

Bicarbonate (Olsen) Phosphorus Troubleshooting

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Soil bicarbonate (Olsen) pH is one of the more difficult soil phosphorus analysis methods. The method is based on the use of use of 0.5 N NaHCO_3 adjusted to pH 8.50 using and soil extraction ratio of 1:20. In the process of extraction, CO_2 from bicarbonate is driven off, pH increases and bicarbonate converts to carbonate. Soil calcium activity is reduced as calcium carbonate is formed increasing the quantity of phosphates ($\text{PO}_4\text{-P}$) in the extraction solution.

The amount of soil phosphate extracted is influenced by the pH of the extraction solution, temperature, extraction time and the spectrophotometric measurement. Deviation from the prescribed method for any one of these variables leads to bias in the amount of PO_4 recovered.

Extraction Solution

The 0.5 N NaHCO_3 adjusted to pH 8.50, is unstable and will increase in pH with time. The extractant solution is typically stable for a period of eight hours and will over 48 to 72 hours increase to a pH of 9.0, dependent on laboratory environmental conditions. Research using NAPT reference soils indicates that an increase in pH of 0.25 units of the NaHCO_3 results in an average 15% increase in the amount of phosphate extracted (Table 1). An increase of 0.50 pH units resulted in an increase of 20% and was soil dependent. Thus for bicarbonate extractable $\text{PO}_4\text{-P}$ it is essential that the bicarbonate extraction solution be prepared fresh, that the pH be adjusted to 8.50 ± 0.05 and it be checked daily to verify pH.

Table 1. Influence of pH on bicarbonate extractable phosphate.

Soil ID	0.50 N NaHCO_3		
	pH 8.50	pH 8.75	pH 9.00
94103 ¹	6.0	8.3	10.3
94107	11.3	13.5	14.5
95102	24.0	32.6	40.4
94101	38.9	45.4	49.6

¹ Soils obtained from 1994 and 1995 former Western States Proficiency Testing Program.

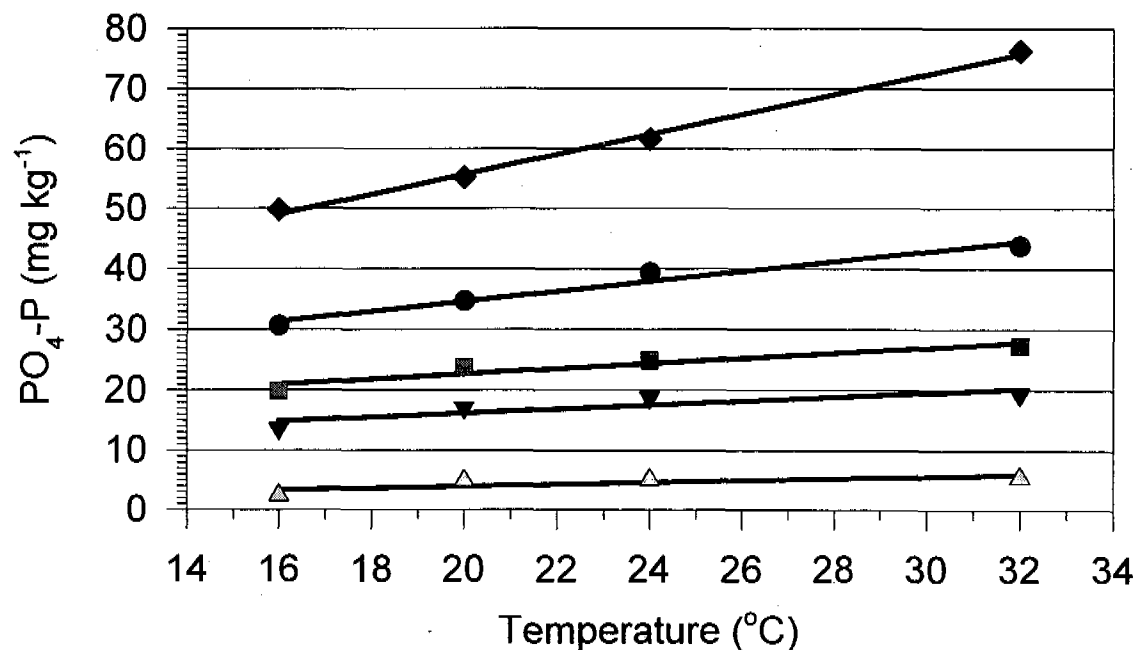


Figure 1. The influence of temperature on the quantity of $\text{PO}_4\text{-P}$ extracted for five standard reference soils.

Extraction Temperature

The extraction of $\text{PO}_4\text{-P}$ is sensitive to the temperature conditions under which the extraction is performed. Surprisingly few in the soil laboratory testing realize the magnitude of influence of temperature. The effect on $\text{PO}_4\text{-P}$ is proportional to the amount in the soil. For a soil with 5.0 mg kg^{-1} of $\text{PO}_4\text{-P}$ at 20°C the amount of $\text{PO}_4\text{-P}$ extracted increases at a rate of $0.15 \text{ mg kg}^{-1} \text{ }^\circ\text{C}^{-1}$ (Figure 1). For a soil with 55.0 mg kg^{-1} of $\text{PO}_4\text{-P}$ at 20°C , the amount of $\text{PO}_4\text{-P}$ extracted increased at a rate of $1.5 \text{ mg kg}^{-1} \text{ }^\circ\text{C}^{-1}$.

Thus an increase in temperature in the laboratory from 20 to 24°C would increase the amount of $\text{PO}_4\text{-P}$ extracted for a soil with a baseline level of 20 mg kg^{-1} at 20°C to 23 mg kg^{-1} at 24°C , resulting in a high bias. When conducting the bicarbonate extraction it is critical to maintain the temperature within a range of $22 \pm 2.0^\circ\text{C}$ and continually monitor and document the temperature of the extraction. High bias recoveries of $\text{PO}_4\text{-P}$ for laboratory QC standard reference checks are likely associated with increased temperatures in the summer, and the reverse in winter.

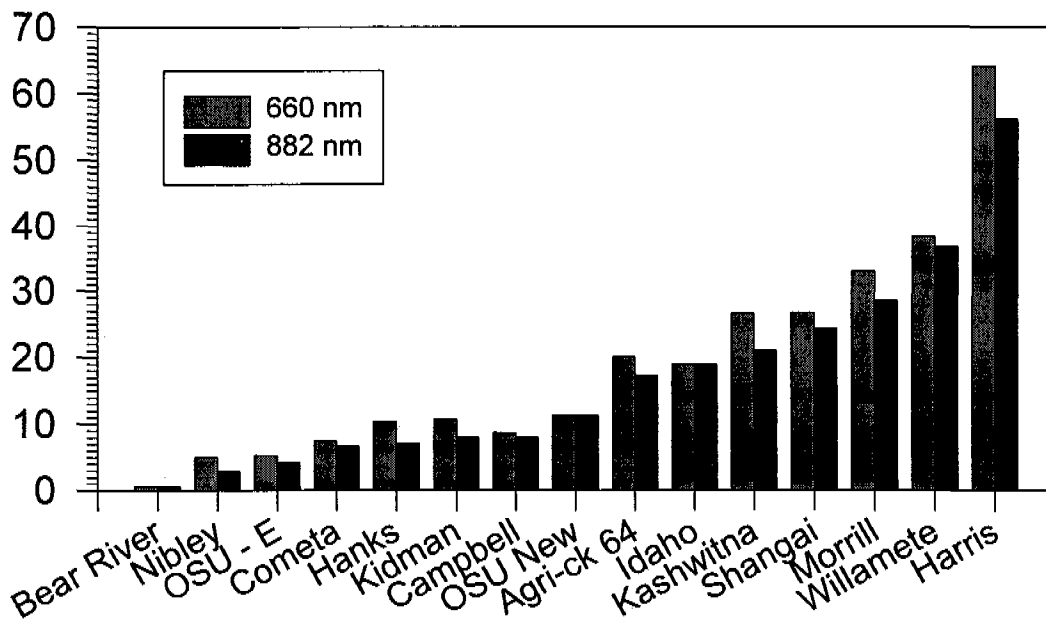
Extraction Time

As the bicarbonate extraction is not quantitative for $\text{PO}_4\text{-P}$, the amount extracted is influenced by extraction time. Although the effect of time is less pronounced than that of extractant pH and temperature, it is none the less worth notation. The bicarbonate method defines the extraction time as 30 minutes and generally most extraction equipment is controlled by electronic timers. Increasing the extraction time to 40 minutes increases the amount of $\text{PO}_4\text{-P}$ by 5%. However laboratories maybe delayed in doing the actual filtration step and have a significant hold time. Hold times of 5-6 minutes have little influence on the amount of $\text{PO}_4\text{-P}$ recovered, whereas hold times of more than 30 minutes are likely lead to a significant $\text{PO}_4\text{-P}$ bias.

Spectrophotometric Measurement

The final step of the bicarbonate method is the spectrophotometric determination of $\text{PO}_4\text{-P}$ by its reaction with ammonium molybdate. When the method was developed it was recommended that the determination be made at 660 nm using a spectrophotometer. However, subsequent research has shown that the 882 nm wavelength is superior and does not have a soil soluble organic interference that is noted for the 660 nm wavelength. Research using fifteen reference soils indicates that the amount of high bias associated with the 660 nm relative to the 882 nm wavelength is highly soil dependent (Figure 2). Thus all laboratories should use the 882 nm for all bicarbonate soil extracts to avoid a high bias.

Figure 2. The influence of spectrophotometric wavelength on $\text{PO}_4\text{-P}$ content.



Additional Comments

The non-equilibrium extraction of $\text{PO}_4\text{-P}$, is based on a soil extraction ratio of 1:20 (soil to extractant). The extraction itself is typically done using a 50 or 100 mL extraction vessel and reciprocating shaker. It is critical that the extraction vessel contain a minimum of 25% dead space (occupied by air) to provide sufficient agitation to insure soil/extract mixing. As the dead space is reduced the amount of $\text{PO}_4\text{-P}$ recovered will decrease as a result of decreased mixing.

Low recoveries of extractable bicarbonate $\text{PO}_4\text{-P}$ (low bias) can generally attributed to two sources: low soil extraction efficiency associated with insufficient agitation; incorrect pH of the ammonium molybdate spectrophotometric complex. It is recommended that a reciprocation shaker be used for the extraction using a vessel described in the previous paragraph. Orbital shakers may provide insufficient soil mixing. Insufficient neutralization of the bicarbonate will lead to a less than optimal pH and low recovery of $\text{PO}_4\text{-P}$.

Specific soils which have high concentrations of extractable bicarbonate soil $\text{PO}_4\text{-P}$, often exceed the high calibration standard. Typically the spectrophotometric method requires 5.0 mL of the bicarbonate extract for the determination of $\text{PO}_4\text{-P}$. For high analysis soils it is recommended to reduce the amount of extract (and standards) to 1.0 mL to ensure the soil is within range of the calibration standards. Note one will need to account for the additional dilution of the extract. For specific very high analysis soils ($> 200 \text{ mg kg}^{-1}$) the aliquot of bicarbonate extract may be further reduced.

Conclusions

Bicarbonate extractable soil $\text{PO}_4\text{-P}$ is non equilibrium method. The pH of the extractant, temperature conditions of the extraction, length of extraction all can influence the amount of $\text{PO}_4\text{-P}$ extracted. Only by careful attention and control of the extraction conditions can the amount of bicarbonate extractable $\text{PO}_4\text{-P}$ be consistent. Bias in recovery values can be attributed to changes in any one or combinations of these factors.

In the soil analysis laboratory only the use of quality control check samples can provide data regarding bias and precision of bicarbonate $\text{PO}_4\text{-P}$.