EVALUATION OF THE BRAY P1 SOIL TEST ON EASTERN RED SOILS IN WISCONSIN

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Introduction

Soil testing for phosphorus (P) is used agronomically to determine the amount of P needed for crop production. Soil test P is also used for determining environmental risks associated with elevated levels of soil P. The Bray P1 soil test method is commonly used in Wisconsin for measuring plant available P and is the required test for regulatory agencies. The Bray P1 extracting solution consists of 0.03 N ammonium fluoride and 0.025 N hydrochloric acid. The ammonium fluoride extracts mostly aluminum bound-P, and no iron-P, and the hydrochloric acid extracts calcium-P (Tandon et al., 1967). Mehlich-3 and Olsen are also widely-used soil test P methods. Mehlich-3 was developed for a wide range of soils including calcareous soils (Wang et al., 2004; Lucero et al., 1998), and Olsen was developed primarily for calcareous soils (Olsen et al., 1954). A calcareous soil is defined as a "soil containing sufficient calcium carbonate (often magnesium carbonate) to effervesce visibly when treated with cold 0.1 N hydrochloric acid" (Brady and Weil, 1999). Mehlich-3 and Bray P1 soil test results are highly correlated in neutral to acid soils with Mehlich-3 extracting slightly more P than Bray P1 in most soils because Mehlich-3 uses a more acidic extracting solution (Tran et al., 1990, Beegle and Oravec, 1990, Lucero et al., 1998; Mallarino, 2003). The Bray P1 soil test method is intended for acid soils, and the validity of its use to predict plant available P levels on the eastern red soils (ERS) in Wisconsin has been questioned due to concerns that the weak acid Bray P1 extracting solution could be neutralized by reaction with carbonates in these soils. Previous studies have found that Bray P1 extracts less P at higher soil pH (Mallarino and Blackmer, 1992; Mallarino, 1997; Atia and Mallarino, 2002) and that Bray P1 does not correlate as well as with Mehlich 3 or Olsen in soils with higher calcium carbonate contents (Hooker et al., 1980; Mallarino, 2003; Hermin et al., 2004). Mallarino (1997) found that Mehlich 3, Olsen, and Bray P1 correlated well with each other until soils reached a calcium carbonate equivalent (CCE) of 4% or higher. Other research indicates that pH alone is not a good indicator of when Bray P will fail; data shows that carbonate content greater than 36 g kg^{-1} (3.6%) is important (Mallarino and Atia, 2005). Mehlich 3 and Olsen soil test P results are well correlated regardless of soil type.

Bray P1 inability to accurately measure available soil P on calcareous soils has generally been attributed to neutralization of the extracting solution by calcium carbonate ($CaCO_3$) followed by precipitation of dissolved calcium with the fluoride (Fixen and Grove, 1990). Soils having greater than 1.25% calcium carbonate equivalent (CCE) have the capability of neutralizing all of the HCl in Bray P1, therefore reducing its effectiveness (Hooker et al., 1980). The Mehlich 3 extracting solution has been found to be less neutralized by free carbonates than Bray P1 (Tran et al., 1990). The Mehlich-3 or Olsen P tests are generally viewed as more appropriate tests for high pH, calcareous soils.

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The eastern red soil (ERS) region of Wisconsin is found in the northeast part of the state. The soils there are known to have high pH values and they have traditionally been thought to have substantial carbonate contents. The studies described above suggest that the Bray P1 test may not perform well on ERS soils, and this research was conducted to evaluate the performance of the Bray P1 method relative to other P soil test methods on these soils.

Materials and Methods

Soil samples collected from the eastern red soil (ERS; n=27) region of Wisconsin were analyzed for soil test P, pH, and carbonate. Soils from Kansas (n=29), Iowa (n=9), and a subsoil formation in southwestern Wisconsin (Rountree; n=2) were included as comparison soils known to have high pH or high carbonate content. The Bray P1 soil test phosphorus method was compared to Mehlich 3 and Olsen performance on these soils.

Soil samples were air dried and ground to pass a 2-mm sieve. Soil P tests included Bray P1 (Frank et al., 1998), Mehlich 3 (Mehlich, 1984) and Olsen (Olsen, 1954). Bray P1 was determined by shaking 2.5 g soil with 25 mL of extractant (0.03 N NH_4F and 0.025 N HCl) for 5 minutes at 180 rpm. Mehlich 3 was determined by shaking 2.5g soil with 25 mL of extractant (0.2N CH_3COOH, 0.25N NH_4NO_3, 0.015N NH_4F, 0.013N HNO_3, 0.001M EDTA) for 5 minutes at 180 rpm. Olsen was determined by shaking 2.0 g soil with 20 mL extractant (0.5 M $NaHCO_3$, pH 8.5) for 30 minutes at 180 rpm. After shaking all samples were centrifuged at 2,000 rpm for 10 minutes and filtered through Fisher P5 filter paper. Phosphorus in the extracts obtained by each method was determined colorimetrically by the ascorbic acid method (Murphy and Riley, 1962) on a Perkin Elmer Lambda 25 UV/VIS spectrometer.

Soil pH was measured in a 1:1 soil to water slurry. Carbonate was measured following the titrimetric method of Bundy and Bremner (1972). Samples between 3 and 8 g of soil were precisely measured into a stoppered 240-mL French square bottle, into which 20 mL of 2M HCl was injected to release the carbonate as carbon dioxide (CO_2). Five milliliters of a 2$\underline{M}$ solution of KOH was used to capture the CO_2, which was then titrated to determine inorganic carbon content. Percent calcium carbonate equivalent (%CCE) was calculated from the inorganic carbon (IC) content using this equation: g IC/g soil * 100.09 g $CaCO_3$/12.011g IC * 100 = %CCE.

Results and Discussion

Figure 1 shows the relationship between pH and carbonate content for all soils evaluated. The pH ranged between 5.4 and 8.3 and the carbonate ranged from 0 to 16.1 %CCE. The pH range of the eastern red soils ranged between 5.3 and 7.6. Most of the ERS soils (hollow diamonds) had less than 2% CCE, with the highest only reaching slightly above 4%. The comparison soils (solid squares) however had carbonate contents up to 16%. These data indicate that soils with high carbonate contents will have pH values above ~7. However, a high soil pH value does not necessarily mean that the soil will have high carbonate content (e.g., some high pH soils have low carbonate contents).

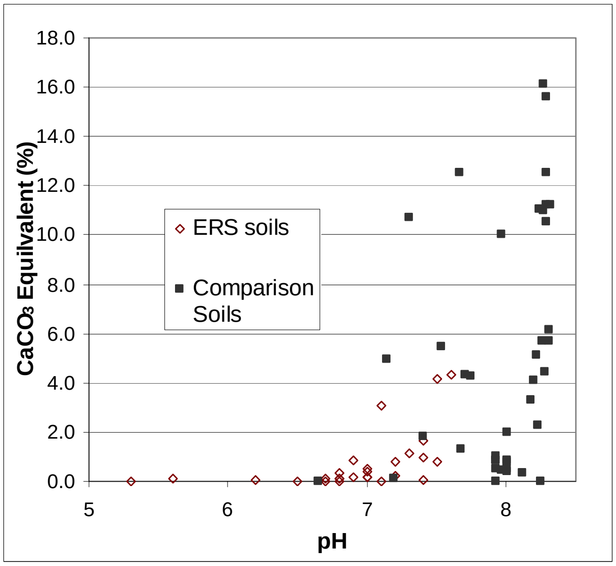

Figure 1. Relationship between pH and %CCE for Wisconsin eastern red soils (ERS) and comparison soils.

Figure 2 shows the relationship between Olsen and Mehlich 3 soil test P values on all soils. The solid circles are those soils with carbonate contents greater than 4% and the hollow squares are those soils with carbonate contents less than 4%. Based on the knowledge of the chemistry of the extractants, both the Olsen and the Mehlich 3 P tests should perform well on most soils including those with substantial carbonate contents. This assumption is supported by the data in Figure 2 showing a generally close linear relationship between soil test P values obtained by the two tests regardless of the soil carbonate content.

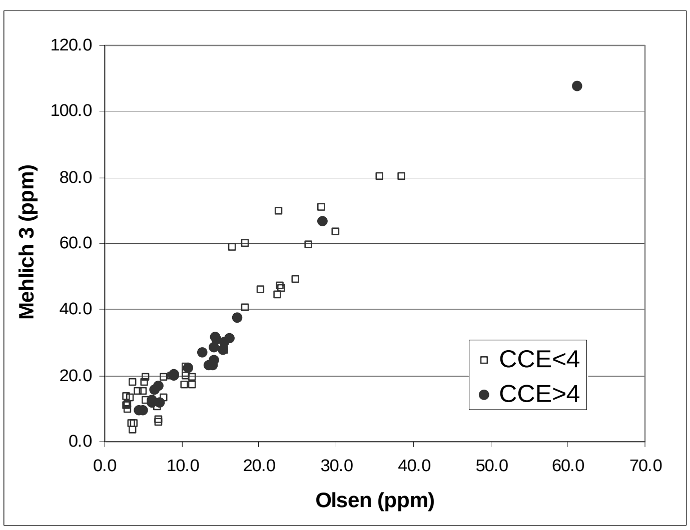

Figure 2. Relationship between Olsen and Mehlich 3 soil test P values for Wisconsin eastern red soils and comparison soils.

Figure 3 shows the relationship between Bray P1 and Mehlich 3 soil test P values on all soils. For many of the soils with carbonate contents greater than 4%, Bray P1 is underestimating the soil test P value likely due to neutralization of the extractant by carbonate. For example, for a substantial group of soils shown in the lower left corner of Figure 3, the Mehlich 3 soil test P values were in the 20 to 30 ppm range while the comparable Bray P1 values were 0 to 10 ppm .

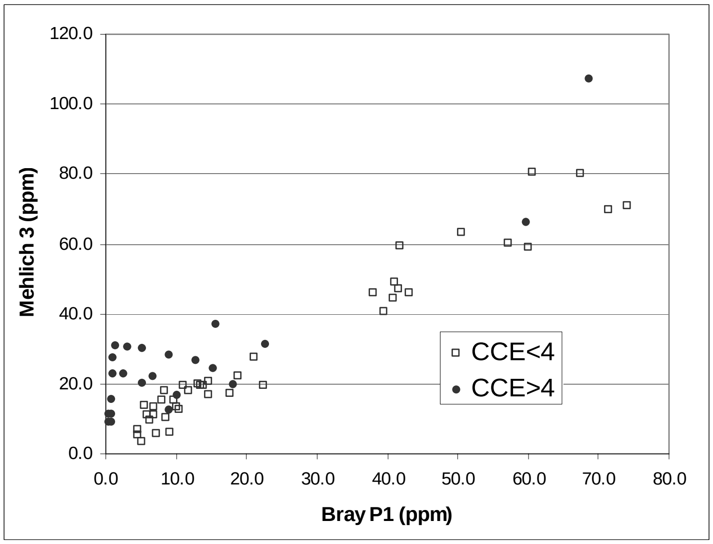

Figure 3. Relationship between Bray P1 and Mehlich 3 soil test P values for Wisconsin eastern red soils and comparison soils.

Figure 4 illustrates the relationship between Bray P1 and Olsen soil test P values on all soils. These results are similar to those shown in Figure 3 for the Bray P1 versus Mehlich 3 relationship in that Bray P1 is underestimating P availability on a substantial number of soils with high carbonate contents.

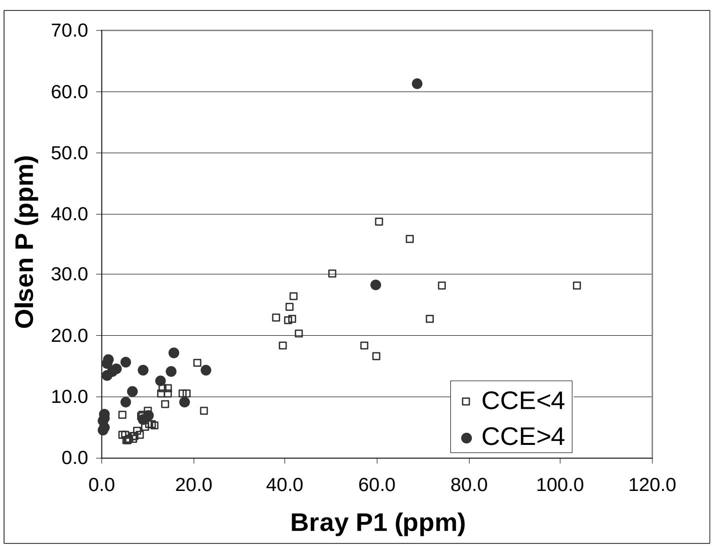

Figure 4. Relationship between Bray P1 and Olsen soil test P values for Wisconsin eastern red soils and comparison soils.

Table 1 summarizes the r^2 values for the soil test P relationships illustrated in Figures 2-4. The r^2 values were similar for the Mehlich 3/Olsen relationship (0.89 compared to 0.88) For the two relationships including the Bray P1 test, the r^2 values decrease from 0.96 to 0.83 when high carbonate soils are included in the analysis. Similarly, in the Bray P1/Olsen relationship, r^2 values declined from 0.77 to 0.66 when high carbonate soils are included. These data indicate that the Bray P1 soil test is unreliable in soils with high levels of carbonate.

Table 1. Compilation of r^2 values for the relationships between soil test P values obtained with various methods for all soils and excluding soils with high carbonate contents.

Comparison	Soils with CCE<4%	All Soils
	------------------------- r^2	-------------------------
M3/Olsen – Figure 2	0.89	0.88
BP1/M3 – Figure 3	0.96	0.83
BP1/Olsen – Figure 4	0.77	0.66

To return to our initial objective of evaluating Bray P1 soil test performance on eastern red soils, Figure 5 shows the relationship between Bray P1 and Mehlich 3 soil P tests for eastern red soils in Wisconsin. The very strong relationship ($r^2 = 0.99$) indicates that the Bray P1 is a valid P test for these soils. The excellent relationship between Bray P-1 and Mehlich 3 tests is likely due to the fact that most of the ERS soils had low carbonate contents.

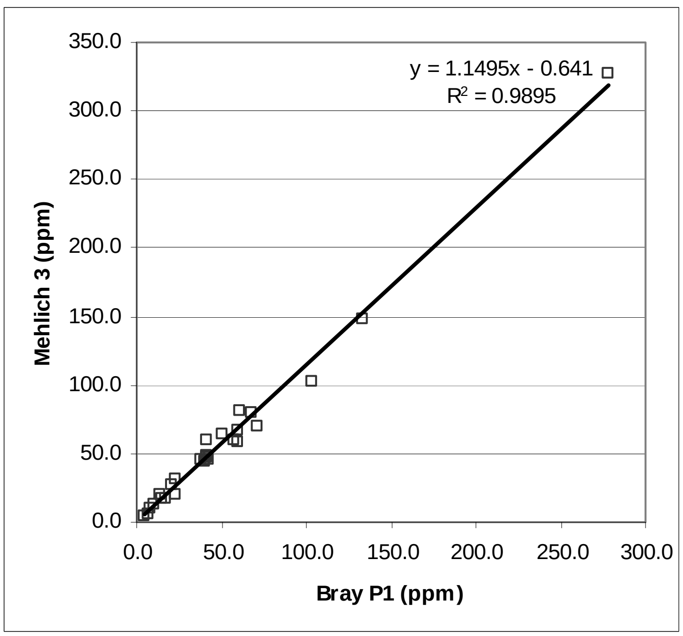

Figure 5. Relationship between Bray P1 and Mehlich 3 P soil test methods on eastern red soils.

Conclusions

The results of this research indicate that the Bray P1 soil P method is not appropriate for assessing P availability in soils with high calcium carbonate contents (over 4% calcium carbonate equivalent). While calcareous soils often have high pH values, pH alone is not a good indicator of soil carbonate carbon content (i.e. some high pH soils have low carbonate contents). Soils analyzed from the eastern red soil region of Wisconsin did not contain enough carbonate to affect Bray P1 soil test performance. Based on this preliminary research, Bray P1 soil test results should still be considered valid estimates of plant available P in this region. Additional analysis of soil samples from the eastern red soil region will continue to verify this conclusion.

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