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Measuring soluble phosphorus in soils, comparisons of methods, and interpretation of results

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The only extensive correlations between soluble P in soils and responses of crops to P fertilizers published in Britain are those for sugar beet made by the late E. M. Crowther and summarized by Warren & Cooke (1962). Since Crowther's work was done, new methods of assessing 'available' P in soils have been developed but they have not been correlated with the results of field experiments. We thought that the following newer extractants were worth testing: (i) a mildly acid sodium acetate-acetic acid buffer solution developed by Morgan (1937) which is now used by some advisory chemists in England ; (ii) 0·5 M sodium bicarbonate solution, developed in U.S.A. by Olsen, Cole & Watanabe (1954), is now used on calcareous soils in many countries; (iii) a neutral 0·01 M solution of calcium chloride in water, suggested by Schofield (1955), measures the ionized phosphate immediately available to crops.

In our work we have analysed soils from field experiments testing phosphate fertilizers both by some older methods and by these modern ones. The values for soluble soil P obtained by seven methods were compared with each other, and with the responses of the crops grown to superphosphate; they were also used to show a possible way of setting limiting values for soluble P that define 'deficient' soils.

EXPERIMENTAL SITES, SOILS AND CROPS

The field experiments, done from 1951 to 1956, were described by Cooke (1956) and by Cooke & Widdowson (1959); they were collaborative work between the U.K. Advisory Services and Rothamsted Experimental Station. The main crops were potatoes, swedes and grass. A few experiments on other crops have been excluded, as have those where the field data were incomplete, or where there was no soil sample; 179 suitable experiments remained. Most of the experiments were in England and Wales, with some in each N.A.A.S. Province, a few were in the east and north of Scotland, and some in Northern Ireland.

The experiments compared phosphate fertilizers, and the sites were chosen by Advisory Soil Chemists in the expectation that the soils were 'deficient' in P. This choice should have excluded all soils 'satisfactory' in 'available' P, but on some fields the crops did not respond to phosphate fertilizer. As the sites did not represent the full range of P-fertility met in practice, the series was unsuitable for general correlations between soil analyses and crop performance; but, as the soils had already been selected as 'P-deficient', the experiments tested drastically the use of the methods of analysis for distinguishing 'deficient' soils.

The results of 66 experiments on swedes, 72 on potatoes and 41 on grass are used in this paper. There were two types of experiments on both swedes and on potatoes, different phosphate fertilizers being compared in each (Cooke, 1956). Type I experiments were mostly in the west, and Type II in the east of U.K.; the two sets of data for each crop were treated separately. Most of the experiments tested 0, 0·33 and 0·66 cwt. P_2O_5/acre as superphosphate and three other phosphates, each applied at 0·5 cwt. P_2O_5/acre. Responses to 0·5 cwt. P_2O_5/acre were calculated by averaging responses to the two rates of superphosphate. The level of soil P influences both yield of crops grown without added P and response to fertilizer P, so both quantities were correlated with soil analyses. The P contents of grass and swedes were treated in the same way as yields, but, as they provided no extra information on the comparisons between methods, details are not discussed here.

ANALYTICAL METHODS

Total P was determined on soil ground to pass a 0·5 mm. round-holed sieve; 'soluble' P was determined on soil passing a 2 mm. round-holed sieve.

Total P

2 g. of soil was digested with 10 ml. of boiling 60 % $HClO_4$ for 5 hr. The digest was diluted with water and boiled again for 15 min. After cooling, washing and filtering, P was determined by a molybdo-vanadate method (Hanson, 1950).

HCl *soluble* P

12 g. of soil was shaken for 1 min. with 28 ml. 0·3N-HCl and filtered. P was determined by a molybdenum blue method (Truog & Meyer, 1929), which was also used with the other methods described below.

H_2SO_4 *soluble* P

2 g. of soil was shaken for 30 min. with 400 ml. of 0·002N-H_2SO_4 containing 3 g. $(NH_4)_2SO_4$ per litre and brought to pH 3·0 (Truog, 1930).

Citric acid (H_3Ci) *soluble* P

10 g. of soil was shaken for 24 hr. with 100 ml. of 1 % (w/v) H_3Ci solution on an end-over-end shaker (additional citric acid was added for calcareous soils (Dyer, 1894)). Before determining P, organic matter was removed by ashing (Metson, 1956).

Acetic acid (HAc) *soluble* P

5 g. of soil was shaken for 6 hr. with 200 ml. of 0·5N-HAc (Williams & Stewart, 1941).

Acetic acid-sodium acetate buffer (HAc–NaAc) *soluble* P

5 g. soil was shaken for 15 min. with 25 ml. of Morgan's solution (at pH 4·8) (Tinsley & Pizer's (1946) modification of Morgan's (1937) method was used).

$NaHCO_3$ *soluble* P

5 g. of soil was shaken for 30 min. with 100 ml. of 0·5M-$NaHCO_3$ solution, buffered to pH 8·5 with NaOH (Olsen *et al.* 1954). Decolorizing carbon was used when needed to give a colourless extract.

P *in equilibrium with* $CaCl_2$ *solution*

20 g. of soil was shaken at intervals during 15 min. with 100 ml. of 0·1M-$CaCl_2$ solution (Schofield, 1955).

RELATIONSHIPS BETWEEN SOLUBLE PHOSPHORUS IN SOILS AND CROP RESPONSE

Increases in crop yields from superphosphate supplying 0·5 cwt. P_2O_5/acre were examined by dividing all experiments on each crop into three groups, each of nearly equal numbers of centres, according to size of response. Table 1 gives average values for each group of soil pH, total soil P, and soluble soil P measured by seven methods. In the swede and potato experiments, but not in the grass series, the more responsive crops tended to be on the more acid soils. The average amounts of total P in the soils were inversely proportional to average responses by swedes and grass to added superphosphate, whereas average responses in the potato experiments were not related to total soil P. In the swede experiments all the methods used to measure soluble P gave lowest average values in the group of experiments giving the largest responses; the HCl and HAc methods gave the largest contrasts between the average values for groups of sites showing large and small responses. All methods were much less successful in differentiating between groups of potato experiments showing low and high

Table 1. *Relationships between soluble soil phosphate and crop responses to applied superphosphate*

	Response to 0·5 cwt. P_2O_5/acre		Average data for groups of soils								
					Soluble P extracted by						
					HCl	H_2SO_4	H_3Ci	HAc	HAc–NaAc	$NaHCO_3$	$CaCl_2$
No. of soils	Range	Average	pH	Total P	Mg P/100 g. of soil						μM P/litre
Swedes (tons/acre of roots)											
22	−0·9– 2·1	1·5	6·1	96	2·31	3·38	8·59	3·91	0·34	1·69	1·29
22	3·1– 6·8	4·4	5·9	84	1·58	3·29	7·50	2·80	0·29	1·71	1·28
22	7·0–20·7	10·8	5·8	76	1·06	1·94	6·62	0·73	0·19	1·12	0·81
All centres 66	−0·9–20·7	5·6	5·9	85	1·65	2·87	7·57	2·48	0·27	1·51	1·13
Potatoes (tons/acre of tubers)											
24	−0·3– 0·9	0·5	6·6	78	1·43	3·13	6·16	2·01	0·43	1·63	1·08
24	0·9– 1·8	1·3	6·2	73	1·31	2·93	4·95	1·56	0·30	1·23	0·91
24	1·8– 7·4	2·9	6·0	74	1·92	3·02	6·50	1·53	0·29	1·27	1·04
All centres 72	−0·3– 7·4	1·6	6·3	75	1·55	3·03	5·87	1·70	0·34	1·36	1·01
Grass (cwt./acre of dry matter)											
14	−2·1– 1·8	0·1	6·2	97	1·90	3·72	6·21	1·55	0·36	1·74	2·73
14	2·6– 5·3	3·4	6·2	88	1·12	2·60	6·48	2·11	0·31	1·32	1·76
13	5·6–13·6	8·6	6·4	78	0·94	2·09	4·51	1·00	0·21	0·90	1·44
All centres 41	−2·1–13·6	3·3	6·3	88	1·33	2·81	5·76	1·57	0·29	1·33	1·99

average responses; HAc, HAc–NaAc, and $NaHCO_3$ all gave lower average values for soluble P in soils of the more responsive group; the other methods failed. In the grass experiments, the HAc and H_3Ci methods gave average values for soluble P that were not regularly related to average responses; the other methods were better and the largest differences between the groups of experiments showing low and high average responses were with the HCl, $NaHCO_3$ and $CaCl_2$ methods.

Correlations were calculated between unmanured yields, increases in yields caused by superphosphate, and the soluble P values obtained by each of the methods used. Many of the correlations between soluble P in soil and crop performance were significant, but few of the coefficients were much greater than 0·5 and detailed data are not presented. As the Type I and Type II potato and swede experiments were treated separately, there were five sets of correlations between soil and crop results. The methods are ranked in Table 2 in order of correlation; 1 represents the highest correlation in each set, and 8 the lowest. Soil analyses and crop performance were poorly correlated in the potato and grass experiments, only three coefficients were significant out of 14 in the grass experiments and two out of 28 in the potato experiments, but half of the correlations in the swede experiments were significant. There were no significant correlations between soluble P in soils and the increases in the P contents of the crops caused by giving superphosphate in any of the groups of experiments, and data are not shown in Table 2. There were, however, many significant correlations between amounts of P taken from soil by crops receiving no superphosphate and the values for soluble P in the soils (Table 2). (The potato crops were not analysed.)

If an analytical method is to be generally useful, it must be consistently good for different crops and different kinds of soil; consistency was tested by listing the numbers of significant correlation coefficients achieved by each method for the sets of data in Table 2:

	Numbers of significant correlations		
	Yield increases from P fertilizer	Yields without P fertilizer	P in crops grown without P fertilizer
With total soil P	1	1	1
With soil P soluble in			
HCl	3	1	3
H_2SO_4	2	2	3
H_3Ci	0	1	1
HAc	0	0	1
HAc–NaAc	2	1	2
$NaHCO_3$	3	2	3
$CaCl_2$	1	1	1

Values for P soluble in $NaHCO_3$ solution were most consistently related to crop performance. Table 2 shows that this method was consistently better than most of the others for predicting both response to added P, and also the amount of P in the unmanured crops, but it was much less successful in predicting yields of grass and potatoes grown without P fertilizer. The other extractants that were generally useful were HCl, H_2SO_4 and HAc–NaAc buffer solution. The H_3Ci, HAc and $CaCl_2$ methods were generally poor, but the $CaCl_2$ method was best for predicting unmanured yields of potatoes in both series.

The relationships between analytical values for soluble P by the seven methods, used singly and together, and the crop data were also examined by partial regression analyses. The results showed that when one of the better methods of extraction was used, no more useful information was obtained by using a second method as well; details are not given here.

RELATIONSHIPS BETWEEN DIFFERENT METHODS OF MEASURING SOIL PHOSPHORUS

In the whole series of 179 soils the ranges of values for pH (in water), total P and soluble P were:

pH	4·4–8·2	
Total P	22–270 mg.P/100 g. of soil	
P soluble in		
HCl	0·04– 7	mg. P/100 mg. soil
H_2SO_4	0·8 –13	mg. P/100 mg. soil
H_3Ci	1·0 –42	mg. P/100 mg. soil
HAc	0·1 –29	mg. P/100 mg. soil
HAc–NaAc	0·1 – 1	mg. P/100 mg. soil
$NaHCO_3$	0·4 – 5	mg. P/100 mg. soil
$CaCl_2$	0·1 –11 μM P/l.	

The methods used to measure soluble P extracted very different proportions of the total P present in the soils but results by methods that dissolve some part of the same fractions of total soil P should be correlated. Relationships between soluble P values given by the seven methods tested are summarized in Table 3 by stating the total number of significant correlations (out of 5) between them. The H_2SO_4 and HCl methods, which had 4 significant coefficients, varying from 0·74 to 0·95, were the two most closely related. The H_2SO_4 method and the HAc–NaAc buffer solution method were also significantly correlated in four of the sets of data but none of the coefficients was high; there were also four significant correlations between the $CaCl_2$ and HAc–NaAc methods. Values obtained by the HAc–NaAc method were most often related significantly to values obtained by other methods. The methods least related to others were those using H_3Ci and $CaCl_2$.

CALCAREOUS SOILS

In the swede and grass experiments 16 of the soils contained more than 1 % $CaCO_3$. There were only eight centres on each crop and soluble P by any method was not significantly related to the responses of the crops to superphosphate. There were two consistent relationships between analytical values obtained by different methods: H_2SO_4 soluble P and HCl soluble P were closely related ($r = 0{\cdot}91^{**}$ in grass experiments and $0{\cdot}87^{**}$ in potato experiments), HCl soluble P was also related to HAc–NaAc soluble P ($r = 0{\cdot}73^{*}$ and $0{\cdot}90^{**}$ in the grass and potato experiments respectively).

USING SOLUBLE SOIL PHOSPHATE VALUES FOR ADVISING ON FERTILIZING

Measurements of soluble P in soils are used in advising on fertilizing, to adjust average recommendations to the needs of crops on individual fields; less than average fertilizer is recommended

Table 2. *Correlations between values for soluble soil phosphorus and crop performance*

(Methods are ranked for degree of correlation, 1 = highest, and marked * for significance ($P = 0{\cdot}05$ or less) of the appropriate coefficient.)

Experimental series	Grass	Potatoes I (West)	Potatoes II (East)	Swedes I (West)	Swedes II (East)
No. of centres...	40	49	24	40	31
Correlations with increases in yield caused by added phosphate					
Total P	5	3	8	5*	4
P soluble in					
HCl	3*	7	7	1*	1*
H_2SO_4	2*	4	5	2*	3
H_3Ci	6	5	6	8	7
HAc	8	6	4	7	5
HAc–NaAc	4	1*	3	3*	6
$NaHCO_3$	1*	2	1	4*	2*
$CaCl_2$	7	8	2	6*	8
Correlations with yields without added phosphate					
Total P	8	6	6	4*	8
P soluble in					
HCl	2	5	5	2*	6
H_2SO_4	3	4	2	1*	3*
H_3Ci	6	8	7	8	2*
HAc	1	3	4	7	4
HAc–NaAc	5	2	3	3*	5
$NaHCO_3$	7	7	8	5*	1*
$CaCl_2$	4	1*	1	6	7
Correlations with P in crops grown without added phosphate					
Total P	8	—	—	4*	8
P soluble in					
HCl	1*	—	—	1*	5*
H_2SO_4	2*	—	—	3*	3*
H_3Ci	7	—	—	8	4*
HAc	6	—	—	7	2*
HAc–NaAc	3*	—	—	5*	6
$NaHCO_3$	4*	—	—	2*	1*
$CaCl_2$	5	—	—	6*	7

Table 3. *Relationships between values for soluble* P *in soils measured by several methods*

(Numbers of significant correlations out of five possible.)

P soluble in	Total P	P soluble in: HCl	H_2SO_4	H_3Ci	HAc	HAc–NaAc	$NaHCO_3$	$CaCl_2$
HCl	1	—	—	—	—	—	—	—
H_2SO_4	0	4	—	—	—	—	—	—
H_3Ci	1	1	1	—	—	—	—	—
HAc	1	1	1	3	—	—	—	—
HAc–NaAc	1	4	4	2	3	—	—	—
$NaHCO_3$	3	3	1	2	1	3	—	—
$CaCl_2$	0	0	0	0	1	4	2	—

on the richer soils and more than average on poor land. Soil analysis used in this way can improve fertilizer efficiency, but Boyd (1961) found that few farmers use soil analyses to adjust their manuring. Most farmers lack confidence in soil analysis for purposes other than liming. This may be partly because unsuitable chemical methods of determining soluble P and K are sometimes used, and, in some areas, there have been too few field experiments testing fertilizers to 'calibrate' the analyses. But probably the main reason is the lack of a generally accepted numerical definition of 'deficiency' in soil P (or K). Interpreting soil analysis is complicated because some crops thrive at levels of soil P inadequate for others, and because responses to fertilizers depend on season, on the health of crops, and on physical properties of soil. Perhaps because of these difficulties, no published work has defined the levels of soil P above which any given crop is unlikely to respond to fertilizer; but this must be done if advice on fertilizing is to be based on soil analyses. Acceptance of pH in planning liming, and non-acceptance of P and K soil analyses in planning fertilizing, may be because pH 7 (or a lower agreed figure) serves as a 'limiting value' to show whether soil contains enough calcium. As there is no obvious value, like the middle point of the pH scale, in setting 'limiting values' for soluble P, the application of soil analysis is hindered.

Most advisers try to use soil analyses by setting a limit for soluble P arbitrarily and recommending heavy fertilizer dressings on soils well below the limit, moderate dressings for soils around the limit, and either light dressings or none at all for those well above. If the limit is placed too low, many spectacular responses will demonstrate the value of soil analysis, but the remaining fields above the limit will include many where moderate, but profitable, responses to fertilizer would have been obtained. If the limit is set too high much fertilizer may be wasted. The occasional soils with 'high' values for soluble P, where P fertilizers nevertheless increase yields profitably, may not be eliminated by using better analytical methods because fertilizers sometimes increase crops on 'rich' soils when attack by a pest or disease, or adverse weather or physical conditions of soil, are overcome by a high concentration of nutrients near to the roots of seedlings or young plants. Because a few anomalous experiments of this kind usually exist in any set of field experiments, tables relating *average* responses to fertilizers with *average* values for soluble P (such as Table 1) cannot be used to set limits for classifying 'deficient' soils. Any method of using soil analyses to advise on P-manuring should have a 'built-in' statement of the degree of confidence associated with limiting values. If the limit is taken as the highest analytical figure where a significant, or alternatively a profitable, response to fertilizer has ever been recorded, farmers will be protected from wrong advice on the basis of existing information; but this limit will usually be so high that fertilizer would be advised on very many fields where the crops would not benefit. The loss caused by heavy manuring of many unresponsive crops may be lessened by setting a limit which rejects a proportion of the experiments where crops responded to fertilizer, soils with the highest soluble-P being rejected first. The proportion of soils to be rejected when setting limits in this way depends on the degree of risk that farmers are willing to take in accepting advice based on the limiting value chosen. Risk of serious loss is lessened when 'optimum' fertilizer dressings are advised on all 'deficient' soils and a small dressing is given to crops on 'non-deficient' soils to insure against advice being wrong by preventing failures on the few anomalous soils.

This method of setting limiting values is illustrated in a simple way in Table 4 which shows, for four methods of analysis and each crop, the highest values at which significant ($P = 0{\cdot}05$) responses to superphosphate were recorded; it also gives the highest values after discarding first one in twenty, and then one in ten, of the experiments; (sites with the highest values for soluble P were rejected in turn from each set of data). This series of experiments was not suitable for setting 'limits' for general advisory work, because the soils did not represent a normal range of phosphate levels; Table 4 is intended only to illustrate a new way of using soil analyses in advisory work. Satisfactory limits could be established if the results of all existing field experiments and related analyses were pooled, the 'best' analytical method selected, and a correct

Table 4. *Selecting limiting values for soluble P to define deficient soils*

(The values listed in each group are the highest for sites where crops responded significantly ($P = 0{\cdot}05$) to superphosphate. There were 21 grass experiments, 46 on potatoes and 57 on swedes.)

	Soluble P (mg.P/100 g. of soil) extracted by			
	HCl	H_3Ci	HAc–NaAc	$NaHCO_3$
	Highest values over all centres			
Grass	2·5	24	0·7	2·1
Potatoes	6·6	34	0·8	3·1
Swedes	5·6	36	0·8	5·3
Highest values after discarding one-twentieth of centres				
Grass	1·9	8	0·4	1·9
Potatoes	5·0	12	0·8	2·8
Swedes	4·3	25	0·6	4·4
Highest values after discarding one-tenth of centres				
Grass	1·8	8	0·3	1·6
Potatoes	3·2	10	0·6	2·2
Swedes	3·3	14	0·4	2·4

statistical process used to establish the limiting values for soil P that define 'deficiency' for each crop. The confidence limits associated with the values should be stated so that farmers know the degree of risk they run in accepting advice. If this can be done farmers will become more confident that soil analysis is a useful advisory tool.

SUMMARY

Soil samples from 179 field experiments testing phosphate fertilizers on potatoes, swedes and grass were analysed for total phosphorus, and for phosphorus soluble in the following solutions: 0·3N-HCl, 0·002N-H_2SO_4, 1% citric acid (H_3Ci), 0·5N acetic acid (HAc), acetic acid-sodium acetate buffer (HAc–NaAc) at pH 4·8, 0·5M-$NaHCO_3$, and 0·01M $CaCl_2$.

Average values for soluble P were closely related to average crop responses to superphosphate in the experiments on swedes, but not in the grass and potato experiments. The extractants that differentiated best between responsive and unresponsive groups of experiments were HAc, HAc–NaAc, and $NaHCO_3$ for potatoes, and HCl, H_2SO_4, HAc–NaAc, $NaHCO_3$ and $CaCl_2$ for grass.

For the experiments as a whole 0·5M-$NaHCO_3$ was the 'best' extractant. The HCl, H_2SO_4, and HAc-NaAc buffer solution methods were roughly equally effective, though inferior to $NaHCO_3$; the other three extractants (HAc, H_3Ci, $CaCl_2$) were of little *general* use. Total P in soil was also related to response to superphosphate, though less well than values for soluble P obtained by the better methods.

Estimates of soluble P by different solvents were often related. Estimates by HCl and H_2SO_4 methods were most closely related; values for P soluble in H_2SO_4 and in HAc–NaAc were also often significantly correlated, as were estimates by HAc–NaAc and $CaCl_2$. The H_3Ci and $CaCl_2$ methods gave results that were least related to those with other methods.

The use of soil analyses in advising on P-manuring is discussed and a tentative method is proposed of establishing the analytical limits for soluble P that define 'deficient' soils. If the confidence attached to the limiting values that separate 'deficient' and 'non-deficient' soils is stated, farmers will be able to assess the risk entailed in accepting advice based on soil analysis.

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REFERENCES

BOYD, D. A. (1961). *Proc. Fertil. Soc.* no. 65.

COOKE, G. W. (1956). *J. Agric. Sci.* **48**, 74.

COOKE, G. W. & WIDDOWSON, F. V. (1959). *J. Agric. Sci.* **53**, 46.

DYER, B. (1894). *J. Chem. Soc.* **65**, 115.

HANSON, W. C. (1950). *J. Sci. Fd Agric.* **1**, 172.

METSON, A. J. (1956). Methods of Chemical Analysis for Soil Survey Samples. *Soil Bur. Bull. N.Z.* no. 12.

MORGAN, M. F. (1937). *Bull. Conn. Agric. Exp. Sta.* no. 392.

OLSEN, S. R., COLE, C. V., WATANABE, F. S. & DEAN, L. A. (1954). *Circ. U.S. Dep. Agric.* no. 939.

SCHOFIELD, R. K. (1955). *Soils & Fert.* **18**, 373.

TINSLEY, J. & PIZER, N. H. (1946). *J. Soc. Chem. Ind., Lond.* (*Trans.*), **65**, 208.

TRUOG, E. & MEYER, A. H. (1929). *Industr. Engng Chem.* (*Anal.*), **1**, 136.

TRUOG, E. (1930). *J. Amer. Soc. Agron.* **22**, 874.

WARREN, R. G. & COOKE, G. W. (1962). *J. Agric. Sci.* (in the Press).

WILLIAMS, E. G. & STEWART, A. B. (1941). *J. Soc. Chem. Ind., Lond.* (*Trans.*), **60**, 291.