

EVALUATION OF PHOSPHORUS EXTRACTED BY ROUTINE
LABORATORY PROCEDURES FROM ARIZONA SOILS

by

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A Thesis Submitted to the Faculty of the
DEPARTMENT OF SOILS, WATER, AND ENGINEERING
In Partial Fulfillment of the Requirements
For the Degree of
MASTER OF SCIENCE
WITH A MAJOR IN AGRICULTURAL CHEMISTRY AND SOILS
In the Graduate College
THE UNIVERSITY OF ARIZONA

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ACKNOWLEDGMENTS

The author wishes to express his gratitude and sincere appreciation to his major professor, Dr. T. C. Tucker, for his assistance in the development and fulfillment of this project. The author also wishes to acknowledge Dr. G. V. Johnson for his engaging discussions and advice.

Special appreciation is extended to the University of Arizona Soil and Water Testing Laboratory for the use of their soil samples and the information which was available on them.

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ABSTRACT

Two hundred thirty alkaline calcareous soil samples from twelve counties in Arizona were selected from the University of Arizona Soil and Water Testing Laboratory. Selection was made on the basis that the soil samples received by the Laboratory represented a diverse range in physical and chemical properties and because of the information which was available on these soils.

Statistical analyses were made on the data to evaluate the degree of association between amounts of phosphorus extracted by the carbon dioxide and sodium bicarbonate method. The correlation between these two procedures was not high ($r = .706$). First and second order partial correlations between carbon dioxide and sodium bicarbonate extracted phosphorus while controlling for variables of saturated paste pH, calcium carbonate equivalent, either separately or together, did not improve the degree of association.

INTRODUCTION

Soil tests have been used for many years to aid in the evaluation of the soil's plant nutrient supplying power and in determining fertilizer needs. A survey of the literature shows that numerous chemical methods and their subsequent modifications have been developed and thoroughly investigated for measuring the phosphorus status in agricultural soils. Despite these efforts, there still exists considerable uncertainty in the application of the various phosphorus tests for soils with varying properties.

For phosphorus, no single chemical soil extraction has been found to be universally suitable for determining an availability index for all soil and crop combinations. Several methods are currently used in the United States. For the sake of uniformity in similar agricultural regions, some of these techniques have been discarded in favor of equal or better methods of evaluation. A reduction in the number of phosphorus extraction methods would be beneficial, providing the reduction does not result in a decrease in the accuracy to predict a soil's fertility status. Uniformity would benefit those concerned with laboratory operations and soil test interpretations. Also, the growers who make use of the tests and fertilizer recommendations would benefit.

The purpose of this investigation was to evaluate the association of two chemical methods for extracting phosphate from alkaline calcareous soils and the affect of soil pH and calcium carbonate on that association.

The methods employed were the extraction with carbon dioxide saturated water and the extraction with buffered sodium bicarbonate solution.

Both methods have been used in Arizona. The latter which was developed primarily for use on alkaline and calcareous soils is currently used extensively in the western United States. The extraction of phosphorus with carbon dioxide saturated water is one of several methods presently used in the state of Arizona.

LITERATURE REVIEW

Introduction

Nelson, Mehlich, and Winters (1953) have shown in a review of soil tests for available phosphorus, that many methods have been developed and evaluated. Of the methods investigated, some have given good results in limited areas. However, none have proven adequate for all possible soil and crop combinations, due to the vast array of such systems.

Fitts and Nelson (1956) listed the four main objectives of a soil test to be: (1) categorizing soils for the purpose of fertilizer and lime recommendations, (2) predicting the probability of a profitable response for a fertilizer application, (3) evaluating soil productivity, and (4) determining specific soil parameters which may be improved by soil admendment or cultural practices. To meet these objectives, the successful soil test should fulfill the following three criteria as proposed by Bray (1948): (1) the extractant used should extract all or part of the available form(s) of a nutrient from soils with differing properties; (2) measurement of the nutrient extracted should be performed with reasonable speed and accuracy; and, perhaps most important, (3) under varying conditions the amount of nutrient extracted should be well correlated with crop response and growth.

Plants chiefly absorb phosphorus as the orthophosphate ion (Hagen and Hopkins, 1955). In soils the orthophosphate ion is complexed with cations and organic compounds. It has been shown that plants vary

in their ability to attain phosphorus from a particular form (Bray, 1948; Russel, Russel, and Marais, 1957; Noggle and Fried, 1960; Fox and Kacar, 1964). This variation may be attributed to the plants rooting pattern, growth rate, metabolic activity and the total phosphorus requirement of the plant (Nelson et al., 1953).

Phosphorus solubility in calcareous soils has been thoroughly investigated and found to be a function of pH and Ca^{++} activity (Burd and Murphy, 1939; Gardner and Kelly, 1940; Pratt and Thorne, 1948; Stanberry, 1948). The effect of added calcium carbonate on phosphorus solubility in solution has also been investigated (Benne, Perkins, and King, 1936; Cole, Olsen, and Scott, 1953). These studies showed that for calcareous solutions and soils a minimum solubility of phosphate occurs near neutrality. Cole et al. (1953) showed that in the acid range, the phosphate solubility is a function of both H^+ and Ca^{++} activities. For alkaline conditions in the presence of solid phase calcium carbonate, it was found that the Ca^{++} activity controlled phosphate solubility.

Due to the diverse soil-phosphorus-plant relationships, methods for evaluating the available phosphorus status of a soil have usually been developed for a particular area where the soils and cultural practices are similar. Some methods have in common, the objective of evaluating the intensity fraction of soil phosphorus, i.e., the concentration of available forms of phosphorus in the soil solution (Mattingly, 1965). To achieve this goal, investigators have used various types of extractants in their evaluations.

Carbon Dioxide Extraction Method for the
Evaluation of Soil Phosphorus

On the basis that plant roots respire carbon dioxide, Mitscherlich (1930) proposed the use of carbon dioxide saturated water for soil testing. Wrangell (1930) utilized carbon dioxide saturated water to extract phosphorus. In a modified procedure, Dirks and Scheffer (1930) reported using a bicarbonate-carbon dioxide saturated solution for extraction. McGeorge (1939) employed the carbon dioxide method to investigate the availability of phosphates on unproductive Arizona soils.

McGeorge, Buchner, and Breazeale (1935) previously suggested that in calcareous soils, the solvent action of carbon dioxide on phosphorus was a function of pH. It was pointed out, that the H^+ activity must be sufficient to overcome the precipitation of calcium phosphates due to the common ion effect of calcium. Thus, on alkaline calcareous soils, the solubility of phosphate will be governed by two opposing reactions when carbon dioxide gas is bubbled through the soil water suspension. These effects are as follows: (1) an increase in Ca^{++} activity, thus promoting a decrease in phosphate solubility, and (2) a decrease in pH resulting in an increase in phosphate solubility (McGeorge et al., 1935). Puri and Asyhar (1936) reported that as the amount of calcium carbonate is increased, the value for available phosphate is lowered. As the carbon dioxide concentration in the suspension water is increased, the phosphate extracted from calcareous soils increased (McGeorge, 1939). In support of these studies, Pearson (1941), found that a change in phosphate concentration occurs as the

rate of carbon dioxide gas passed through the suspension is increased for a given extraction time. Also, if the soil:water suspension is allowed to set before bubbling with carbon dioxide gas, the amount of extractable phosphate increased. Stanberry (1948) showed that for a calcareous fine sandy loam, both the common ion effect of calcium and the hydrogen ion activity affected phosphorus solubility. He found that for pH 8.5 and 5.8 carbon dioxide saturated suspensions, the phosphorus concentration was higher than those of intermediate pH values. Maximum values of phosphorus solubility were found to be associated with the highest phosphate fertility levels and the longest extraction times.

Sodium Bicarbonate Extraction Method for the
Evaluation of Soil Phosphorus

Olsen, Cole, and Watanabe (1954), using a 0.5 M sodium bicarbonate extracting solution adjusted to pH 8.5, proposed a new method for assessing available soil phosphorus. Since secondary precipitation reactions occur as the H^+ activity is increased in calcareous soils, due to an increase Ca^{++} activity, the authors sought to reduce the effect of the opposing reactions on phosphate solubility. Thus, if the Ca^{++} activity was decreased, secondary precipitation reaction would decrease resulting in an increase in soluble phosphorus. The authors showed that the Ca^{++} activity would be suppressed based on mass-action law calculations for calcite in systems free of salt interactions. Thus, the main effect of sodium bicarbonate in calcareous soil suspension is to decrease the calcium ion activity, resulting in an increased soil phosphorus solubility. These complex interactions of the soil solution result from the numerous simultaneous equilibria that exist among the solution phase ions,

between solution and solid phase ions and between dissolved and free soil gasses. Adams (1974) proposed a set of reactions for a calcareous soil containing gypsum. Figure 1 is a representation of this scheme.

Phosphate solubility was found to be independent of extraction time between 30 and 120 minutes (Olsen et al., 1954). Breland and Sierra (1962) found that phosphorus extracted after 2 to 5 minutes was significantly less than 10, 20, and 30-minute periods. For a continuous and constant shaking rate over an extraction period of 30 minutes, it was found that the amount of extractable phosphorus increased as the temperature increased from 14 to 33 C (Stone, 1971). Consequently, Stone recommended that temperature control should be considered when using the sodium bicarbonate technique. He also found that the effect of shaking rate was not a critical factor in the amount of phosphorus extracted.

Relationships of Carbon Dioxide and Sodium Bicarbonate
Extractable Phosphorus as an Index to
Plant Available Soil Phosphorus

Using the carbon dioxide method, Ensminger and Larson (1944) found a good correlation between extractable phosphorus and crop response on alkaline soils of Idaho. Stanberry (1948) showed that carbon dioxide extracted phosphate from calcareous soils of Washington, correlated well with the Neubauer method (Thornton, 1935). In a comparison of carbon dioxide and sodium bicarbonate as extractants, Tolman, Johnson, and Gaddie (1956) correlated yields of sugar beets with extractable phosphorus for soils of several western states. They found that both methods were adequate, however, the sodium bicarbonate

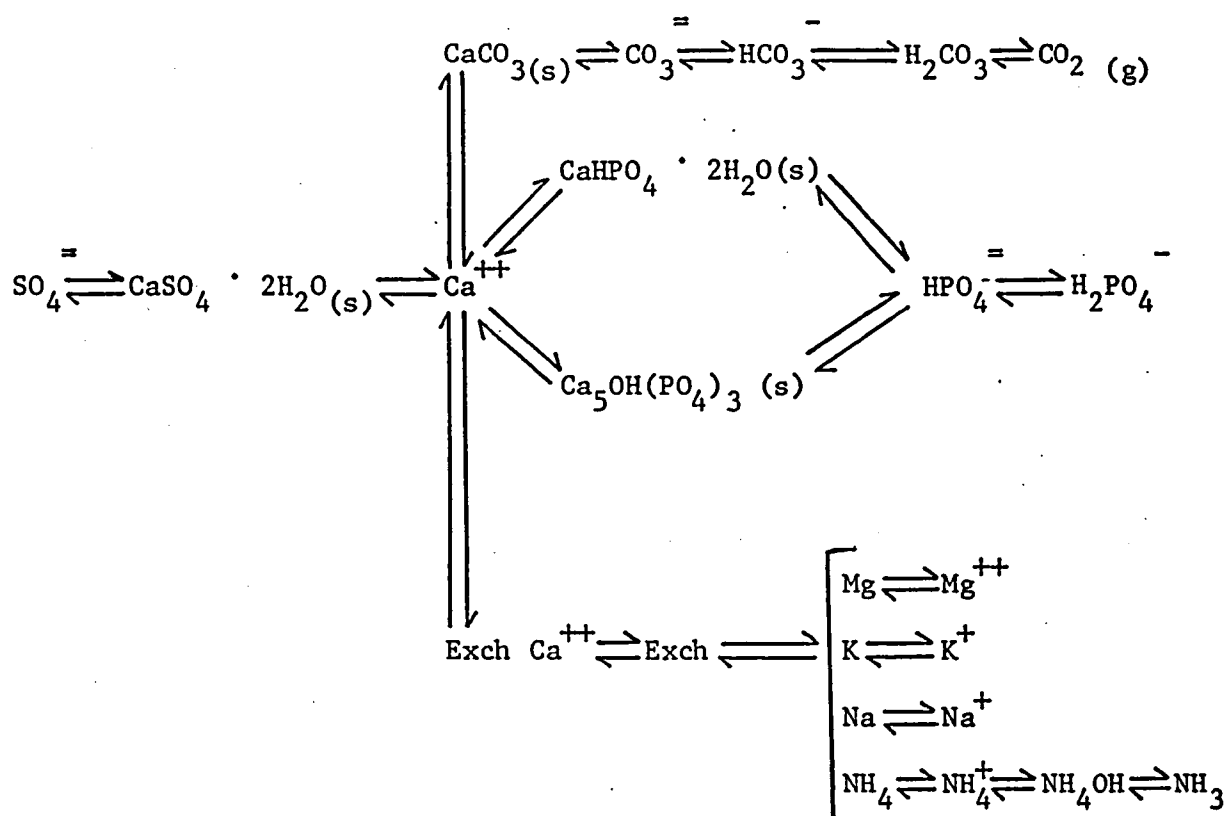


Fig. 1. Calcium equilibria in a calcareous soil containing gypsum.

procedure gave better results over a more diverse range of soils and extracted approximately three times more phosphorus.

Olsen et al. (1954) reported very good correlation between sodium bicarbonate soluble phosphorus and 'A' values, i.e., amount of nutrient available in the soil (Fried and Dean, 1952), for a wide variety of soils and crop conditions. In a study of New Mexico soils it was found that the sodium bicarbonate extraction more favorably correlated with plant uptake than the carbon dioxide extraction (Pack and Gomez, 1956). They also obtained a correlation coefficient (r) of 0.465, significant at the one percent level, between amounts of phosphorus extracted by the two methods. Smith, Ellis, and Grava (1957) obtained significant correlation between sodium bicarbonate extractable phosphorus and crop response on calcareous soils in Kansas. Other investigators have also obtained good correlation between 'A' values and extractable phosphorus by the sodium bicarbonate method (Thompson and Pratt, 1954; Moser, Sutherland, and Black, 1959; Martin and Mikkelsen, 1960).

In Arizona, two in-depth studies have been made comparing extractable phosphorus methods and crop response. Jones (1959) found that uptake of phosphorus and yields of tomato plants were more closely related to carbon dioxide soluble phosphorus than sodium bicarbonate extracted phosphorus. This study was carried out in the greenhouse using 11 different soils. In field studies with cotton and sorghum, a very small degree of association between percent sufficiency for yield and soil phosphorus extracted by the two methods was observed. Jones found a highly significant correlation between amounts of phosphorus extracted by the two methods ($r = 0.565$). More recently, Holanda (1972)

extensively investigated chemical procedures for evaluating available soil phosphorus. From his investigation he found that soil phosphorus extracted by the sodium bicarbonate method significantly correlated with percent yield sufficiency, whereas the carbon dioxide method did not. In his study twelve soils were investigated using tomato plants for yield data. For both methods, extractable phosphate was positively associated with plant yield and phosphate uptake. Using multiple correlation analysis, Holanda suggested that the predictability of methods as indicators of plant response could be improved when various chemical and physical soil parameters are used. A highly significant correlation ($r=0.71$) between extractable phosphate by the carbon dioxide and sodium bicarbonate methods was found by Holanda.

MATERIAL AND METHODS

Soil Analysis

Two hundred and thirty soil samples from twelve counties in Arizona received for analysis by the Soil and Water Testing Laboratory at The University of Arizona, Tucson, were selected for this investigation. The soil samples selected had previously been evaluated for soil pH and carbon dioxide extractable phosphate by the Soil and Water Testing Laboratory. Soil pH was determined on saturated pastes as described by United States Salinity Laboratory Staff (1954) and ranged from pH 7.1 to 9.1. Carbon dioxide extractable phosphate as described by Puri and Asyhar (1936) were determined by the Testing Laboratory and ranged from 0.80 to 207.7 ppm extractable phosphate.

The air-dried soils selected were mixed thoroughly and further analyzed for calcium carbonate equivalent (Allison and Moodie, 1965). Extractable phosphate was also determined by the method of Olsen et al. (1954). The phosphomolybdate blue color was developed in the buffered sodium bicarbonate extracts using the procedure of Murphy and Riley (1962) as modified by Watanabe and Olsen (1965). All measurements of optical density were made with a Bausch and Lomb Spectronic 20 spectrophotometer adjusted to a wavelength of 820 mu.

Statistical Analysis

Simple correlation analyses were used to measure the degree of association between phosphate extracted by the carbon dioxide and sodium

bicarbonate methods. Also, partial correlations were determined for the variable pair, extracted phosphate by carbon dioxide and by sodium bicarbonate, by controlling for the pH variable only, the calcium carbonate equivalent only and for both pH and calcium carbonate equivalent.

RESULTS AND DISCUSSION

Soil Analysis

The analytical values for the soils studied are presented in Table 1. Soil pH varied from 7.1 to 9.1 with a mean value of 7.65. The carbonate content of the soils, expressed as calcium carbonate equivalent, ranged from 0.03 to 16.9 percent with a mean value of 4.07 percent.

Phosphate extracted by the carbon dioxide and sodium bicarbonate methods ranged from 0.26 and 0.6 ppm P to 67.8 and 236.6 ppm P, respectively. These data are presented in Table 1 and are plotted in Figure 2. The sodium bicarbonate method extracted more phosphate than the carbon dioxide method from all but nine of the soil samples (Table 2). For those soils, neither the pH nor the calcium carbonate equivalent values appear to be responsible for the effect. Apparently other soil factors were responsible for the higher values of extracted phosphate obtained by the carbon dioxide method rather than the sodium bicarbonate method in these particular soils.

Statistical Evaluations

Partial correlation coefficients are presented in Table 3 for the four variables studied; calcium carbonate equivalent, pH, and carbon dioxide and sodium bicarbonate extractable phosphate.

A reasonable degree of correlation should be found between the two extraction methods studied if the same chemical forms and/or the same relative proportions of these forms were extracted. Correlations

Table 1. Carbon dioxide and sodium bicarbonate extractable phosphate, calcium carbonate equivalent, and pH of selected Arizona soils.

Soil Sample Number ^a	Phosphate Extraction Method		CaCO ₃ Eq.	Saturated Paste pH
	CO ₂	NaHCO ₃		
	----- ppm P -----		(%)	
1-1	0.7	3.7	3.55	7.7
1-2	1.4	3.3	0.35	8.2
1-3	0.6	3.3	0.30	8.1
1-4	0.3	3.7	0.35	8.3
1-5	1.4	8.8	2.63	8.2
1-6	1.5	4.8	1.43	8.2
1-7	0.6	2.0	0.18	7.6
1-8	0.3	1.8	0.18	7.7
1-9	1.2	7.8	2.63	7.4
1-10	0.8	8.8	7.78	7.2
1-11	1.2	7.4	4.80	8.0
1-12	1.6	7.4	6.45	7.9
1-13	1.6	9.3	3.88	7.8
1-14	1.6	6.4	10.03	7.7
1-15	0.4	14.4	16.90	7.5
1-16	1.5	6.4	4.10	7.7
1-17	1.4	1.6	10.00	8.1
1-18	1.5	4.6	7.83	7.8
1-19	1.1	4.6	2.39	7.9
1-20	0.8	4.0	4.20	7.8
1-26	1.0	3.7	11.18	7.6
1-27	1.6	4.2	6.38	7.8
1-29	0.9	7.6	8.93	7.6
1-32	0.4	0.6	5.90	7.4
1-33	0.4	2.7	5.45	7.3
1-34	0.8	5.3	5.80	7.7
1-35	0.4	9.1	11.18	7.7
1-36	1.2	15.3	6.73	7.9
1-37	0.7	3.7	2.38	7.5
1-38	0.8	3.3	4.58	7.5
1-41	1.4	8.3	3.83	7.4
1-42	1.6	4.6	4.53	7.7
1-43	1.4	2.9	4.40	7.8
1-44	1.6	3.7	4.28	7.5
1-45	1.4	3.1	4.28	7.6
1-46	1.6	4.2	4.80	7.6
1-47	0.9	2.9	4.05	7.7
1-48	1.4	4.2	4.05	7.6
1-49	1.6	6.9	4.35	7.7
1-50	1.5	4.2	7.08	7.7
2-1	2.7	8.8	1.15	8.0

Table 1, Continued. Extractable phosphate, CaCO₃ equivalent, and pH.

Soil Sample Number ^a	Phosphate Extraction Method		CaCO ₃ Eq.	Saturated Paste pH
	CO ₂	NaHCO ₃		
	----- ppm P -----		(%)	
2-2	2.6	11.9	2.25	8.2
2-3	2.2	5.5	0.30	7.6
2-4	1.7	13.0	0.53	7.6
2-5	1.7	2.7	2.60	7.9
2-6	2.4	11.4	0.18	7.6
2-7	2.3	10.1	3.70	7.8
2-8	2.8	7.1	0.75	7.6
2-9	1.8	7.4	1.33	8.0
2-10	2.2	7.8	0.30	7.1
2-11	1.7	8.3	0.18	7.1
2-12	2.6	7.1	0.48	7.7
2-13	2.7	8.8	2.55	8.0
2-14	1.9	4.1	7.30	7.9
2-15	1.7	4.1	3.48	7.9
2-16	2.9	10.3	11.23	7.9
2-17	2.5	5.7	2.43	7.6
2-18	2.6	14.1	3.48	7.6
2-19	2.4	8.1	11.13	9.1
2-20	2.8	83.3	4.40	7.8
2-21	2.5	17.0	3.86	7.7
2-22	3.0	3.3	1.18	7.9
2-23	2.6	4.6	3.30	7.9
2-24	2.6	5.1	2.78	7.9
2-25	2.6	2.2	3.13	7.9
2-26	2.5	3.7	3.30	7.9
2-27	2.5	3.7	3.65	8.0
2-28	2.5	9.8	2.00	7.8
2-29	2.2	2.5	2.15	8.0
2-30	2.1	11.4	10.55	7.8
2-31	2.9	5.5	0.35	7.2
2-32	1.7	5.3	10.03	7.5
2-33	1.8	6.4	4.98	7.6
2-35	2.3	11.9	6.43	7.5
2-36	2.5	3.3	4.40	8.0
2-37	3.2	2.0	0.13	7.6
2-38	2.1	23.6	5.20	7.4
2-39	2.1	9.3	3.30	7.9
2-40	2.4	20.2	5.05	7.8
2-41	2.4	9.3	1.58	7.5
2-42	3.2	6.4	1.90	7.7
2-43	1.9	5.3	3.83	7.7
2-44	2.0	4.6	3.65	7.7

Table 1, Continued. Extractable phosphate, CaCO₃ equivalent, and pH.

Soil Sample Number ^a	Phosphate Extraction Method		CaCO ₃ Eq. ³	Saturated Paste pH
	CO ₂	NaHCO ₃		
	----- ppm P -----		(%)	
2-45	1.7	3.7	4.05	7.7
2-46	1.9	6.0	3.78	7.7
2-47	2.0	6.4	3.43	7.7
2-48	1.7	4.8	3.35	7.6
2-49	1.7	5.5	3.30	7.6
2-50	2.1	5.3	3.53	7.7
3-1	4.2	9.7	1.68	8.1
3-2	4.1	11.9	0.18	8.1
3-3	4.0	34.2	0.30	7.7
3-5	3.5	19.4	0.65	7.4
3-6	3.2	11.6	1.78	7.8
3-7	2.9	8.1	1.40	7.6
3-8	4.7	9.2	0.65	7.8
3-9	4.4	16.8	10.30	8.0
3-10	3.8	20.1	4.50	7.6
3-11	4.3	8.9	3.65	7.9
3-14	3.4	12.5	0.80	7.2
3-15	4.0	10.8	0.80	7.3
3-16	4.7	8.1	5.98	8.0
3-20	3.4	10.8	2.93	7.5
3-21	3.4	9.2	1.13	7.5
3-22	4.5	21.1	6.38	7.5
3-23	3.9	7.1	0.80	7.7
3-24	3.6	34.7	0.53	7.4
3-25	4.1	14.9	0.93	8.0
3-26	4.6	15.2	3.00	7.5
3-27	3.6	13.4	2.40	7.6
3-28	3.7	37.7	5.00	7.8
3-29	4.6	11.4	3.58	7.6
3-30	3.5	14.9	1.93	7.7
3-31	4.1	5.8	1.90	7.3
3-32	3.5	8.9	6.20	7.6
4-1	5.0	23.4	6.78	7.6
4-4	5.0	5.1	0.40	7.9
4-6	5.1	3.9	3.20	7.7
4-7	5.0	19.8	0.53	7.6
4-8	5.6	17.8	10.15	7.7
4-9	5.2	27.7	3.60	7.3
4-10	5.2	9.5	0.28	7.2
4-11	5.3	10.4	1.25	7.1
4-12	4.9	10.8	11.03	8.3

Table 1, Continued. Extractable phosphate, CaCO₃ equivalent, and pH.

Soil Sample Number ^a	Phosphate Extraction Method		CaCO ₃ Eq.	Saturated Paste pH
	CO ₂	NaHCO ₃		
	----- ppm P -----		(%)	
4-13	6.5	31.4	3.20	7.5
4-15	6.3	17.4	5.65	7.6
4-16	6.2	33.0	1.05	7.6
4-17	4.9	30.6	2.05	7.2
4-18	4.9	23.9	4.93	7.8
4-19	5.9	20.4	4.25	7.8
4-20	6.1	20.8	1.05	7.4
4-21	6.0	50.7	5.58	7.5
4-22	5.9	23.9	5.45	7.4
4-23	6.2	31.1	4.45	7.5
4-24	5.5	10.8	9.88	7.5
5-1	7.0	18.7	0.88	8.2
5-2	7.0	20.4	0.33	7.5
5-3	6.7	15.8	2.93	7.8
5-4	7.8	120.4	8.70	7.3
5-5	7.8	81.8	8.58	8.0
5-6	6.7	23.0	0.80	7.3
5-7	7.4	30.7	6.70	7.6
5-8	7.6	25.3	4.13	7.8
5-11	7.4	34.3	1.05	7.4
5-12	6.5	16.6	10.70	7.6
5-13	7.5	21.7	4.85	7.7
5-14	6.9	39.4	1.40	7.2
5-15	7.7	7.9	1.65	7.2
5-16	7.8	28.2	5.63	7.4
5-17	6.9	58.4	6.28	7.5
5-18	6.9	45.5	5.23	7.5
5-19	7.8	32.7	4.75	7.6
5-20	6.5	46.8	5.03	7.6
5-21	6.5	39.4	5.75	7.5
5-22	7.8	13.8	1.30	7.6
6-1	8.4	42.9	5.48	7.7
6-2	9.4	40.1	1.70	7.9
6-5	9.5	77.4	8.68	7.6
6-6	8.9	37.4	10.28	7.7
6-7	9.1	47.3	2.43	7.4
6-13	8.8	77.4	9.60	7.7
6-14	8.6	39.4	0.70	7.1
6-15	9.1	3.0	0.03	7.6
6-16	9.0	3.7	11.05	8.1
6-17	9.1	32.2	0.70	7.7
6-19	8.5	47.3	5.43	7.7

Table 1, Continued. Extractable phosphate, CaCO₃ equivalent, and pH.

Soil Sample Number ^a	Phosphate Extraction Method		CaCO ₃ Eq. ³	Saturated Paste pH
	CO ₂	NaHCO ₃		
	----- ppm P -----		(%)	
6-20	9.5	60.3	4.70	7.7
6-21	9.1	18.0	1.03	7.3
6-22	8.8	48.1	5.35	7.5
6-23	9.5	114.9	6.48	7.5
6-24	9.3	70.0	5.78	7.5
6-25	8.8	29.5	6.20	7.5
6-26	8.8	67.2	5.15	7.5
6-27	8.9	47.5	9.20	7.7
7-3	11.4	12.7	0.30	7.7
7-4	9.8	31.2	8.13	8.1
7-5	10.1	10.3	2.63	8.1
7-6	10.6	25.6	3.35	7.7
7-8	9.8	3.3	11.05	7.5
7-9	10.8	22.9	1.03	7.3
7-10	10.6	117.1	0.50	7.6
7-11	11.1	35.9	0.30	7.3
7-12	10.4	12.7	0.10	7.3
7-13	10.8	26.3	5.30	7.4
7-14	11.1	71.0	5.55	7.7
7-15	10.4	32.7	6.35	7.8
7-16	10.4	61.0	4.65	7.5
7-17	10.8	64.9	2.95	7.4
7-18	10.1	26.3	5.48	7.4
7-19	10.4	68.3	5.88	7.5
7-20	10.1	46.8	5.28	7.5
7-21	10.4	65.6	5.35	7.5
8-1	19.2	47.1	0.70	7.6
8-2	15.2	55.4	0.83	7.6
8-3	14.4	80.2	7.75	7.7
8-4	12.4	38.3	4.15	7.7
8-5	17.6	107.5	8.13	7.7
8-6	13.4	67.5	7.00	7.6
8-7	12.7	66.1	7.73	7.8
8-8	13.4	63.4	5.15	7.7
8-9	13.4	59.4	8.08	7.7
8-10	14.7	68.4	7.15	7.7
8-11	20.2	103.3	7.20	7.7
8-12	12.1	29.1	5.03	7.7
8-13	11.7	48.0	7.00	7.7
8-14	12.7	77.3	9.00	7.6
8-15	30.3	94.2	8.93	7.6

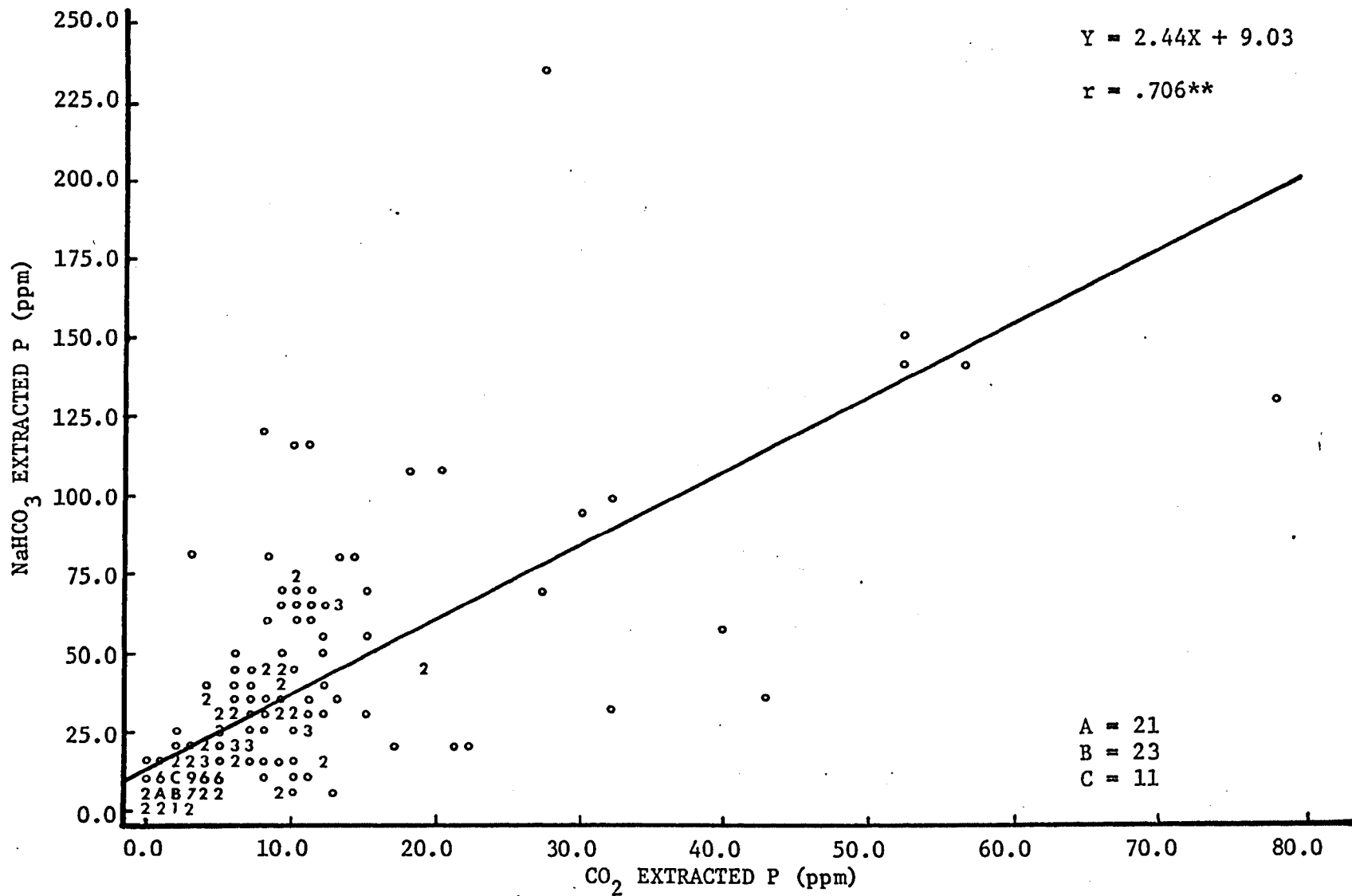


Fig. 2. Scatter diagram for extracted phosphate by the carbon dioxide and sodium bicarbonate method.

Table 2. Carbon dioxide and sodium bicarbonate extractable phosphate, calcium carbonate equivalent, and pH for those soils in which carbon dioxide extractable phosphate was highest.

Soil Sample Number ^a	Phosphate Extraction Method		CaCO ₃ Eq.	Saturated Paste pH
	CO ₂	NaHCO ₃		
	----- ppm P -----		(%)	
2-25	2.6	2.2	3.13	7.9
2-37	3.2	2.0	0.13	7.6
4-6	5.1	3.9	3.20	7.7
6-15	9.1	3.0	0.03	7.6
6-16	9.0	3.7	11.05	8.1
7-8	9.8	3.3	11.05	7.5
8-20	13.1	8.6	0.05	7.4
8-28	32.0	29.2	1.23	7.6
8-38	24.1	18.3	1.03	7.4

^aSoil sample numbers as in Table 1.

Table 3. Partial correlation coefficient for the variables pH, carbon dioxide and sodium bicarbonate extractable phosphate, and calcium carbonate equivalent represented by V_1 , V_2 , V_3 , and V_4 , respectively.

Sample Range ^a	Partial Correlation Coefficients							
	Zero Order					First Order, Variable Pair (V_2, V_3)		Second Order, Variable Pair (V_2, V_3)
	Variable Pair					Controlled Variables		Controlled Variables
	(V_1, V_2)	(V_1, V_3)	(V_2, V_4)	(V_3, V_4)	(V_2, V_3)	V_1	V_4	V_1 and V_4
1	.186	-.034	-.028	.343**	.101	.110	.127	.105
2	.262	-.030	-.105	.110	.165	.180	.180	.219
3	.358	-.065	.322	.053	-.067	-.047	-.089	-.068
4	-.139	-.236	-.056	-.015	.322	.300	.322	.301
5	.007	-.089	.035	.540*	.203	.204	.219	.223
6	.123	-.184	-.061	.291	.315	.346	.348	.459
7	-.301	-.091	-.642**	-.113	.177	.157	.137	.128
8	.095	.027	-.324*	.381*	.558**	.557**	.778**	.812**
1-8	-.156*	-.200**	-.084	.171**	.706**	.697**	.773**	.727**

^aSample range indicates range of carbon dioxide extracted phosphate as follows:

Sample Range	CO ₂ Extracted Phosphate
	-- ppm PO ₄ --
1	0-5
2	5-10
3	10-15
4	15-20
5	20-25
6	25-30
7	30-35
8	> 35
1-8	> 0

*Significant at the .05 level.

**Significant at the .01 level.

for zero order partials between the two extraction methods were not significant for data grouped into sample ranges except for the highest extractable phosphate range. Ranges were based on amounts of carbon dioxide extractable phosphate. When the data was not grouped, the degree of association ($r=.706$) between the two methods was highly significant for extractable phosphate. The predictability of associating the variance in extractable phosphate by one procedure with the variance of the other procedure based on the coefficient of determination ($r^2=.499$) is 49.9 percent.

For each sample range, the first and second order partial correlations between the variable pair carbon dioxide and sodium bicarbonate extractable phosphate were not significant for all but the highest extractable phosphate group. This highly significant correlation was not improved by adjusting for either pH or calcium carbonate equivalent. For the second order partials, the degree of association between the variable pair was slightly further improved by controlling both the soil pH and calcium carbonate equivalent variables. The first and second order correlations did not improve the degree of association between the variable pair carbon dioxide and sodium bicarbonate extractable phosphate when all data points for all ranges were considered.

On the soils at the Cotton Research Center and the Mesa Experimental Farm in Arizona, Abbott (personal communication, 1974) indicated that a highly significant degree of association ($r=.98$) between extractable phosphate by the carbon dioxide and sodium bicarbonate methods. Although the phosphorus fertility management on

the soils in these two areas has differed, the soils have similar properties. The soils in this study represented a more diverse range in soil properties which may account for the lower degree of association. Zero order partial correlations between calcium carbonate equivalent and each extraction method were significant for only a few of the sample ranges studied. The zero order partial correlations between soil pH and each extraction method for all sample ranges were not significant. Perhaps this may best be explained by examining the action and conditions of the two extraction procedures. The sodium bicarbonate method employs a pH 8.5 buffered extractant to soil ratio of 20:1. Any effect the soils studied would have on the suspension pH would be negligible, thus the effect of soil pH would not appreciably affect the amount of phosphate extracted. Since the extracting solution is 0.5 M sodium bicarbonate, the common ion effect between the phosphate and calcium ion is reduced. The influence of calcium ion activity is reduced due to an increase in bicarbonate which results in precipitation of calcium in the carbonate form (Olsen et al., 1954). Since the common ion effect would be reduced, differences in soil calcium carbonate content would not be expected to have an appreciable effect on the amount of phosphate extracted by the sodium bicarbonate method. The action of carbon dioxide as an extractant is considerably more complex. As carbon dioxide gas is bubbled through the soil suspension, carbonic acid is produced. Since soils vary in their buffering capacity (Bradfield, 1941), the effect of the carbonic acid produced will differ. As the pH is decreased in alkaline calcareous soils due to an increase in carbonic acid, the phosphate solubility will tend to increase. However, the

increased carbonic acid results in an increase in calcium ion activity causing a decrease in phosphate solubility due to the common ion effect (Stanberry, 1948; Olsen et al., 1954). Thus, due to variation in soil buffering capacities, different soils will vary in soil suspension pH and calcium ion activity as they approach equilibrium for a given extraction time and temperature. Therefore, significant correlations between soil pH or calcium carbonate equivalent and either sodium bicarbonate or carbon dioxide extracted phosphorus would not necessarily result.

The likelihood of significant correlations between extractable phosphate and plant response on growth on alkaline calcareous soils would appear to be favored using the sodium bicarbonate method. The variability of the pH and calcium ion activity in the suspensions of the sodium bicarbonate extractions would be appreciably minimized as compared to the carbon dioxide extraction suspensions. By minimizing the effect of pH and calcium ion activity, the sodium bicarbonate would be expected to extract the same forms or relative proportions of phosphate from different soils. Thus, upon correlation with a yield response function, the phosphate extracted from different soils should represent similar indexes of availability.

SUMMARY

To evaluate the merits of one phosphorus extraction method over another, it is necessary to correlate the amount of phosphorus extracted with crop response and growth. Correlations between percent yield sufficiency and carbon dioxide or sodium bicarbonate extracted phosphorus for greenhouse conditions for Arizona soils have not been good (Jones, 1959; Holanda, 1972). For the diverse range of alkaline calcareous Arizona soils in this study, the degree of association of amounts of extractable phosphate as determined by these two methods were not well correlated. This suggests that these methods extract different forms of phosphorus and/or relative proportions of these forms. The degree of association was not improved appreciably by controlling the variables of saturated paste pH, calcium carbonate equivalent, or both. To better evaluate the validity of either method more research data are needed from field experiments on a large number of soils with varying properties. If either carbon dioxide soluble or sodium bicarbonate extractable phosphate values better correlate with a yield response function, the results of this study indicate the other method would not correlate similarly.

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