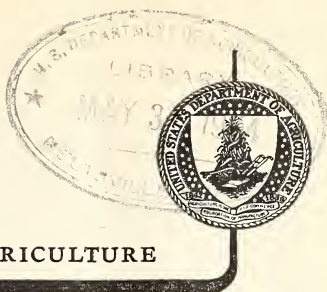# Historic, archived document

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Estimation of Available Phosphorus in Soils by Extraction With Sodium Bicarbonate [1]

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INTRODUCTION

Relatively few methods employing either an alkaline or acid extractant have been proposed for measuring readily available phosphorus on both acid and alkaline soils. Das (*9*)[3] recommended a 1-percent K_2CO_3 solution for extracting phosphates on both acid and calcareous soils. Hockensmith and coworkers (*14*) modified this method and reported that K_2CO_3 is the most satisfactory of several extractants studied for indicating the crop response to applied phosphate on calcareous soils. On acid soils Gardner and Kelley (*13*) reported that

[3] Italic numbers in parentheses refer to Literature Cited, p. 18.

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the K_2CO_3 method was unsuitable, since it extracted relatively much more phosphorus than was available to plants.

Rhoades (23) leached soils with a solution of 0.01 N Na_2CO_3 buffered with sufficient H_3BO_3 added to give it the same pH as the soil. For most calcareous soils this solution was largely a mixture of sodium bicarbonate and sodium borate with pH values between 7 and 8.5. This method was not proposed for acid soils.

A new method for extracting soil phosphorus with sodium bicarbonate solutions is described in this circular. The relationship of the extractable phosphorus to yield response in greenhouse and field experiments and to a measure of plant available phosphorus, or the 'A' value (12), is shown. The $NaHCO_3$-soluble phosphorus is compared with the methods of Bray (4), Truog, CO_2-soluble (26), and H_2O-soluble (2) by means of correlation analysis with 'A' values.

DEVELOPMENT OF METHOD

THEORETICAL BASIS

Several studies have been conducted to show the relationship of pH to phosphate solubility in calcareous soils (6, 13, 22, 26) and in systems containing excess $CaCO_3$ (1, 7). The results show that the solubility of the calcium phosphate is a function of pH and Ca^{++} activity, with a minimum solubility between pH 7 to 7.5 and an increase in solubility on both the alkaline and acid side of this pH range. On the alkaline side the solubility of phosphorus in the presence of solid phase $CaCO_3$ is a function of the Ca^{++} activity, whereas on the acid side of the minimum solubility range in pH the solubility of phosphorus is a function of both the H^+ activity and the Ca^{++} activity (7). An increase in H^+ activity increases the solubility of phosphorus and an increase in Ca^{++} activity decreases the solubility of phosphorus.

One of the objectives in research on soil tests has been to eliminate or diminish the secondary precipitation reactions that may occur during the extraction process with dilute acids (8). McGeorge and others (18) stated that the solvent action of CO_2 on phosphorus in calcareous soils was mainly a function of reaction and that the H^+ activity must be sufficient to overcome the common ion effect of Ca^{++} in precipitating a calcium phosphate. Thus, two reactions with opposite effects on phosphate solubility occur when CO_2 is bubbled through a calcareous soil:water suspension, i. e., an increase in solubility caused by a decrease in pH and a decrease in solubility when precipitation of a calcium phosphate occurs as a result of the increase in Ca^{++} activity. Stanberry (26) showed that both reactions affected phosphate solubility on a calcareous Sagemoor fine sandy loam, since the concentration of phosphorus was higher at both pH 8.5 and 5.8 than at intermediate pH values. Time-of-extraction studies on this same soil with CO_2 showed that there was a maximum solubility of phosphorus in 5 and 30 minutes, respectively, for low and high phosphate fertility levels. A decrease in solubility of phosphate following the maximum level led to the conclusion that a calcium phosphate precipitated from supersaturated solutions of the CO_2 extract.

Secondary precipitation reactions may occur with extractants that increase the H^+ activity of the calcareous soil:water system, because a concomitant increase in the Ca^{++} activity occurs. Since the solubility of phosphate may be increased in this system with a decrease in Ca^{++} activity, the secondary precipitation reactions should be largely eliminated with an extractant that decreases the Ca^{++} activity.

Gardner and Kelley (13) indicated that in the presence of $CaCO_3$ and excess carbonate ions the increase in phosphorus solubility in 1-percent K_2CO_3 solutions on calcareous soils was a result of the repression of the Ca^{++} activity. The K_2CO_3 method is not applicable to acid soils, however, probably because forms of iron and aluminum phosphates unavailable to plants are dissolved as a result of the high pH of the extracting solution.

The Ca^{++} activity in a soil:water system is repressed with $NaHCO_3$ solutions at pH 8.5, and the undesirable effects of the high pH of 1-percent K_2CO_3 solutions are avoided. The ratio of HCO_3^- to $CO_3^=$ is 63 to 1 in a solution of $NaHCO_3$ at pH 8.5. The influence of $NaHCO_3$ concentration on the molar concentrations of HCO_3^-, $CO_3^=$, and Ca^{++} in a $CaCO_3-H_2O$ system at pH 8.5 is shown in table 1. The calculations are based on the mass-action law, using 4.82×10^{-9} as the solubility product of calcite (11) with no corrections for salt effect. In a 0.5 molar solution of $NaHCO_3$, the equilibrium calcium concentration is 857 times smaller than in a pure $CaCO_3-H_2O$ system in equilibrium with atmospheric CO_2. The main effect of the $NaHCO_3$ in calcareous soils, therefore, is to decrease the Ca^{++} activity, which in turn increases the solubility of phosphorus.

In acid and neutral soils the phosphorus present in the form of calcium phosphates would probably become more soluble in the presence of $NaHCO_3$, owing to a repression of the Ca^{++} activity, assuming that solid phase $CaCO_3$ would be formed at pH 8.5. Since the calcium phosphates are known to be the most available forms of phosphorus in these soils, the $NaHCO_3$ method may be applicable to acid and neutral as well as to calcareous soils.

The main effect of the $NaHCO_3$ on acid and neutral soils probably would be through ionic competition of HCO_3^-, $CO_3^=$, and OH^- ions for phosphate adsorbed on the surface of soil particles. According to Kurtz and others (16) the replacing ability of HCO_3^- for phosphate was greater than the replacing ability of acetate or sulfate ions on acid soils. Laatsch (17) stated that HCO_3^- ions displaced sorbed phosphate from colloidal surfaces in soils.

TABLE 1.—*Influence of $NaHCO_3$ concentration on the molar concentrations of HCO_3^-, $CO_3^=$, and Ca^{++} in a $CaCO_3-H_2O$ system at pH 8.5*

$NaHCO_3$	HCO_3^-	$CO_3^=$	Ca^{++}
[1] 0. 0	0. 0014	2.30×10^{-5}	5.30×10^{-4}
. 01	. 0098	1.56×10^{-4}	3.09×10^{-5}
. 10	. 0984	1.56×10^{-3}	3.09×10^{-6}
. 50	. 492	7.80×10^{-3}	6.18×10^{-7}

[1] Solubility of calcite in H_2O at atmospheric pressure of CO_2 (11).

The amount of phosphorus on the surface of soil particles, which readily exchanges with P^{32} in the soil solution, was shown to be highly correlated with plant available phosphorus, or 'A' values (21).

The relationship between the surface or exchangeable phosphorus measured by P^{32} and the phosphorus soluble in $NaHCO_3$ is shown in
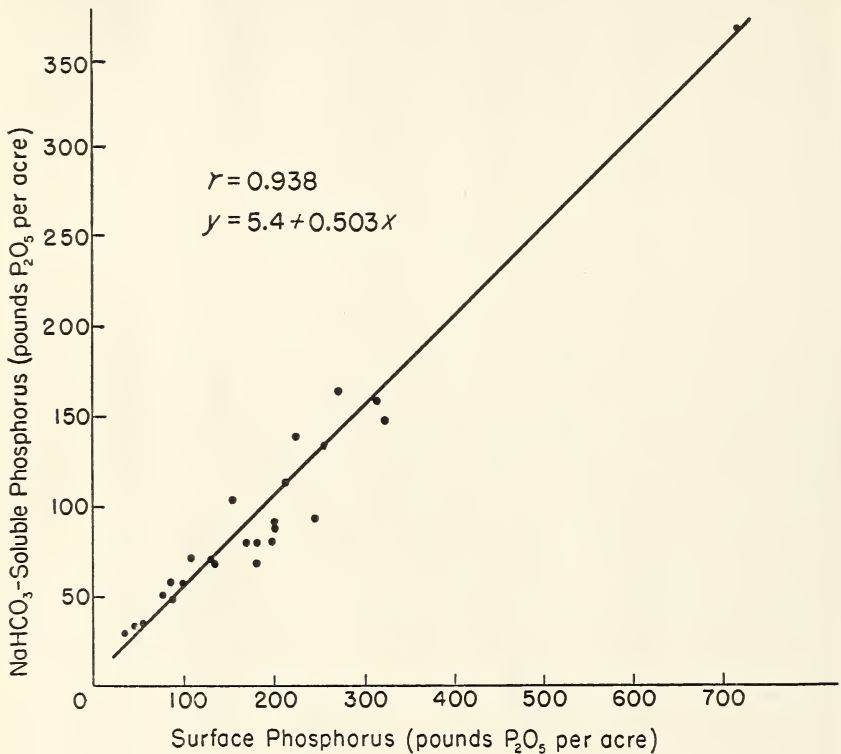
FIGURE 1.—Relationship between surface phosphorus and phosphorus soluble in 0.5 molar $NaHCO_3$ solutions on 25 soils.

figure 1 for 25 soils. The pH of these soils ranged from 5.0 to 7.6. The $NaHCO_3$ extracts about 50 percent of the surface phosphorus. The data indicate that the $NaHCO_3$-soluble phosphorus is closely related to a form of phosphorus, which in turn is highly correlated with the amount of phosphorus available to plants.

EXTRACTION DETAILS

Time of Extraction

Five soil types, representing acid to highly calcareous soils, were selected for this study (table 2). Samples from plots receiving applications of phosphate in the field are included to illustrate the effect of phosphate-fertility level. The extracting solution was 0.5 molar $NaHCO_3$ solution at pH 8.5 and the soil: solution ratio was 1:20.

Equilibrium is not reached in any of the samples over a 2-hour extraction period (fig. 2); however, the curves tend to level off after 30 minutes on the low-phosphate-fertility soils. The absolute differences between the low- and high-phosphate-fertility levels become greater as the extraction time increases; the percentage difference, however, remains about the same for all extraction periods studied. The correlation coefficients between 'A' values and NaHCO₃-soluble phosphorus were essentially the same for 30-, 60-, and 120-minute extraction periods for experiments 4 and 5 described later. Correlations for shorter extraction periods were not determined.

TABLE 2.—*Calcium carbonate content, pH, and phosphate treatment of soil types used for time-of-extraction studies*

Soil No.	Soil type and treatment	CaCO₃	pH
		Percent	
326_____	Davidson silty clay loam [1]_____	_____	5. 3
318_____	Cecil loam [1]_____	_____	5. 7
333_____	Owyhee silt loam_____	_____	7. 0
335_____	Owyhee silt loam, plus phosphate_____	_____	7. 1
151_____	Pryor silty clay_____	0. 51	7. 7
145_____	Pryor silty clay, plus manure_____	1. 15	7. 6
428_____	Millville loam_____	55. 8	8. 2
433_____	Millville loam, plus phosphate_____	55. 8	8. 2

[1] Data on yield response of soils to phosphate in the greenhouse indicated that the Cecil loam had a higher phosphate-fertility level than the Davidson silty clay loam.

pH of Extractant

An increase in the pH of the extracting solution from 8.5 to 9.0 causes an increase in phosphorus solubility. The effect of the pH increase is greater on acid than on alkaline soils (table 3). Correlation coefficients for the phosphate soluble in NaHCO₃ compared with 'A' values showed very little difference between pH 8.5 and 9.0. The relative differences in the extractable phosphorus are less at pH 8.5 than at pH 9 as the soil pH changes (table 3). The level of extractable phosphorus in relation to crop response, therefore, would be more uniform at pH 8.5 than at pH 9 for a group of soils varying in pH.

Method of Extraction

The following method is recommended for extracting soils with NaHCO₃ solutions: (*a*) Prepare a 0.5 molar NaHCO₃ solution adjusted to pH 8.5 with NaOH. (*b*) Shake 5 gm. of soil with 100 ml. of the NaHCO₃ solution and 1 teaspoon of carbon black (Darco G–60 or other suitable carbon black) for 30 minutes. The rate of shaking should be constant. Add more carbon black to the flask after shaking if filtrate is not clear. (*c*) Filter through Whatman No. 40 or other suitable paper. (*d*) Add 5 ml. of the filtrate to a 25-ml. volumetric flask and determine phosphorus by the Dickman and Bray method (*10*). The molybdate reagent is modified by adding an extra 50 ml. of concentrated HCl per liter to neutralize the NaHCO₃ in a 5-ml.
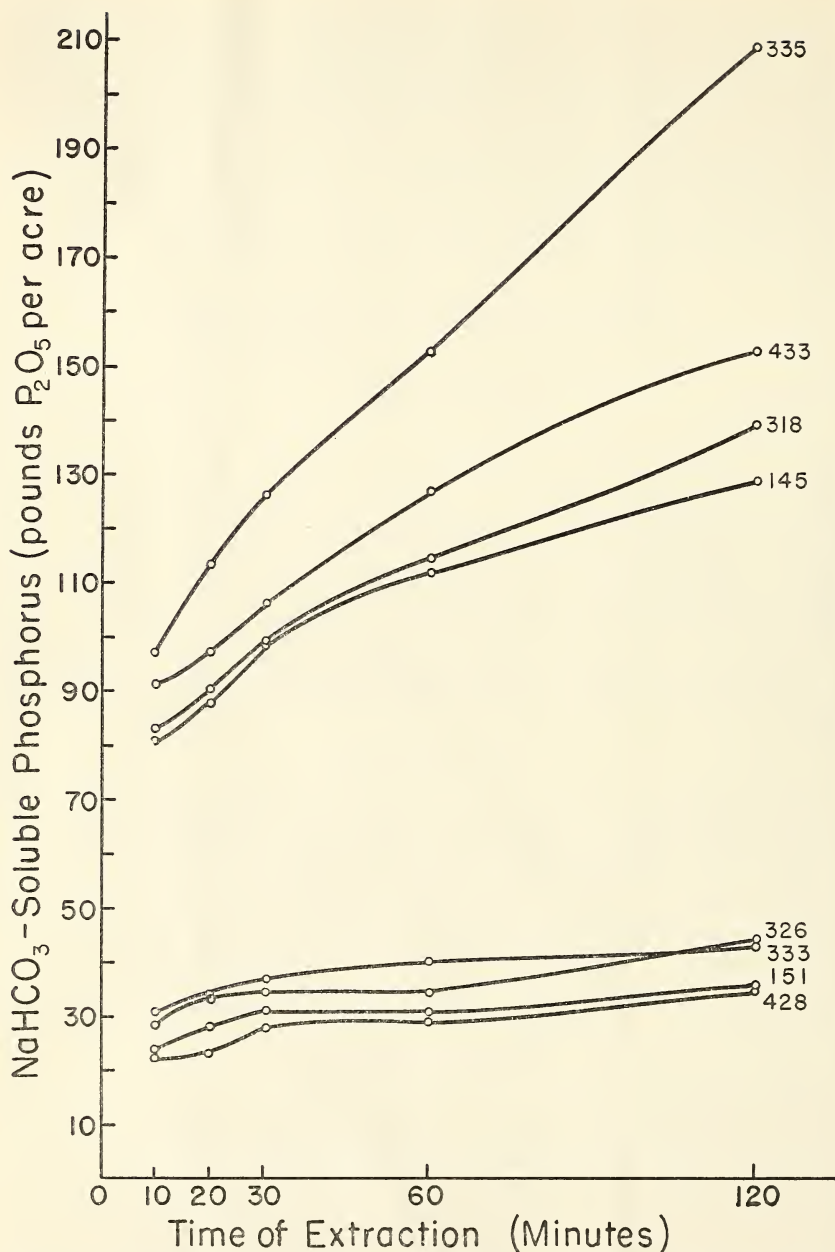
FIGURE 2.—Relation of effect of time of extraction on NaHCO₃-soluble phosphorus in pounds P₂O₅ per acre from several soil types to phosphate-fertility level.

aliquot. (*e*) On some soils high in extractable phosphorus it may be necessary to take less than a 5-ml. aliquot. If so, the total volume should be made up equivalent to 5 ml. of the $NaHCO_3$ solution in order to maintain the proper acidity for developing the color. The standard curve should be prepared with the $NaHCO_3$ included. (*f*) The carbon black (Darco G–60) releases phosphorus when treated with $NaHCO_3$. Therefore, the carbon black is pretreated once with the $NaHCO_3$ solution by leaching, washing with water, and drying.

TABLE 3.—*Effect of pH of the $NaHCO_3$ extracting solution on the mean amount of phosphate extracted from soils varying in pH*

Number of soils	pH range of soils	Pounds P_2O_5 per acre soluble in $NaHCO_3$ at—	
		pH 8.5	pH 9.0
41	4.5 to 6.0	101	150
23	6.1 to 7.0	71	89
10	7.1 to 7.6	46	52

It may be well to indicate a few precautions to be observed in extracting soils. If the flask containing the aliquot is shaken too vigorously after the addition of the molybdate reagent, some solution may be lost as a result of rapid evolution of CO_2. After CO_2 evolution has subsided, wash down the neck of the flask and dilute to about a 20-ml. volume. Add 1 ml. of the dilute $SnCl_2$ solution, shake immediately, dilute to volume, and mix well. Failure to observe this precaution with respect to the $SnCl_2$ will give erratic results. The pH of the $NaHCO_3$ solution tends to increase on standing if exposed to the atmosphere. Changes in pH of the $NaHCO_3$ solution can be prevented by the addition of mineral oil.

EVALUATION OF METHOD

SOIL SAMPLES

Laboratory and greenhouse studies were conducted on six groups of soil samples to obtain a measure of yield and 'A' value. Response data from field experiments were available from a part of these samples. The greenhouse studies on the six groups of soils are described by experiment number. The samples were collected from the surface 6 inches of soil. Nitrogen and potash were added in amounts considered to be sufficient for maximum growth in all experiments. The crops grown on these soils were harvested at the heading-out stage, except in experiment 6.

Experiment 1

Soil samples were collected from 74 locations in the United States and Saskatchewan, Canada. The pH values were less than 6 on 41 samples, between 6.1 and 7 on 23 samples, and above 7.1 on 10

samples. Free calcium carbonate was found in 12 samples. The experiment was conducted during the summer of 1951 at Beltsville, Md., to measure the yield and 'A' value for each soil.[4] Superphosphate containing P^{32} was thoroughly mixed with the soil at the rate of 40, 80, and 160 pounds P_2O_5 per acre. The crop was German millet.

The 'A' values used for the correlation studies in both experiments 1 and 2 were the average values for the various rates of P_2O_5 added. With most soils the 'A' value was essentially the same for each rate of P_2O_5 added.

Experiment 2

An additional 40 soil samples were collected from various sections of the United States, and an experiment similar to the one described previously was conducted in the summer of 1952 at Beltsville, Md. The 80-pound P_2O_5 rate was omitted in this experiment. The pH values were less than 6 on 23 samples, between 6.1 and 7 on 5 samples, and above 7.1 on 12 samples. The crop was German millet.

Experiment 3

A group of 38 soils representing 28 different soil types was obtained from various locations in Colorado. Saturated paste pH values were between 6 and 7 for 3 soils and the rest ranged from pH 7 to 8.4. The calcium carbonate content ranged from none on the 3 acid soils to 9.6 percent. Phosphorus was mixed with the soil at the rate of 80 pounds of P_2O_5 per acre. The phosphorus in the form of H_3PO_4 containing P^{32} was adsorbed on a resin, IR–4B. A separate experiment on several soils showed that the phosphated resin acted essentially the same as superphosphate as a source of phosphorus for the plants. This experiment was conducted during the summer of 1952 at Fort Collins, Colo., using German millet as a crop.

Experiment 4

Thirty soil samples from long-term rotation plots at three locations were selected. One-half of the samples were from plots that had received either manure or phosphate, and the other half had received no phosphorus applications for 10 years or more. All these samples contained free calcium carbonate. The rate of application and the form of the phosphate were the same as in experiment 3. This experiment and experiment 5 were conducted at Fort Collins in the spring and fall of 1952, using oats as a crop.

Experiment 5

Thirty soil samples, representing 10 soil types and 3 levels of available phosphorus, were selected from 10 locations. The samples were obtained from field plots that had received 0, 120, and 240 pounds of P_2O_5 per acre 1 year previous to sampling time. All of the soil pH values were above 7, but 4 of the soil types did not contain any free calcium carbonate and the remaining 6 were calcareous.

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[4] The greenhouse experiments 1 and 2 were conducted by Maurice Fried, Beltsville, Md.

Experiment 6

Thirty soil samples from as many different locations were collected from Oregon.   Phosphorus was mixed with the soil at the rate of 100 pounds of P_2O_5 per acre.   The phosphorus in the form of H_3PO_4 containing P^{32} was adsorbed on a resin, IRA–400.   The crop was Sudan grass, and the experiment was conducted in the summer of 1952 at Corvallis, Oreg.   The Sudan grass was harvested after 7 weeks' growth.[5]

Yield data from this experiment are not discussed, since only three soils showed a significant response to applied phosphate.

RELATION OF PHOSPHATE-FERTILITY LEVEL TO YIELD RESPONSE

The acceptable standard for determining the relative value of soil tests is the yield response of crops to applied phosphorus in greenhouse and field experiments.   With the latter, especially, the assurance that the yield response measured was a result of differences in phosphate-fertility levels was not always evident.   Furthermore, the relationship between phosphate-fertility level and the soluble phosphate by the soil test, on the soils showing no yield response of crops, was indeterminate.

The method of Fried and Dean (*12*) for determining the plant available phosphorus, or 'A' value, permits a measurement to be made both on soils responding and not responding to applied phosphorus; the relationship, therefore, between 'A' value and phosphate soluble in chemical extractants can be determined for a wide range of phosphate-fertility levels.   The 'A' value is defined as the amount of soil phosphorus that is as available to the plants as the phosphorus in a standard phosphate fertilizer which has been mixed with the soil.   Since the 'A' value is used in this study for comparing the relative value of various soil extractants for phosphorus, the relationship between 'A' value and yield response is shown.

Greenhouse Experiments

The relationship between the percentage of soils showing a significant (5-percent level) crop yield increase from applied phosphorus and the 'A' value is shown in figure 3.   A total of 212 samples are compared.

Where 'A' values were below 50 pounds P_2O_5 per acre, all greenhouse soils showed crop yield increases from phosphate fertilization. In the range from 50 to 100 pounds P_2O_5 per acre, 98 percent of the soils showed a crop response to phosphorus.   As the 'A' values increased the proportion of soils showing response decreased rapidly. When the 'A' value was about 200 pounds P_2O_5 per acre 50 percent of the soils showed benefit from phosphorus.   With more than 300 pounds P_2O_5 per acre only 3 percent of the soils responded to phosphorus.   Thus, the 'A' value will predict accurately the crop behavior when the 'A' values are either low or high, but the predic-

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[5] This greenhouse experiment was conducted by Albert Hunter and Lawrence Alban, Oregon State College, Corvallis.
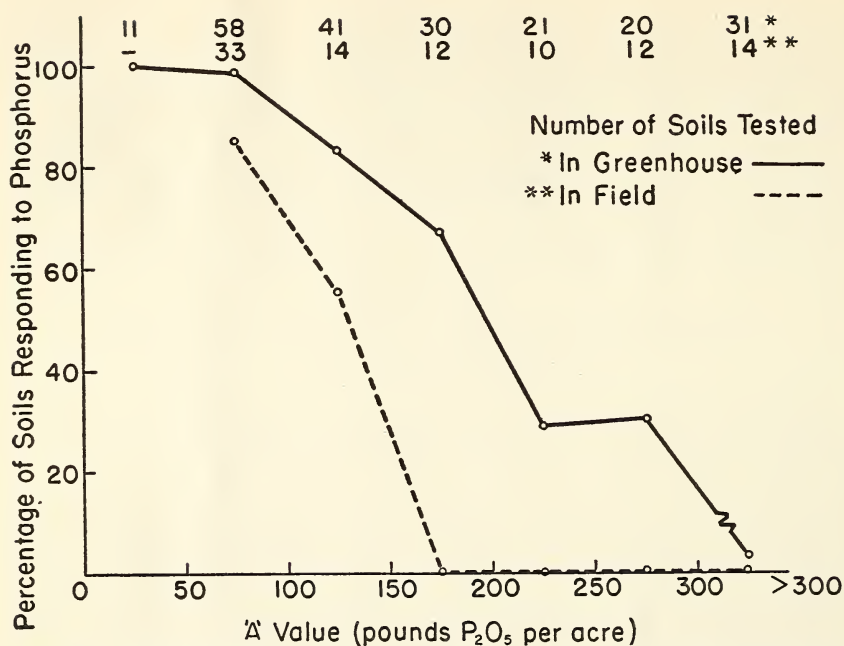
FIGURE 3.—Relationship for greenhouse and field experiments between percentage of soils showing a yield increase from phosphorus and 'A' value.

tion is uncertain when the 'A' value is around 200 pounds P_2O_5 per acre.

If the crop yield on the untreated soils is expressed as a percentage of the maximum yield, or yield from largest P_2O_5 rate used, a quantitative relationship with the 'A' value can be obtained by correlation analysis for the number of soils showing significant increases in crop yield from phosphate fertilization. The linear relationship between the 'A' value and percentage of maximum yield for each greenhouse experiment is shown in table 4. All the correlation coefficients are highly significant at the 1-percent level, but the r^2 values indicate that a large proportion of the variance in percentage of maximum yield is related to factors other than 'A' value.

A method for determining the phosphate-fertility level is most useful if it can be used to predict the crop behavior to additions of fertilizer. The standard error of estimate and the r^2 values (table 4) indicate that only a fair degree of precision may be expected for predicting percentage of maximum yield from 'A' values. The predictions would be expected to be more accurate for soils similar in the physical and chemical properties affecting plant growth and less accurate when these properties differ greatly. For example, the elimination of one soil from experiment 1 increases the r value from 0.690 to 0.721. The lack of high precision in predicting percentage of maximum yield from 'A' values does not necessarily mean the 'A' value fails to measure the phosphate-fertility level in the soil, because there may have been uncontrolled factors other than available phosphorus affecting plant growth.

TABLE 4.—*Linear correlations between 'A' values and percentage of maximum yield on the soils showing a significant increase in yield from added phosphorus*

Experiment No.	Number of soils	Correlation coefficient (r)	Coefficient of determination $(r^2) \times 100$	Standard error of estimate
1_____	43	0. 690	48	21. 4
2_____	34	. 841	71	14. 3
3_____	21	. 758	57	13. 8
4_____	22	. 798	64	15. 3
5_____	16	. 828	69	9. 5

The question arises as to whether the true relationship between percentage of maximum yield and the 'A' value is linear or curvilinear.   The percentage figures were converted to angles (*25, p. 449*) and also used in the form of log $(A-y)$, where A=maximum yield, or 100, and y=percentage of the maximum yield (*3, 24*).   These transformations showed either a slight decrease, no change, or a slight increase in the correlation values with respect to the various experiments.   Percentage-of-maximum-yield figures larger than 89 were not used, since the yield increase was not significantly different from the untreated soil.   If percentage-yield figures between 89 and 98 are included, the logarithmic relationship, log $(A-y)$, shows the best fit of the data plotted against 'A' values; however, the accuracy in measurement in this range is very poor.   The linear relationship between percentage of maximum yield and 'A' values within the range of values indicated previously appears to fit the data equally as well as a curvilinear relationship.

From a practical standpoint, the prediction from 'A' value as to whether or not a yield response may be expected meets most of the requirements of a test to determine phosphate-fertility levels.   The prediction from 'A' values of the percentage of maximum yield is a further refinement, which may be satisfactory on a limited group of soils; but, until the various factors affecting plant growth can be controlled better, any attempt to apply this relationship to a large number of soils will decrease the accuracy of the prediction.   The maximum yield, for example, ranged from 10 to 31 gm. dry weight in experiment 1 under conditions where N, P_2O_5, and K_2O were added in amounts considered to be sufficient for maximum growth.

Field Experiments

Data on crop response to added phosphate in the field were available from 66 locations from experiment 1 and 29 samples from experiments 4 and 5.   The relationship between 'A' value and the percentage of soils responding to phosphate is indicated by the broken line in figure 3.   When the 'A' value was less than 100 pounds P_2O_5 per acre, 85 percent of the soils gave a phosphate response.   None of the soils gave a phosphate response when the 'A' value was above 150 pounds P_2O_5 per acre, if a response for both field and greenhouse experiments were taken as a criterion of response.   Actually, there

were 3 dryland wheat soils from Canada and 2 from Washington on which a field response but no response in the greenhouse was obtained. Four other soils from various locations also fell in this category.

Comparing soils from the field and greenhouse experiments, a response to phosphate was measurable in the greenhouse at higher levels of 'A' values than in the field (fig. 3). This result would be expected as a result of the smaller soil volume available to the plant roots in a greenhouse pot compared with field conditions.

MEASUREMENT OF NaHCO₃-SOLUBLE PHOSPHORUS IN RELATION TO YIELD RESPONSE

All the soils responded to added phosphate in the greenhouse and 90 percent of them in the field when the extractable phosphorus was less than 25 pounds P_2O_5 per acre (fig. 4). When the extractable phosphorus was between 25 and 50 pounds P_2O_5, 90 percent of the soils responded to phosphate in the greenhouse in contrast to only 50 percent in the field. These differences between field and greenhouse response are similar to those noted previously for the 'A' value comparisons in figure 3, and probably they are the result of the same effects.
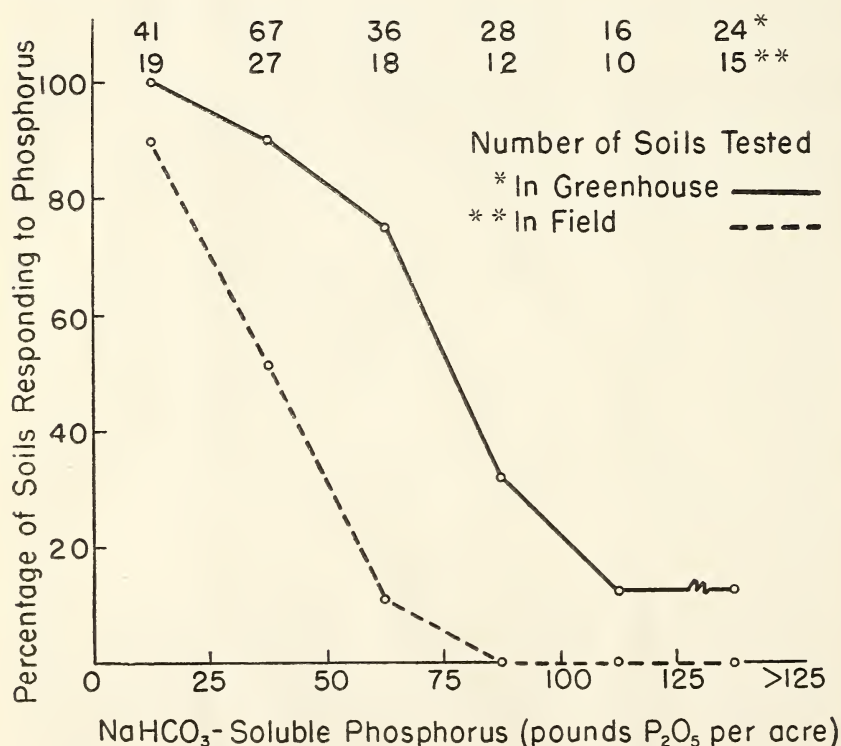

FIGURE 4.—Relationship between NaHCO₃-soluble phosphorus and the percentage of soils responding to phosphate in field and greenhouse experiments. The soils are the same as those compared in figure 3.

A similar comparison between field and greenhouse response was reported by Jenny and coworkers (15) for the relationship between the percentage of maximum yield of lettuce in pots and the number of field tests responding to phosphate. Most of the field tests responded to phosphate when the percentage of maximum yield of lettuce was less than 20 percent. When the percentage of maximum yield of lettuce was 40 percent or more, only a small percentage of the field tests responded to phosphate.

The average value of $NaHCO_3$-soluble phosphorus for the 33 soils showing a phosphate response in the field (fig. 4) was 26 pounds P_2O_5 per acre. The values ranged from 15 to 53 pounds P_2O_5 per acre. The average 'A' value for these same soils was 80 pounds P_2O_5 per acre, with a range of 45 to 137.

CORRELATION OF 'A' VALUES WITH VARIOUS METHODS

The amount of phosphorus extracted by the various methods was correlated with 'A' values for six groups of soils (table 5), although not all of the methods were tested for each group. The $NaHCO_3$ method consistently gave a high correlation with 'A' value for all groups of soils, whereas the other methods were either lower than the $NaHCO_3$ method or variably correlated with the different groups of soils. The r^2 values for the 74 samples in experiment 1 were 0.882, 0.562, and 0.059 for the $NaHCO_3$, Bray, and CO_2 methods, respectively. This comparison supplies convincing evidence of the close relationship between 'A' values and $NaHCO_3$-soluble phosphorus for a group of soils containing both acid and calcareous types.

TABLE 5.—*Correlations between the amount of phosphorus extracted by various methods and 'A' values in 6 experiments*

Method	Correlation coefficient (r) for experiment—					
	1	2	3	4	5	6
$NaHCO_3$_____	0. 939	0. 903	0. 874	0. 936	0. 935	0. 866
Bray [1]_____	. 750	. 940	. 802	. 903	. 898	--------
H_2O_____	--------	--------	. 716	. 965	. 837	. 751
CO_2_____	. 243	--------	. 628	. 881	. 774	. 638

[1] Extracting solution is 0.025 N HCl plus 0.03 N NH_4F.

A further breakdown of the 74 soils based on their cation exchange–anion exchange (C/A) ratios is possible. According to Mehlich (20) the C/A is a qualitative measure for distinguishing between clay minerals of the 2:1 and 1:1 lattice types. When the C/A is greater than 2 or less than 1, the clay minerals are predominately 2:1 and 1:1, respectively. Previous experience with soil-test methods has led to the view that a given method is suitable only to soils with similar chemical and physical properties; however, when such separations into categories are made, the usual basis is the presence or absence of calcium carbonate.

The CO_2 method differs in its relationship to 'A' values as the C/A changes, but the $NaHCO_3$, Bray, and Truog methods are not appreciably affected (table 6). The $NaHCO_3$ method shows the highest correlation with 'A' value for all three groups of soils separated according to C/A ratios.

The main objective of a soil test for available phosphorus is to estimate the phosphorus-fertility level. Assuming that the 'A' value
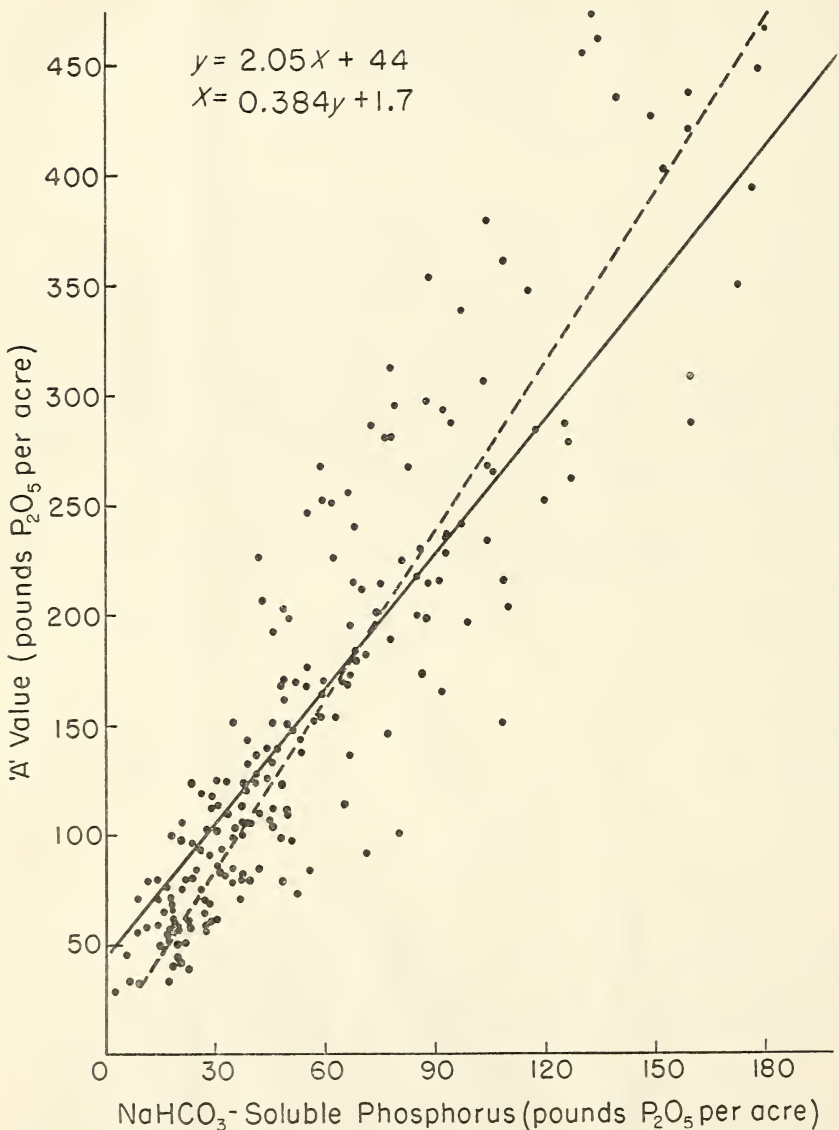

FIGURE 5.—Relationship between $NaHCO_3$-soluble phosphorus and 'A' values.

is a measure of the phosphorus-fertility level in a soil, the accuracy with which 'A' values may be predicted from $NaHCO_3$-soluble phosphorus can be determined from the regression line relating these two variables.   The relationship between these 2 values for 212 samples (samples with 'A' values larger than 450 are not shown in the graph, but they are included in the regression equation) for the first 5 greenhouse experiments, is shown in figure 5.   The correlation coefficient was 0.887 for the combined 212 samples.   The equation of the regression line minimizing the Y components of deviation is $Y = 2.05X + 44$, and the standard error of the estimate is ± 69 pounds P_2O_5 per acre. The equation for the regression of $NaHCO_3$ values on 'A' values is $X = 0.384Y + 1.7$.

TABLE 6.—*Effect of cation exchange–anion exchange ratios on the relationship between the amount of soluble phosphorus and 'A' values on 74 soils, experiment 1*

Cation–anion exchange ratio	Number of soils	Correlation coefficient (r) for method[1] —			
		CO_2	Truog	Bray	$NaHCO_3$
C/A, <1:1_____	16	0. 096	0. 661	0. 772	0. 917
C/A, 1:1 to 2:0_____	19	. 297	. 553	. 798	. 954
C/A, >2:1_____	39	. 463	. 694	. 763	. 953
	74	. 243	. 548	. 750	. 939

[1] Correlations for the CO_2 and Bray methods were supplied through the courtesy of J. W. Fitts; C/A ratios were determined by A. Mehlich.

More than 94 percent of the soils on which the plants responded to phosphate in the greenhouse have 'A' values less than 250 (fig. 3), so the major interest in 'A' values will be in this range.   In addition, the error of measurement for 'A' values is larger for the high than for the low values.   An error estimate for 'A' values from $NaHCO_3$ values based on a wide range of 'A' values would be too high for the low and too low for the high ranges of measurements.   Therefore, the error of estimate for predicting 'A' values from $NaHCO_3$ soluble phosphorus was determined from the number of soils showing 'A' values less than 250 as well as for the total number of comparisons. This equation, $Y = 1.7X + 45$, is calculated from the 159 comparisons where the 'A' value is less than 250.   The standard error of the estimate is ± 30 pounds P_2O_5 per acre.

DISCUSSION

A useful chemical extractant for plant available phosphorus ('A') in soils will (1) measure all or a definite proportion of the various forms of phosphorus in the same relative amounts as they are absorbed by plants during the growing season, (2) correlate to a high degree with plant uptake of phosphorus and yield response to added phosphorus over a wide range of soil types, (3) minimize the secondary

precipitation and adsorption reactions that may occur during the extraction, and (4) be adaptable to rapid, routine-test procedures.

Some of the currently used soil tests for phosphorus satisfy requirements (3) and (4) but fall short in varying degrees for (1) and (2). The chief incentive to develop a better test is the failure of a given method to apply to a wide variety of soils. If the limits of soil conditions and plant growth under which a given test works are known, satisfactory results may be expected, but too often these limitations are not adequately defined. The large number of soil-test methods used by various agencies not only indicates that each test will apply to a limited range of soils but also strongly implies a lack of agreement as to which test is best for a given group of soils with similar chemical and physical properties.

In this study attempts were made to find a chemical extractant that measured not only a definite proportion of the various forms of phosphorus available to plants but also minimized the secondary precipitation reactions occurring during the extraction process. The data presented indicate that the two major mechanisms of the extraction process are: (1) Calcium phosphates increase in solubility in $NaHCO_3$ at pH 8.5, as a result of the repression of the Ca^{++} activity (common ion effect of $CO_3^=$ ions in the presence of solid phase $CaCO_3$); and (2) the HCO_3^-, $CO_3^=$, and OH^- ions replace phosphate ions on the surface of the soil particles. The phosphorus available to plants is considered to be derived chiefly from various forms of calcium phosphates and from the phosphorus on the surface of soil particles that readily exchanges with P^{32} in the soil solution. Probably a large proportion of the calcium phosphates available to plants is also present on the surface of the soil particles (21).

Acid extractants, such as CO_2, weak organic acids, or mineral acids, are likely to be affected by secondary reactions on calcareous soils, whereas the $NaHCO_3$ method is essentially free from secondary reactions. To illustrate this difference, a calcareous soil-water system saturated with CO_2 will show a pH near 6.1 (27) if the $CaCO_3$ is in excess. When the soil-to-water ratio is 1:10 the $CaCO_3$ content must exceed 0.9 percent to be in excess, if the system is in equilibrium with 1 atmosphere of CO_2. If the $CaCO_3$ content of the soil is less than 0.9 percent, all of the $CaCO_3$ will dissolve and the pH will decrease below 6.1. As a result, the extractions will not be made at the same pH, but will depend on the $CaCO_3$ content of the soil. The pH of the $NaHCO_3$ solution does not change when shaken with soil. These effects, in addition to those noted previously under the heading "Theoretical Basis," page 2, probably contribute to the lower correlation values found between CO_2-soluble phosphorus and 'A' values.

Evidently the Bray method is less subject on calcareous soils to interfering secondary reactions than the CO_2 method. This difference is probably accounted for by the short extraction period used in the Bray procedure rather than by any essential differences in the chemical reactions involved. The extraction period is 5 minutes for the Bray procedure compared with 20 to 30 minutes for the CO_2 method. According to Burd (5) a short extraction period reduces secondary precipitation reactions of calcium phosphates in calcareous soils.

The lower correlation values (table 5) for the Bray method compared to $NaHCO_3$ on the calcareous soils are associated with a tendency for the Bray method to give low values for extractable phosphorus on soils high in $CaCO_3$.

Water-soluble phosphate has been used in California with considerable success as an indicator of crop response (2, 19). In this study the water-soluble phosphate gave a higher correlation with 'A' values than $NaHCO_3$ in one experiment, but a considerably lower correlation than $NaHCO_3$ in three other experiments. The data indicate that the water-soluble phosphate tends to give lower correlations with 'A' values as the number of soil types compared increases.

RECOMMENDATIONS

The level of phosphorus soluble in $NaHCO_3$, at which most of the soils respond to applied phosphate, is lower for the field than for the greenhouse experiments (fig. 4). Based on field experiments, using a 1:20 soil-to-solution ratio, the relationship between expected yield response to applied phosphate and the level of $NaHCO_3$-soluble phosphorus is as follows: Below 25 pounds P_2O_5 per acre, a response; 25 to 50 pounds, a probable response; above 50 pounds, a response unlikely. These values were obtained from experiments using wheat, oats, and alfalfa. The values may be expected to apply also for crops with similar phosphorus requirements, but the values may need to be lower for corn and higher for potatoes.

SUMMARY

A new method for extracting soil phosphorus with 0.5 molar solutions of $NaHCO_3$ at pH 8.5 is described. The method is adaptable to rapid, routine, soil-testing procedures.

A theoretical basis for development of the method is described. The extraction mechanism is based on the increased solubility of calcium phosphates as a result of lowering the Ca^{++} activity in solution. Also, the $NaHCO_3$ extracts about one-half of the amount of phosphorus on the surface of soil particles, which readily exchanges with P^{32} in the soil solution.

Secondary precipitation and adsorption reactions are greatly minimized in the $NaHCO_3$ extractions.

Evaluation of the method is based on 212 soil samples from greenhouse and 95 soil samples from field experiments. The relationships between yield response of crops to phosphate and 'A' values determined in the greenhouse experiments are indicated.

The $NaHCO_3$ method was compared with the Bray, Truog, water-soluble, and CO_2-soluble phosphorus methods by means of correlation analysis with 'A' values from six experiments. The $NaHCO_3$ method gave the highest correlations with 'A' values with two exceptions— one compared to the Bray and one compared to the water-soluble methods.

Recommendations are given concerning the relation of the expected crop response in the field to the level of phosphorus soluble in $NaHCO_3$.

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