

## **Water-Soluble Phosphorus as Affected by Soil to Extractant Ratios, Extraction Times, and Electrolyte**

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**Abstract:** One of the most important nutrients for plant production is phosphorus (P). However mismanagement of fertilizer or manure can lead to P build-up in surface soils and elevate P loss in runoff possibly resulting in accelerated eutrophication. Concern of excess P in runoff has increased interest in water-soluble soil P and its use in determining potential for runoff P loss. Several variations of this procedure are currently in practice causing difficulty in comparing research findings. This study evaluated the effectiveness of several common variations of the water-soluble P procedures. Water-soluble soil P was analyzed for 10 soils using four different soil to solution ratios (1:2, 1:5, 1:10, 1:50) and four extraction times (10, 30, 60, and 900 min.). In addition, calcium chloride solutions (0.005 M, 0.01 M, 0.02 M) were compared to deionized water (DW) as extractant. The average amount of water-soluble P increased with wider soil to solution ratio, whereas the extraction time had no effect on the amount of P extracted. Water-soluble P extracted by the various soil to solution ratios and extraction times was significantly related to Mehlich 3 P ( $r^2 > 0.83$ ;  $p < 0.001$ ). These findings suggest that a standardized procedure be used for water-soluble P analysis.

**Keywords:** Phosphorus, water-soluble phosphorus, soil to extractant ratio, extraction time

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## INTRODUCTION

Phosphorus (P) is considered one of the most important plant nutrients in plant/soil systems and is often a limiting nutrient in plant production. As a result, P is properly applied to agricultural land as either commercial fertilizer or manure with application rates based on soil analyses developed to determine the amount of P available to a plant during the growing season. The major P extraction methods include Mehlich3 (Mehlich 1984), Bray-Kurtz P1 (Bray and Kurtz 1945), and Olsen et al. (1954). Each of these tests is suited for different geographic regions and soil properties and is limited to nutrient assessment for plant production.

Phosphorus often is the limiting nutrient of biological productivity in surface water environments as well as terrestrial environments (Sharpley et al. 1994). As a result, P inputs to surface water environments can lead to accelerated eutrophication (Sharpley et al. 1999). Prior to the United States Clean Water Act of 1972, the main source of P pollution was attributed to point sources (i.e., industry, sewage, drainage pipes, etc.). However, agricultural runoff is now considered to be a primary source of P pollution because many point sources are largely under control (Daniel et al. 1994). High concentrations of P may occur in runoff from agricultural fields with high soil surface P content. Through years of fertilizer and manure mismanagement practices, P may build up in the surface soil to levels far exceeding the requirements for plant production. Rainstorms and subsequent runoff events transport dissolved reactive P (DRP) and particulate P (PP) to nearby waterways. Over time, P concentrations of local water bodies may elevate and result in eutrophication. This concern has led to increased interest in a soil P test that may better assess a soil's affinity to contribute to nonpoint source P pollution (Pote et al. 1996). One such analysis is water-soluble soil P.

Water-soluble soil P has been studied in great detail because it represents the amount of P readily available to plants (Kuo 1996) and may be the most appropriate environmental estimator of P concentrations in runoff compared with other soil test methods developed for crop production (Pote et al. 1996). Because water is the solvent and transport medium for P loss from soils, it is expected that estimates of water-soluble P be the most highly correlated to DRP concentrations in runoff vs. other soil P extractants (Hooda et al. 2000). Pote et al. (1996) showed that water-extractable P was better correlated to DRP and bioavailable P (BAP) in runoff from simulated rainfall than Mehlich3, Bray-Kurtz P1, and Olsen P extraction methods. Hooda et al. (2000) also found that water-extractable P was better correlated to soil desorbed P than Olsen, Mehlich 3, Ammonium Oxalate, and Iron Oxide-coated paper P extractions.

Currently, there is no widely accepted method for determining water-soluble P. Previous studies have used different procedures to determine water-soluble P (Pote et al. 1996; Olsen and Sommers 1982; Thompson et al. 1960) by using different soil to solution ratios or different extraction

times. Some methods used wider soil to solution ratios and longer extraction times, such as 1:20/1 h (Mackay et al. 1984), 1:25/1 h (Sharpley et al. 1996), 1:105/15 h (Thompson et al. 1960), 1:100/15 h (van Diest 1963), and 1:60/1 h (van der Paauw 1971), whereas others used narrower soil to solution ratios and shorter extraction times: 1:10/5 min Olsen and Sommers 1982, 1:10/5 min (Kuo and Jellum 1987), 1:1.25/1 h (Olsen and Watanabe 1970), and 1:10/1 h (Kuo 1996). It is difficult to compare the effectiveness of the different water-soluble soil P methods because these studies were performed on different soils with no wide comparisons. In addition, other methods have used a solution of  $\text{CaCl}_2$  as an extracting solution to aid in filtration (Kuo 1996) or to more closely simulate the ionic concentration of other sources of water commonly used for rainfall simulation studies, such as tap water or pond water.  $\text{CaCl}_2$  extraction solutions generally do not extract as much P from the soil as deionized water.

Varying the soil to solution ratio has produced conflicting results in regard to the amount of P extracted (Chapman, Edwards, and Shand 1997). Many of these studies (Hope and Syers 1976, Barrow and Shaw 1979b, White 1966) evaluated the effects of soil to solution ratios on soil adsorption of P. Hope and Syers (1976) found that adsorption was lowest with a wide soil to solution ratio, whereas White (1966) found that adsorption was lowest with a narrow soil to solution ratio. Barrow and Shaw (1979b) compared narrow to wide soil to solution ratios while varying shaking technique (i.e., gentle vs. vigorous) and reported that with gentle shaking extending the shaking time ratio had no effect on the amount of P extracted. Chapman et al. (1976) investigated the effect of soil to solution (1:1.5–1:15.4) ratios on the fractions of P extracted with water and found that DRP increased with wider soil to solution ratios without varying extraction/shaking time. In addition, Hesketh and Brookes (2000) studied the effect of soil to solution ratios on  $\text{CaCl}_2$ -extractable P of selected European soils and reported that P extracted increased as the soil to solution ratio widened. However, these studies used multiple long extraction times, which would be unreasonable for routine and efficient lab analysis. Objectives of this study were to 1) evaluate the effect of different soil to solution ratios and extraction times on water-soluble P using deionized water as the extracting solution, 2) evaluate the effect of varying  $\text{CaCl}_2$  concentrations on soluble P, and 3) determine the relationship between water-soluble P extracted with deionized water (DW) and Mehlich 3-extractable P.

## MATERIALS AND METHODS

### Study Soils

Ten surface soils (0–15 cm), varying in physical and chemical properties as well as Mehlich3-extractable P content, were collected from the state of

**Table 1.** Chemical and physical properties of soils studied

Soil	Name	Mehlich 3 P (mg kg <sup>-1</sup> )	pH	% Clay
Darnell	Udic Haplustept	17	5.4	11
Dalhart	Aridic Haplustalf	26	7.1	12
Pond Creek	Pachic Argiustoll	89	5.0	28
Dougherty	Arenic Haplustalf	132	5.3	8.0
Lebron	Fluvaquentic Hapludoll	63	7.7	59
Sallisaw	Typic Paleudalf	311	5.5	22
Stigler	Aquic Paleudalf	204	5.1	28
Dennis	Aquic Argiudoll	624	5.9	8.0
Kirkland	Udertic Paleustoll	694	6.4	13
Richfield	Aridic Argiustoll	364	6.4	8.0

Oklahoma (Table 1). The soils were air-dried and sieved to pass a 2.0-mm screen prior to chemical and physical analyses. Soil properties (pH, texture, and Mehlich3 P) were measured on the collected samples. Soil pH was determined in a 1:1 soil to DW suspension (Thomas). Soil texture was determined by the hydrometer method (Gee and Baude 1986). Duplicate analyses were conducted in the measurement of physical and chemical properties.

### Water-Soluble Phosphorus

Deionized water (DW) was used to extract and evaluate water-soluble P by varying the soil to solution ratios and extraction times. Soil to solution ratios were 1:2, 1:5, 1:10, and 1:50 soil to DW while extraction times were 10, 30, 60, and 900 min. Soil was placed in a 50-mL centrifuge tube with varying volumes of deionized water, shaken for the specified time on an end-to-end shaker at 150 oscillations per minute, and then centrifuged at 14,470 g for 10 min. The clear supernatant was analyzed colorimetrically for P by using the molybdenum-blue method (Murphy and Riley 1962). A total of 16 treatments were evaluated in the study of water-soluble P using DW as the extracting solution. Duplicate analyses were conducted on all study soils.

### Method Comparison

In addition, methods for extraction of soluble P were compared by using DW and three concentrations of CaCl<sub>2</sub> (0.005 M, 0.01 M, and 0.02 M). Soils were

extracted and analyzed as described above with the exception of a single soil to solution ratio of 1:10 and only one extraction time of 10 min were used. Based on the preliminary results, the soil to solution ratio of 1:10 and shaking time of 10 min were chosen to determine soluble P, which is similar to the method used for Mehlich3 P and is an efficient combination for commercial laboratories to use. Duplicate analyses were conducted on all study soils.

### **Correlation Between Water-Soluble Phosphorus and Mehlich 3 P**

The relationship between water-soluble P and Mehlich 3-extractable P was investigated by using more than 100 Oklahoma soils varying in physical and chemical properties as well as Mehlich 3 P. Mehlich 3 P was determined by extracting 1 g of soil with 10 mL of Mehlich 3 solution and shaking for 5 min. Duplicate analyses were conducted on all study soils.

### **Statistical Analysis**

Analysis of variance techniques were used with PROC MIXED in PC SAS Version 8.2 SAS Institute 2001 to assess the effects of extraction time and soil to solution ratio on the response of P extracted. The experimental design was a  $4 \times 4$  factorial in a randomized complete block design with subsampling. Soil was considered the random blocking factor and the treatment structure consisted of the factorial combination of four levels of extraction time and four levels of ratio. Two replicates for each combination of soil, extraction time, and ratio were obtained, and these replicates were considered subsamples in the model. The simple effects of ratio given extractant and extractant given ratio were examined with a SLICE option in an LSMEANS statement, and multiple comparisons at a 0.05 significance level were made when the simple comparison was significant. Satterthwaite's approximation for the denominator degrees of freedom was used when necessary.

Analysis of variance techniques were used with PROC MIXED in PC SAS Version 8.2 SAS Institute 2001 to assess the effects of extracting solution on the response of P. The experimental design was a randomized complete block design with subsampling. Soil was considered a random blocking factor, and the treatment was four levels of extractant. Two replicates for each combination of soil and extractant were obtained, and these replicates were considered subsamples in the model. Multiple comparisons at a 0.05 significance level were made when the treatments were significant in the analysis of variance. The relationship between water-soluble P and Mehlich3 P was determined by using PROC CORR (SAS Institute 2001).

## RESULTS AND DISCUSSION

### Physical and Chemical Properties

Study soils varied in physical and chemical characteristics. Soil pH ranged from 5.0 to 7.7, whereas Mehlich 3 P ranged from 17 to 694 mg/kg (Table 1). Percentage clay ranged from 8 to 59%.

### Water-Soluble Phosphorus

There was no significant interaction between soil to solution ratio and shaking time ( $p > 0.05$ ). The overall mean P extracted (averaged across all extraction times) was not significantly different ( $p > 0.05$ ) between the soil to solution ratios of 1:2 and 1:5. However, differences did occur within the wider ratios tested. The overall mean amount of P extracted by the 1:10 ratio was significantly greater ( $p < 0.05$ ) than the narrower ratios of 1:2 and 1:5, and the 1:50 ratio extracted a larger amount of P ( $p < 0.05$ ) than all other soil to solution ratios tested (Table 2). These results are consistent with the findings of Chapman et al. (1997) who investigated soil to solution ratios of 1:1.5–1:15.4 and reported that the amount of extracted P per unit weight of soil increased as the soil to solution ratio widened. There was no significant difference in the overall mean amount of P extracted (averaged across all soil to solution ratios) by the different shaking times ( $p > 0.05$ ) (Table 2). The results of our study are similar to those of Barrow and Shaw (1979b) who compared narrow to wide soil to solution ratios while varying shaking technique (i.e., gentle vs. vigorous) and reported that with gentle shaking extending the shaking time had no effect on the amount of P extracted.

**Table 2.** Statistical analysis of the mean amount of water soluble phosphorus extracted (mg kg<sup>-1</sup>) for different soil to deionized water ratios and shaking times

Extraction time (min)	Soil to solution ratios				Mean
	1:2	1:5	1:10	1:50	
10	6.26aA	9.89aAB	18.2aBC	26.4aC	15.2a
30	6.87aA	12.3aA	18.2aA	29.7aB	16.8a
60	6.81aA	12.9aAB	20.7aB	32.9abC	18.4a
900	8.10aA	15.0aAB	23.4aB	42.4bC	22.2a
Mean	7.01A	12.5A	20.2B	32.9C	

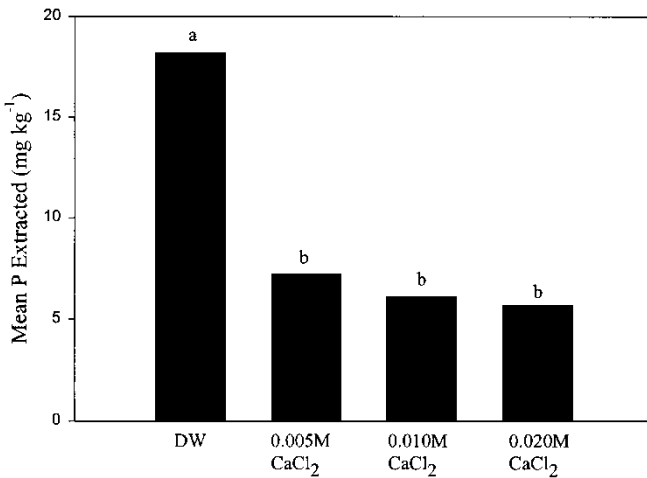
Lower case letters are used for mean comparisons among rows, and upper case letters are used for mean comparisons among columns. Ratio means with the same upper case letter are not significantly different at  $\alpha = 0.05$ , whereas time means with the same lower case letter are not significantly different at  $\alpha = 0.05$ .

**Method Comparison**

There have been many studies using different water-soluble P methods, yet few compare different water-soluble P tests. Four extraction solutions differing in salt concentrations were used to extract soluble P. Significantly less P was extracted by CaCl<sub>2</sub> ( $p < 0.05$ ) compared with the extraction using DW (Figure 1). Although extractable P decreased slightly with increasing the concentration of the CaCl<sub>2</sub> solution, there was no significant difference ( $p > 0.05$ ) in the amount of P extracted by the different CaCl<sub>2</sub> solutions from 0.005 M to 0.020 M. Results of this study differ from those of Barrow and Shaw (1979a) who used one soil and found that P desorption increased with increasing CaCl<sub>2</sub> concentrations.

**Relationships Between Water-Soluble Phosphorus and Mehlich 3 P**

More than 100 Oklahoma soils varying in physical and chemical properties including P content were used to develop a relationship between water-soluble P and Mehlich3 P. The water-soluble P extracted by the various soil solution ratios and extraction times was significantly related to Mehlich 3 P ( $r^2 > 0.83$ ;  $p < 0.001$ ) (Table 3). In addition, the water-soluble P extracted by the method chosen for the method comparison (1 : 10 soil to solution, 10 min) was highly correlated with Mehlich 3 P ( $r^2 = 0.88$ ;  $p < 0.001$ ) (Figure 2). These results agree with those found by other investigators who



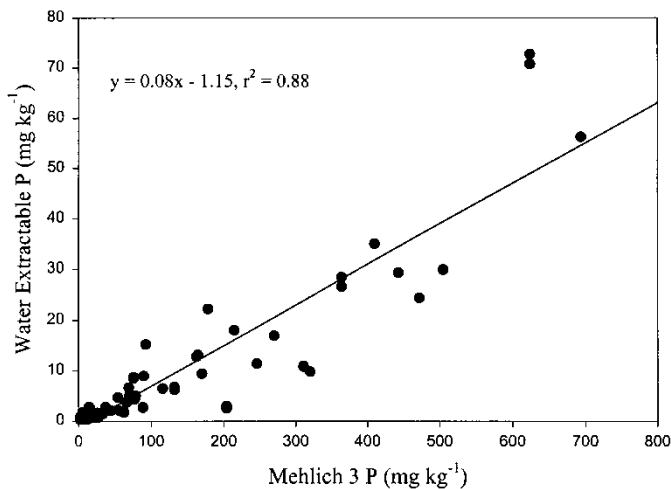
**Figure 1.** Mean amount of phosphorus extracted by using different extracting solutions for 10 Oklahoma soils at a 1:10 soil to solution ratio and a 10-minute extraction time.

**Table 3.** Correlation coefficients ( $r^2$ ) between water-soluble P and Mehlich 3-extractable P for different soil to deionized water ratios and shaking times

Extraction time	Soil to solution ratios			
	1:2	1:5	1:10	1:50
10 min	0.95 <sup>a</sup>	0.88 <sup>a</sup>	0.92 <sup>a</sup>	0.83 <sup>a</sup>
30 min	0.96 <sup>a</sup>	0.97 <sup>a</sup>	0.95 <sup>a</sup>	0.83 <sup>a</sup>
1 h	0.96 <sup>a</sup>	0.96 <sup>a</sup>	0.96 <sup>a</sup>	0.90 <sup>a</sup>
15 h	0.95 <sup>a</sup>	0.96 <sup>a</sup>	0.96 <sup>a</sup>	0.96 <sup>a</sup>

<sup>a</sup>Statistically significant ( $p < 0.001$ ).

have found that highly significant relationships exist between water-soluble P and Mehlich 3 P (Burt et al. 2002, McDowell and Sharpley 2001, Sims et al. 2002). Deionized water appears to extract only about 7% of the amount of P that Mehlich 3 extracts. Pote et al. (1996) showed that water-extractable P was better correlated to dissolved reactive P (DRP) and bioavailable P (BAP) in runoff from simulated rainfall than Mehlich 3 P but did not correlate water-soluble P with Mehlich 3 P. In addition, Hooda et al. (2000) found that water-extractable P was better correlated to soil desorbed P than Olsen, Mehlich 3, Ammonium Oxalate, and Iron Oxide-coated paper P extractions. The Mehlich 3 extraction determines the amount of P available during



**Figure 2.** Linear correlation between water-soluble P (extraction time = 10 min and soil to solution ratio = 1:10) vs. Mehlich 3 P for several Oklahoma soils ( $n = 100$ ). \* $p < 0.001$ .

the crops growing season and has been widely used to assess nutrient sufficiency for plants. Conversely, the water-soluble extraction determines the amount of P immediately available and is a more appropriate environmental estimator of P concentrations in runoff.

## CONCLUSIONS

Narrow soil to solution ratios (1 : 2 and 1 : 5) had no significant effect on the mean amount of P extracted. A 1 : 10 soil to solution ratio extracted a larger amount of P than the narrower ratios and a 1 : 50 ratio extracted significantly more P than all other ratios tested. Extending the extraction time from 10 min to 900 min had no effect on the amount of P extracted using DW for the majority of soil to solution ratios with the exception of the 1 : 50 ratio. Within that ratio, slightly more P was extracted by the extended time of 900 minutes compared with other times. The addition of  $\text{CaCl}_2$  in the extracting solution caused a decrease in the mean amount of P extracted. DW extracted the greatest amount of P for the extractants tested. Water-soluble P was highly correlated with Mehlich 3 P for all the tested soil solution ratios and extraction times. Knowledge of these differences will assist researchers in better comparing results of past studies in which differing procedures were used to determine water-soluble P in soils. This finding suggests a standardized procedure would prove beneficial and should be used for water-soluble P analysis.

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