Fig. 4. Correlation between yield response of potatoes to potash fertilizer and rate of release of non-exchangeable potassium

References

1. ARNOLD, P. W. and CLOSE, B. M. (1961). Release of non-exchangeable potassium from some British soils cropped in the Glasshouse. *J. Agric. Sci.*, **57**, 295.
2. PRATT, P. F. (1951). Potassium removal from Iowa soils by greenhouse and laboratory procedures. *Soil Sci.*, **72**, 107.
3. EAGLE, D. J. (1963). Potassium availability to plants. *Nature*, **198**, No. 4880, 558.
4. BARBER, T. E. and MATTHEWS, B. C. (1962). Release of non-exchangeable soil potassium by resin equilibration and its significance for crop growth. *Can. J. Soil Sci.*, **42**, 266.
5. BRAY, R. H. (1948). *Diagnostic Techniques for Soils and Crops*, (Washington, D.C.:American Potash Institute).

Discussion

Dr. Shone suggested that ions from the soil could displace hydrogen ions on the resin which would cause the development of quite acid conditions, resulting in the degradation of the soil clay material and thereby the release of some potassium from a non-exchangeable form.

Mr. Eagle thought that the resin technique had the same effect as a percolation technique using distilled water, measuring only the release of non-exchangeable potassium.

Analytical methods for potassium and their correlations with crop response

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THIS report gives the results of investigations made by the N.A.A.S. Soil Scientists to compare the value of methods of soil analysis in predicting crop responses to potassium fertilizer.

The earliest of the series of investigations was with Reference Soils drawn from potato experiments done in the years 1955–58, and compared the routine methods then in use in regional laboratories. The results are summarized in Table 1.

Table 1

Comparison of methods and laboratories
(Reference Soils 1955–58; potatoes, tons per acre)
(Percentage of variance of K responses accounted for by regression on soil K)

Method	Laboratory	Ratio 1:	Shake	Per cent reduction of variance
Morgan's	Starcross	5	5 min	35
	Wye	2	2 min	32
	Wolverhampton	5	30 min	30
1 per cent Citric acid	Leeds	10	3 hr	37
	Reading	10	16 hr	35
	Shardlow	10	24 hr	35
0·5N Acetic acid	Aberystwyth	40	1 hr	32
	Bangor	40	1 hr	33
	Cardiff	40	1 hr	37
N Ammonium nitrate	Cambridge	5	—	30

Table 2

Methods compared in 1962 investigations

Method	Laboratory	Ratio 1:	Shake min
0·5M NaHCO₃ (Olsen)	Leeds	20	30
0·01M CaCl₂	Aberystwyth	5	30
0·3N HCl	Shardlow	2·5	1
Morgan's reagent	Bristol	5	15
Modified Morgan's	Cambridge	5	30

Table 3

Comparison of five methods of soil determination
(Reference Soils 1955–61; potatoes, tons per acre)

	D.F.	Total Variance	Variance after fitting regression on soil K determinations					
			D.F.	Leeds Olsen's	Aberystwyth $CaCl_2$	Shardlow HCl	Bristol Morgan's	Cambridge Mod. Morgan's
Soil K only Single regression line	113	2·02	112	1·58	1·43	1·59	1·46	1·36
Soil K and soil-group (a) Single regression line	101	1·24	100	1·13	1·11	1·12	1·10	1·12
(b) Separate regressions for each soil-group	—	—	88	1·07	1·10	1·03	0·99	1·06

No method proved materially better than any other, and all were able to account for about a third of the variance of responses to K, after allowing for experimental error.

Soil K determinations were also made in the 1962 investigation on soil P. The methods compared are given in Table 2. With these additional results the value of the methods of soil analysis could be compared both before and after classification into groups corresponding to soil series. Table 3 shows the variance of the responses K_2–K_0 before and after fitting a linear regression of K-response on log soil K; the first line of the Table is for all the soils taken together, the second line gives the corresponding variances within soil groups (series). Comparison of the total variance (before fitting the regression) with the variance within groups shows that soil group alone accounted for about 40 per cent of the total variance; most of the reduction in variance can be attributed to difference in soil texture of the group.

Some methods of soil K determination (e.g., Morgan's) appeared distinctly more useful than others when soil groups were not taken into account, but within soil groups there was little to choose between the methods tested, which with common regression lines, only accounted for about 10 per cent of the remaining variance. The slight additional reductions with separate regression lines were not significant.

Recently a further investigation, including other methods of determination of soil K, was made. Some additional soil series were included whilst some series which gave only small responses to potash were omitted. The methods tested are set out in Table 4 and the results are given in Table 5 on the same basis as Table 3.

Table 4

Analytical methods investigated in 1963

Laboratory	Method	Shake	Soil: Extractant ratio 1 :
Wolverhampton*	N Nitric acid (see Pratt, *Soil Science*, **72**, 107)	(10 min boil)	10
Bangor	0·5N acetic acid	1 hr	40
Newcastle†	N Ammonium acetate (modified Peech and English technique)	(leached)	25
Aberystwyth‡	0·01M Calcium chloride (see P. W. Arnold, *Proc. Fertil. Soc.* **72**, 36)	15 min	2
Shardlow	1 per cent Citric acid	24 hr	10
Cambridge	0·5N Ammonium acetate-acetic acid (modified Morgan's reagent)	30 min	5
Bristol	Sodium acetate-acetic acid (Morgan's reagent)	15 min	5
Wye	Sodium acetate-acetic acid (Morgan's reagent)	2 min	2

Notes from laboratories:

* No analytical difficulties were experienced with this technique and the results were reproducible provided that the boiling time was kept constant.

† No difficulties were experienced with this method, but being a leaching technique the requirements for glassware and laboratory space are higher than those for a normal technique.

‡ The only difficulty with this method was that with peat soils the narrow soil: extractant ratio provided insufficient filtrate for analysis and also created shaking difficulties.

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Table 5

Comparison of methods of soil K determinations, 1963 potatoes, tons per acre

	D.F.	Total Variance	D.F.	Wolver-hampton Nitric acid	Bangor Acetic acid	Newcastle N ammon. acetate	Abery-stwyth CaCl₂	Shardlow Citric acid	Cambridge Mod. Morgan's	Bristol Morgan's	Wye Morgan's
						Variance after fitting regression on soil K determination					
Soil K only Single regression line	114	2·91	113	2·41	1·99	2·44	2·02	1·97	2·18	1·99	1·89
Soil K and soil-groups (a) Single regression line	103	2·48	102	2·14	1·65	2·14	2·06	1·75	1·83	1·78	1·76
(b) Separate regression for each soil group	—	—	91	2·05	1·61	2·28	2·18	1·72	1·84	1·72	1·75

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Because of the exclusion of soils relatively unresponsive to K, soil groups alone were less effective than in the previous investigation. When soil groups are not taken into account, the results from the methods tested in both years are similar, the regression accounted for one quarter to one third of the total variance for all soils taken together for the three methods 0·1M CaCl₂ (Aberystwyth), Morgan's (Bristol) and the modified Morgan's (Cambridge). Of the additional methods tested, the results for acetic acid (Bangor), citric acid (Shardlow) and Morgan's (Wye) differed only slightly from the rest, while nitric acid (Wolverhampton) and N ammonium acetate (Newcastle) were somewhat less effective.

The 1963 investigation also included other groups of experiments for which there were bulk soil samples; these give information on potash responses for various crops. A description of the experiments is given in App. 1 p. 61. The results in App. 2 p. 62 have been treated as in previous tables except that it was impossible to distinguish between soils because of lack of information. The Table shows the variance of the K responses after fitting a linear regression on the soil K determinations; a + in the table implies that the mean square for regression (1 d.f.) was approximately equal to or was less than the remainder mean square, or that the regression coefficient was positive (i.e., response increased with increasing soil K levels).

The Table shows that in general the methods tested were less successful both for potatoes and for other crops than they were for the potatoes on the Reference Soils. For some of the fifteen groups of experiments the average response to K was small; for five of them (Nos. 3, 5, 6, 9 and 13) the experimental error variance was almost as great as, or was greater than the between-centre variance of the K responses, indicating that virtually all the apparent differences in response from centre to centre could be ascribed solely to experimental error.

For the three remaining groups of experiments on cereals, none of the methods was of any value in two of the groups, but for the combine-drilled wheat experiments (No. 1) the citric acid method accounted for almost one third of the variance. However, the mean response to K in the five groups of experiments, taken together, was so small that it would scarcely repay the cost of the fertilizer. It is very doubtful if, in these circumstances, even a reliable method of soil analysis would be economical.

For the sugar beet experiments, all methods except CaCl₂ (Aberystwyth) and citric acid (Shardlow) were of some value for the Chalky Boulder Clay soils (No. 7); none was effective for Dr. Tinker's experiments (No. 8).

For the groups of experiments on fodder crops the nitric acid method (Wolverhampton) was the only successful method for two of the three groups (rape and kale, Nos. 11 and 12) and was as good as any other method for the third group (swedes, No. 10).

Nitric acid (Wolverhampton) was also the only method to show any success in the Yorks. and Lancs. experiments on grass (No. 15), and although not very successful in the hay experiments (No. 14) was slightly better than any other method.

There was no consistent difference between the three variants of Morgan's method (Bristol, Wye and Cambridge). For only three of the ten groups (sugar beet, No. 7, swedes, No. 10, hay, No. 15) did they have any value, and in these groups other methods were equally or more effective.

The nitric acid method was included to see whether it could be used simultaneously with one of the other methods which measure 'Exchangeable' K, but no further reduction in variance resulted from pairing methods in this way.

The general conclusion to be drawn from the foregoing results is that even for a K responsive crop like potatoes, none of the methods tested was of great value. For the less responsive crops most of the methods were almost completely ineffective.

Discussion

When questioned on the importance of sampling errors in connection with soil analysis, *Dr. Boyd* thought that the routine soil sampling errors and the laboratory errors had now been reduced to very reasonable values. There was always the risk that a single core might strike a pocket of fertilizer, or, under grazed conditions, an area which had recently received urine; as it was not possible to recognize these areas, the risk of large errors was reduced by increasing the number of cores per sample.

Dr. Boyd explained that he did not favour expressing responses as a percentage of the yield without fertilizer, because this yield was determined by many factors other than soil K content. If, as often happened, these factors were positively correlated with soil K content, the prediction value of soil K could be much exaggerated.

Dr. Pizer suggested that the reason why soil analysis appeared to be ineffective was that in the period prior to 1951 when the amount of potassic fertilizer used was limited it was not difficult for soil analysis methods to pick out the deficient sites; subsequent to 1951 the rate of use of potassic fertilizer had increased considerably and there was now the difficulty that sampling may or may not pick up the residues of applied potassic fertilizers. The depth of sampling was also of great importance since some of the applied potassium might still be available to crops though at a depth below the conventional sampling depths.

Dr. Boyd stressed the problem of the depth of sampling quoting sugar beet trials where the correlation between soil analysis and crop response was very disappointing. It was possible that the sugar beet was drawing on potassium reserves other than those in the top 6 in. of soil which had been sampled for analysis.

Appendix 1

Details of experiments included in 1963 investigation

Series Ref. No.	Crop	Source and description of data	No. of centres	Years	Crop units (per acre)	Mean resp. to K
1	Wheat	N.A.A.S. S.W. Reg. (Chalky soils, K combine drilled)	12	1958–60	Cwt grain	1·1
2	Wheat	N.A.A.S. S.W. Reg. (Chalky soils, K broadcast)	12	1956–58	Cwt grain	1·2
3	Barley	N.A.A.S. S.W. Reg. (Chalky soils, K combine drilled)	11	1958–60	Cwt grain	0·4
4	Barley	N.A.A.S. S.W. Reg. (Oolitic soils, K broadcast)	12	1956–58	Cwt grain	−0·2
5	Barley	N.A.A.S. S.W. Reg. (Oolitic soils, K combine drilled)	7	1960–62	Cwt grain	−0·3
6	Potatoes	N.A.A.S. E. Reg. (Peaty soils, K broadcast over ridges)	22	1952–54	Tons total tubers	0·9
7	Sugar beet	N.A.A.S. E. Reg. (Chalky Boulder Clay soils)	28	1949–51	Tons clean beet	0·7
8	Sugar beet	Dr. Tinker	35	1957–60	Cwt total sugar	1·3
9	Sugar beet	Dr. Tinker	19	1958–61	Cwt total sugar	3·7
10	Swedes	N.A.A.S. Wales	22	1953–59	Tons D.M.	0·66
11	Rape	N.A.A.S. Wales	10	1956–62	Cwt D.M.	1·7
12	Kale	N.A.A.S. W. Mids., S.E. and S.W. Regs.	6	1960–62	Cwt D.M.	4·4
13	Kale	N.A.A.S. Wales	11	1956–61	Tons Fresh Wt.	0·5
14	Hay	N.A.A.S. Wales	16	1952–60	Cwt D.M.	3·4
15	Grass	N.A.A.S. Yorks. and Lancs. Reg.	14	1953–61	Cwt D.M.	2·5

Appendix 2

Results of 1963 investigations, excluding Reference Soil Potatoes

Ref. No.	Crop	D.F.	Total variance	Variance after fitting regression on soil K determination							
				Nitric acid	Acetic acid	Amm. acet.	CaCl₂	Citric acid	Mod. Morgan	Morgan (Bristol)	Morgan (Wye)
1	Wheat CD	11	2·37	+	2·00	1·80	+	1·59	+	+	+
2	Wheat BC	11	1·10	1·08	+	+	+	1·03	+	+	+
4	Barley BC	11	0·97	+	+	+	0·85	+	0·31	0·35	0·40
7	Sugar beet	27	0·51	0·31	0·29	0·31	0·46	0·46	0·43	0·46	0·56
8	Sugar beet	34	4·90	+	0·46	+	0·58	0·44	+	+	+
10	Swedes	21	0·64	0·40	+	0·37	+	+	+	+	+
11	Rape	9	2·61	1·43	+	+	+	+	+	+	+
13	Kale	5	8·75	0·88	+	+	+	+	+	+	+
14	Hay	15	10·33	9·56	10·17	10·09	9·99	9·67	10·19	9·76	9·75
15	Grass	13	1·64*	1·26	+	+	+	+	+	+	+

Note: A plus sign (+) implies that the residual mean square was not reduced by the regression or that the regression coefficient was positive.
*Experimental errors not deducted.

The determination in soils of potassium and magnesium and their uptake by crops

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AN examination of the methods used in Europe for the routine determination of potassium in soils indicates that while there are many differences in actual techniques most workers make an assessment of exchangeable potassium contents[1]. Water soluble potassium is determined in some laboratories where the majority of soils have high levels of exchangeable potassium. Magnesium determinations are not normally made on a routine basis but where they are made the extracting solution is usually the same as for potassium.

The most popular extractants for potassium assessments appear to be Morgan's sodium acetate-acetic acid reagent and normal neutral ammonium acetate, but dilute solutions of mineral or of organic acids are commonly used, as are lactate extractants of the Egnér types, bicarbonate solutions like those used by Olsen, and dilute solutions of salts such as calcium chloride.

The method which has been used for many years in Northern Ireland[2] involves shaking air-dry soil overnight on an end-over-end shaker with N/2 acetic acid (soil: solution ratio 1 : 40) and determining potassium in the filtrate. This was originally done by the Lundegårdh flame emission technique using a medium quartz spectrograph. For this purpose it was usual to use 20 grammes air-dry soil and 800 ml acetic acid solution. The filtered extract was evaporated to small bulk, organic matter destroyed by hydrogen peroxide and the residue was dissolved in a measured volume dilute hydrochloric acid. The solution was diluted, filtered and adjusted to volume for spectrographic analysis. In recent years a flame photometer has been used to determine potassium directly in the acetic acid extract. Good agreement has been found between the results of the two methods. The sensitive flame photometer has made it possible to economize considerably in time and reagents, the smallness of acetic acid volume being limited only by the limitation in accuracy of measuring a small weight representative of the soil being analysed. Suitable amounts are 2·5 g air dry soil and 100 ml of acetic acid.

This method has been found to remove effectively exchangeable potassium and other exchangeable metal ions from the soil and a single extraction removes some 60–75 per cent of the total potassium which can be removed by successive extractions with this reagent (Table 1).

The amounts of potassium removed from the agricultural soils in Northern Ireland by this method vary widely. It is unusual to find values for surface horizons less than 4 mg K_2O per 100 g air-dry soil and only about two per cent of soils show values of more than 25 mg K_2O per 100 g soil though values of more than twice this level are sometimes obtained. In advisory work, soils with less than 8 mg (0·17 m.e. per cent) of acetic-soluble potassium as K_2O per 100 g are regarded as low and those with values of more than 15 mg (0·32 m.e. per cent) are classed as high. It is of interest to record that up till 1955 when the last detailed examination of data was made some 38 per cent