

PROCEDURAL EFFECTS ON NaHCO_3 EXTRACTABLE SOIL P¹

D. T. Westermann and R. S. Ehlers²

INTRODUCTION

Fertilization practices for optimum crop production will partially depend upon reliable and accurate soil test results. A number of soil test procedures have been developed and calibrated for most plant nutrients. Among them is the NaHCO_3 procedure for estimating plant available soil P. This procedure was first³ published by Olsen and coworkers in 1954, and is widely accepted and used in the U.S. and other countries, especially for neutral and calcareous soils.

An effort to standardize soil testing procedures and reporting units was initiated by a Soil and Plant Testing Workgroup, sponsored by the PNWPF Association, in 1968 with a sample exchange program (James, 1986). There has been a significant improvement in reported soil test results among the active laboratories since this project was started. No attempt is being made by this Workgroup to standardize the recommendations made by the individual laboratories.

Significant sources of variability in reported soil test results could include (a) sampling problems, both in the field and in the laboratory, (b) different sample preparation methods, (c) laboratory errors, (d) individual laboratory modifications of specific methods, and (e) the natural population variance. The objective of this report is to evaluate the effect of selected procedural modifications on NaHCO_3 extractable soil P. The modifications were in (1) extracting conditions, (2) NaHCO_3 solution characteristics, and (3) colorimetric procedure.

METHODS AND MATERIALS

The general procedure used for NaHCO_3 extractable soil P is published elsewhere (Olsen and Sommers, 1982). The specific procedure we used is as follows:

1. Add 100 ml of 0.5 M NaHCO_3 , pH 8.5, to 5 g air-dried soil with approximately 1-g carbon black³ (natural gas furnace processed) added in a 125 ml, wide-mouthed, polyethylene bottle.
2. Shake 30 min on a reciprocating shaker, oscillating at about 140 cycles per minute in a constant temperature room ($70^\circ\text{F}/22^\circ\text{C}$).
3. Immediately filter through Whatman 42 filter paper.
4. To a 5 ml aliquot of the filtrate add 5 ml of 0.5 N H_2SO_4 , degas by shaking under vacuum.
5. Add 11 ml of distilled water and 4 ml of a freshly prepared Murphy-Riley ascorbic acid solution (Murphy and Riley, 1962), and mix.
6. Determine P concentration after 30 min with a spectrophotometer at a wavelength of 815 m μ .

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²Soil Scientist and Biological Technician, respectively. USDA-ARS, Snake River Conservation Research Center, Kimberly, Idaho 83341.

Some precautions in using the ascorbic acid molybdate solution are discussed by Watanabe and Olsen (1965). The NaHCO_3 extracting solution should be kept at the same temperature as that during the actual extraction process.

Six Portneuf silt loam soil samples were obtained from a residual P experiment at Kimberly, Idaho, air-dried at 90°F (32°C), crushed to pass a 2 mm sieve, and stored in plastic bags until sampled for analysis. These soil samples were non-saline, non-sodic, and contain between 3 and 15% acid-equivalent CaCO_3 , and between 5 and $43 \mu\text{g/g}$ (ppm) NaHCO_3 extractable P. Two internal reference soil samples (Portneuf) were also used for selected parts of this study. An additional 26 soil samples, representing soils found in the Pacific Northwest, were used for evaluating the effect of carbon black.

RESULTS AND DISCUSSION

Extracting Conditions

The NaHCO_3 extractable P increased linearly with shaking time up to 120 min (Fig. 1). Extension of the shaking time to 16 hr for the 1:100 dilution ratio increased the extractable P to 16 and $80 \mu\text{g/g}$ for soils 4 and 6, respectively. The slope of the increase was almost 8-fold greater for the soil with the greater extractable P concentration. This indicates that the absolute time effect is dependent upon the relative P concentration. The P concentration would be $742 \mu\text{g/g}$ (0.023 M) if complete equilibrium was achieved between hydroxyapatite and the NaHCO_3 solution (Lindsay, 1979). The NaHCO_3 solution is thought to extract primarily surface sorbed P (Olsen et al., 1954).

The P extracted increased curvilinearly (Fig. 1) as the dilution ratio increased from 10 to 100, with the larger increase occurring in the soil with the highest P concentration. The effect of dilution ratio on extractable P was not affected by shaking time.

A 30 min delay in filtering, after 30 min shaking, increased the P extracted an average of 9% (Fig. 2) across all six soil samples. This was nearly equivalent to an additional 30 min shaking time (Fig. 1 vs. Fig. 2).

The P extracted by NaHCO_3 in 30 min increased linearly as the extraction temperature increased from 45°F to 95°F ($7-35^\circ\text{C}$). This temperature effect (slope) was greater as the relative extractable P concentration increased. The slope of the temperature effect for eight soils was plotted against the P extracted at a standard temperature (Fig. 3). This relationship shows that about 0.94% more P would be extracted with each degree ($^\circ\text{F}$) increase between 45 and 95°F . This extraction temperature effect was also reported by Olsen et al. (1954).

Subsamples from bulk soils 4 and 6 were ground to pass a 0.5 mm sieve. The samples (0.5 and 2 mm) were then extracted with NaHCO_3 at two shaking speeds. The fast speed was about 140 cycles per minute, while the slow speed was about 60 cycles per minute, barely enough to keep the soil particles in suspension. Neither soil particle size nor shaking speed significantly affected the extractable P on the low P soil (Table 1). Shaking speed had no effect on the high P soil but the extractable P was significantly increased by the smaller particle size. This effect could be due to a greater surface area or to greater dissolution rate of the smaller particle sizes by the NaHCO_3 .

NaHCO_3 Solution Characteristics

The solubility of P minerals in soils is pH dependent. The recommended pH of the NaHCO_3 solution is 8.5. A bulk NaHCO_3 solution prepared in advance should be covered with mineral oil to prevent CO_2 loss and be stored in a polyethylene container (Olsen and Sommers, 1982). The extractable P did not change by increasing the NaHCO_3 pH from 8.0 to 8.5, but did significantly increase when the extractant solution was pH 9.0 (Table 2). This might have occurred because

Ca^{++} activity decreases when the pH is above 8.3 (Lindsay, 1979).

The effect of the molality of NaHCO_3 (pH 8.5) on extractable P is shown in Table 3. Generally there was only a small extractable P increase as the NaHCO_3 concentration increased from 0.4 to 0.5 M, but was significantly increased by the 0.6 M solution in three of six soils.

Colorimetric Procedure

The Mo blue methods for determining P concentrations are based on the principle that a phosphomolybdate complex forms in an acid solution that can be reduced to a blue color by ascorbic acid, SnCl_2 , or some other reducing agent. The intensity of the blue color is affected by P concentration, acidity, arsenates, silicates, and other substances that influence the formation of the phosphomolybdate complex and the oxidation-reduction conditions (Jackson, 1958).

It is recommended that the Murphy-Riley ascorbic acid solution be prepared as required as it is generally not stable for more than 24 hr. We measured P concentrations with freshly prepared and 24 hr old ascorbic acid solutions and found no significant differences. The ascorbic acid solution was stored at our laboratory temperatures ($65-80^\circ\text{F}$) for the 24 hr interval. Its deterioration is probably temperature and light dependent.

The effect of acidification on the formation of the blue complex was evaluated by adjusting the pH of the NaHCO_3 aliquot from 8.5 to 1.0 before adding the ascorbic acid solution. This pH range³ had no effect on the P concentrations determined in the soil extracts used in this study. The color development was generally slower as the pH varied either way from 5.0. Silicate interferences and the hydrolysis of organic P compounds to inorganic orthophosphates may be significant in acidic solutions ($\text{pH} < 1.0$).

The NaHCO_3 extract may contain sufficient soluble organic compounds to interfere with³ the P analysis. This interference is corrected by adding carbon black to the extracting bottles prior to shaking. Watanabe and Olsen (1969) found no interferences from soluble organic compounds when using the Murphy-Riley ascorbic acid reagent. This hypothesis was tested on 32 soils from the Pacific Northwest (Fig. 4). In general, about 4% more extractable P was obtained when carbon black was used in the extraction process. A statistical analysis (t-test on the 32 paired soil samples) showed that this was not a significant difference. No P was extracted by the NaHCO_3 solution from the carbon black material itself. Some organic coloring was present in some of the soil extracts after filtering without carbon black but it generally did not contribute to any additional absorption at the wavelengths used for the Murphy-Riley ascorbic acid procedure. Maximum sensitivities for measuring the blue color complex occur at two wavelengths, 710 and 910 $\text{m}\mu$.

CONCLUSIONS

The NaHCO_3 method is widely used as an index of available P in calcareous and neutral soils. The relationship between the P extracted and expected yield responses to P fertilization are well established for most major U.S. crops. In addition, high correlations are generally found between extractable P and plant P uptake.

Major sources of variability found by this study would be the extraction temperature, and contact or extraction time. A 10°F difference caused a 9-10% difference in extractable P concentrations. Contact time after shaking was almost as important as shaking time. Shaking speed and soil particle size may have significant effects for certain soils (Rovira and Stace, 1970). Sodium bicarbonate pH differences would generally not be significant in laboratories using the procedure on a daily basis. Comparison of the P concentrations extracted from two internal soil standards over time showed that a high degree of reproducibility is possible with this procedure ($s_{\bar{x}} = 0.4$).

LITERATURE CITED

1. Jackson, M. L. 1958. Soil chemical analysis. Prentice-Hall, Inc., Englewood Cliffs, NJ.
2. James, D. W. 1986. Soil test P availability within and between laboratories. Abstracts Western Phosphate Conference. Moscow, ID. 20-21 March, 1986.
3. Lindsay, W. L. 1979. Chemical Equilibria in Soils. John Wiley & Sons, NY, pp. 163-209.
4. Murphy, J. and J. P. Riley. 1962. A modified single solution method for the determination of phosphate in natural waters. Anal. Chim. Acta. 27:31-36.
5. Olsen, S. R., C. V. Cole, F. S. Watanabe, and L. A. Dean. 1954. Estimation of available phosphorus in soils by extraction with sodium bicarbonate. USDA Circ. 939.
6. Olsen, S. R., and L. E. Sommers. 1982. Phosphorus. in C. A. Black et al. (Ed.) Methods of Soil Chemical Analysis, Part 2, Agronomy 9:403-430. Am. Soc. Agron., Inc., Madison, WI.
7. Rovira, A. D., and H. C. T. Stace. 1970. Effect of particle size on bicarbonate-extractable phosphate in a sandy Terra Rossa soil. J. Aust. Inst. Agr. Sci. 36:292-293.
8. Watanabe, F. S., and S. R. Olsen. 1965. Test of an ascorbic acid method for determining phosphorus in water and NaHCO_3 extracts from soil. Soil Sci. Soc. Am. Proc. 29:677-678.

Table 1. Soil particle sizes and shaking speed on NaHCO_3 -P (Portneuf silt loam).

Soil Particle Size	Shaking Speed	Soil No.	
		4	6
		Extractable P	
		- $\mu\text{g/g}$ -	
<0.5 mm	Slow	6.9a	46.2c
	Fast	7.1a	45.8c
< 2 mm	Slow	6.9a	40.7d
	Fast	7.2a	42.3d

Means within a soil followed by the same letter are not significantly different at the 5% level.

Table 2. NaHCO_3 pH effect on extractable P

Soil	pH		
	8.0	8.5	9.0
----- $\mu\text{g P/g}$ -----			
4	7.0a	7.0a	8.1b
6	43.1c	41.7c	48.0d

Means within a soil followed by the same letter are not significantly different at the 5% level.

Table 3. NaHCO_3 molality effect on extractable P

NaHCO_3 Molality	Soil No.					
	1	2	3	4	5	6
----- $\mu\text{g P/g}$ -----						
0.4	4.3a	10.4b	36.2d	6.3f	18.6g	39.8h
0.5	4.8a	11.4bc	39.0d	6.6f	20.1g	39.8h
0.6	5.7a	14.2c	43.0e	8.1f	21.4g	44.5i

Means within a soil followed by the same letter are not significantly different at the 5% level.

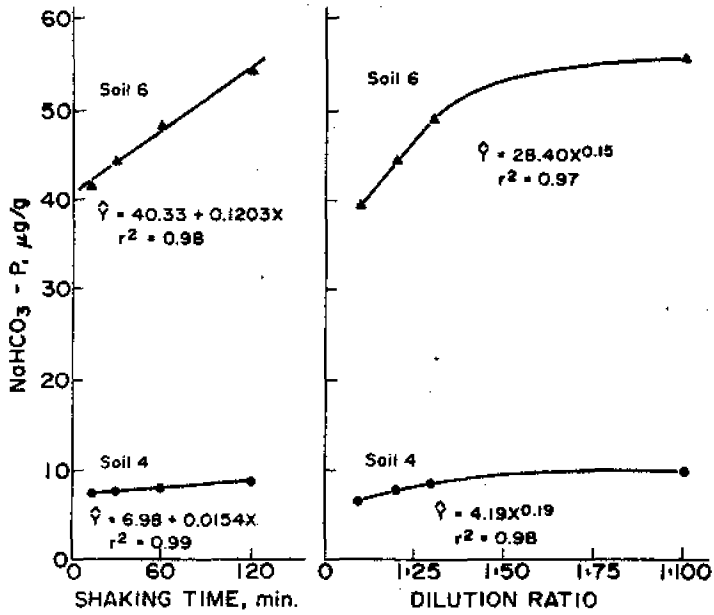


Fig. 1. Effect of shaking time and dilution ratio on P extracted by NaHCO₃.

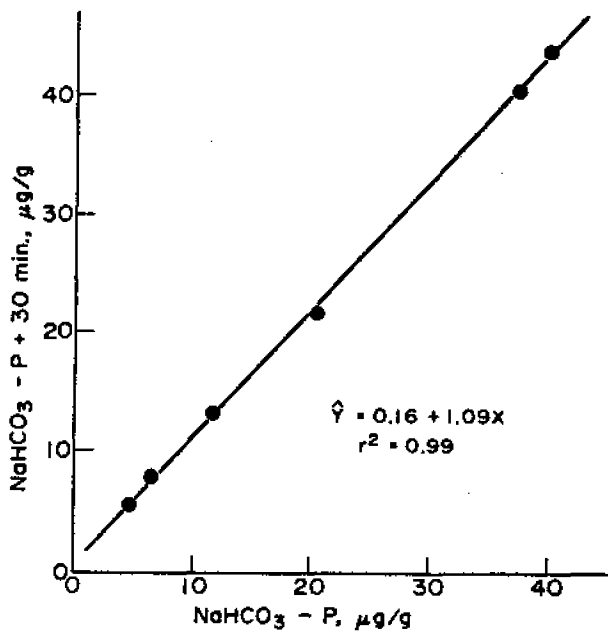


Fig. 2. Effect of an additional 30 min contact time after 30 min shaking time on NaHCO₃ extractable P.

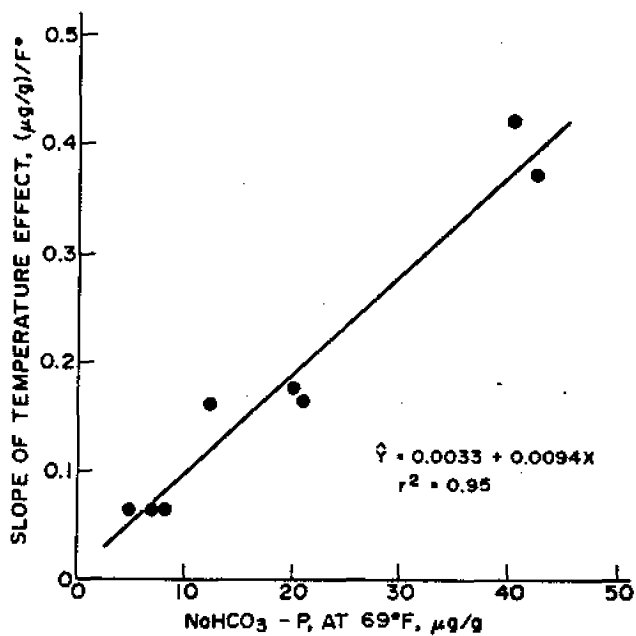


Fig. 3. The relationship between the change in the ratio of P concentration to extraction temperature and the relative NaHCO₃ extractable P concentration.

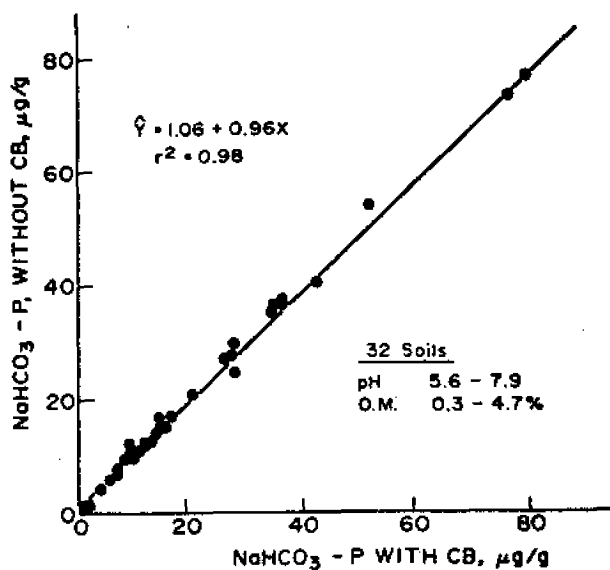


Fig. 4. Effect of carbon black (CB) on NaHCO₃ extractable P.