, D. N., and N. T. Wilkinson. 1958. The colorimetric determination of phosphorus. *Analyst* 83:406–414.
- Jackson, M. L. 1958. Soil chemical analysis. Prentice-Hall, Inc., Englewood Cliffs, N. J.
- Khin, A., and G. W. Leeper. 1960. Modifications in Chang and Jackson's procedure for fractionating soil phosphorus. *Agrochimica* 4:246–254.
- Mehra, O. P., and M. L. Jackson. 1960. Iron oxide removal from soils and clays by a dithionite-citrate system buffered with sodium bicarbonate. *Proc. 7th Nat. Conf. Clays*, 1959, 5:317–327.
- Muir, J. W. 1952. The determination of total phosphorus in soil, with particular reference to the control of interference by soluble silica. *Analyst* 77:313–317.
- Saunders, W. M. H. 1959. Aluminum extracted by neutral citrate-dithionite reagent. *Nature* 184:2037.
- Smith, A. N. 1965. Distinction between iron and aluminum phosphate in Chang and Jackson's procedure for fractionating inorganic soil phosphorus. *Agrochimica* 9:162–168.
- Walker, T. W., and A. F. R. Adams. 1958. Studies on soil organic matter: I. Influence of phosphorus content of parent materials on accumulations of carbon, nitrogen, sulphur, and organic phosphorus in grassland soils. *Soil Sci.* 85:307–318.
- Watanabe, F. S., and S. R. Olsen. 1962. Colorimetric determination of phosphorus in water extracts of soil. *Soil. Sci.* 93:183–188.