

# Soil Phosphorus Extracted by Bray 1 and Mehlich 3 Soil Tests as Affected by the Soil/Solution Ratio in Mollisols

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*Different relationships between soil-test methods results have been reported in several agricultural regions. Differences in the same soil-test procedure (e.g., soil/solution ratio) exist between soil-testing laboratories from different agricultural regions. Our objectives were to (1) determine the effect of soil/solution ratio on the amount of phosphorus removed by Bray 1 and Mehlich 3 methods, (2) compare the amounts of phosphorus removed by Bray 1 and Mehlich 3 in Mollisols from the Pampean region, and (3) determine whether soil/solution ratio affects the relationship between Bray 1 and Mehlich 3. Soil phosphorus availability was determined with two extractants (Bray 1 and Mehlich 3), using two soil/solution ratios (1:10 and 1:8, wt/v) in 72 soils (noncalcareous, loess-derived Mollisols) from the Pampean region. The amount of phosphorus removed was 20–24% greater when using 1:10 than 1:8 (wt/v) soil/solution ratio. This effect was significantly greater in Bray 1 than in Mehlich 3 ( $p = 0.04$ ). When compared using the same soil/solution ratio, Mehlich 3 removed 4 to 8% more phosphorus than Bray 1. The soil/solution ratio used in the comparison affected the relationship between both extractants. The difference between extractants was slightly greater with a soil/solution ratio of 1:8 than of 1:10 ( $p = 0.03$ ). Our results showed that even when using the same method, changes in the procedure (like soil/solution ratio) may cause different soil-test results and also differences in the relationship between two extracting solutions. Therefore, reported relationships between two methods are only valid for the soils and region where the relationship was developed and should not be extrapolated to other regions, even with similar soils.*

**Keywords** Phosphorous, soil fertility, testing methodology

## Introduction

Soil phosphorus (P) availability is usually assessed by the soil exposure to different solutions that attempt to remove a proportion of the plant-available P. Most extracting solutions remove the phosphate ions dissolved in the soil solution and also a proportion of the adsorbed and soluble inorganic P forms. Soil-test calibration involves field research to determine the relationship between soil test and crop response or yield, which gives a

Received 11 May 2009; accepted 14 April 2010.

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meaning to the soil-test measurement (Fixen and Grove 1990). Two of the most widespread soil P tests in neutral to acidic (noncalcareous) soils are Bray 1 (Bray and Kurtz 1945) and Mehlich 3 (Mehlich 1984). As the Bray 1 method came historically before the Mehlich 3, in some agricultural regions soil-test calibration had already been done using the Bray 1 method when the Mehlich 3 became available. It is important to note that the interpretation of soil-test results is limited to those crops and soil types to which the soil test has been calibrated.

Because the Mehlich 3 method has several advantages over other methods, it became gradually more accepted by many laboratories all over the world, sometimes replacing the Bray 1 method. One advantage of the Mehlich 3 method is that it can be used to determine not only P but also other nutrients (Mehlich 1984). Adoption of multielement extractants reduces chemical costs and labor. Another advantage is that the Mehlich 3 test performs well in a wider soil pH range than Bray 1. It is generally accepted that the Bray 1 method is more appropriate for acidic soils and the Olsen method is more suitable for calcareous soils. It was reported that the amount of P extracted by Mehlich 3 correlated closely with Bray 1-extractable P in soils with pH less than 7.4 and with Olsen-extractable P in soils with pH 7.4 or greater (Mallarino 1997). Many soil-test laboratories have adopted the Mehlich 3 procedure in an attempt to improve operational efficiency and be more cost-effective. However, the change in soil-test method requires new calibration data from field trials to interpret the results in terms of crop response. A simpler approach is to determine the relationships of the already calibrated soil test and the new one. If a strong correlation between both tests is found, the new extraction method could be incorporated into the diagnosis and recommendation system already developed based upon the standard test (Gartley et al. 2002).

Studies involving the comparison of Mehlich 3 and Bray 1 methods have shown good correlations between the amounts of extractable P, especially in noncalcareous soils. However, reported relationships in the literature have been very variable (Table 1). These studies have shown that Bray 1 extracted more P than Mehlich 3 in some soils (Herlihy, McCarthy and Brennan 2006), similar amounts in other soils (Kleinman et al. 2001; Mallarino and Blackmer 1992; Mallarino 1997, 2003; Mehlich 1984; Michaelson, Ping, and Mitchell 1987; Tran et al. 1990; Wolf and Baker 1985), and less P in others (Eckert and Watson 1996; Ketterings and Flock 2005; Michaelson, Ping, and Mitchell 1987; Wendt 1995). In some studies, soil characteristics helped to explain part of the observed variation in the relationship between Mehlich 3 and Bray 1. Tran et al. (1990) observed that the regression relating Mehlich 3 and Bray 1 was improved when oxalate-extractable aluminum (Al), the maximum phosphate adsorption capacity of soils, or pH was included as a second variable in the equation. Wendt (1995) improved the relationship between Mehlich 3 and Bray 1 when exchangeable calcium (Ca) was included. Michaelson, Ping, and Mitchell (1987) reported that Mehlich 3 extracted 12% more P than Bray 1 in loess-derived soils and 66% more P in volcanic ash-derived soils. Herlihy, McCarthy, and Brennan (2006) observed distinct relationships between soil-test methods for each soil series or association, which preclude the use of a single conversion equation across all soils.

Other sources of variation of the relationships between Mehlich 3 and Bray 1 results reported in different agricultural regions could be the distinct modifications of the methods protocols adopted by soil-test laboratories in different regions. While the soil/solution ratio was originally 1:7 (wt/v) in Bray 1 (Bray and Kurtz 1945) and 1:10 (v/v) in Mehlich 3 (Mehlich 1984), in almost all studies cited in Table 1 the soil/solution ratio was 1:10 (wt/v) for both extractants. In the north central region of the United States the soil/solution ratio commonly used is 1:10 (wt/v), whereas in the Southeast it is 1:10 (v/v), which is

**Table 1**  
Reported relationships between P extracted by Mehlich 3 (M-3) and Bray 1 (B-1) methods

Soil type	Soil/solution ratio (wt:v)		Slope <sup>a</sup>	Range Bray 1 mg kg <sup>-1</sup>	n	r <sup>2</sup>	Source
	M-3	B-1					
Diverse (pH < 7.5)	1:8.5 <sup>b</sup>	1:8.5 <sup>b</sup>	1.04		105	0.92	Mehlich 1984
Noncalcareous (Ultisols, Mollisols, Alfisols)	1:10	1:10	0.87	3–213	91	0.97	Wolf & Baker 1985
Noncalcareous (loess derived)	1:10	1:10	1.01–1.18	3–105	192	0.92–0.96	Michaelson et al. 1987
Volcanic ash-derived soils	1:10	1:10	1.26–1.88	1–74	193	0.85–0.91	Michaelson et al. 1987
Diverse (mostly Inceptisols and Spodosols, pH: 4.4–7.8)	1:10	1:10	1.09	4–251	82	0.96	Tran et al. 1990
Noncalcareous (mostly Mollisols)	1:10	1:10	1.11	2–59	25	0.72	Mallarino & Blackmer 1992
Noncalcareous (Alfisols, Ultisols, Oxisols, pH < 6.1)	1:8.5 <sup>b</sup>	1:8.5 <sup>b</sup>	1.37	1–60	98	0.91	Wendt 1995
Noncalcareous (glacial till-derived)	1:10	1:10	1.2–1.4	2–70		0.90–0.98	Eckert & Watson 1996
Noncalcareous (mostly Mollisols, pH < 7.4)	1:10	1:10	0.97	1–96	> 100	0.90	Mallarino 1997
Diverse (pH: 4.2–8.6)	1:10	1:10	1.12	1–114	24	0.88	Kleinman et al. 2001
Diverse (pH: 4.4–7.4)	1:8.5 <sup>b</sup>	1:7 <sup>b</sup>	1.19	2–252	300	0.97	Gartley et al. 2002
Noncalcareous	1:10	1:10	1.19	4–63	77	0.97	Mallarino 2003
Noncalcareous (pH < 7.4, glacial till-derived)	1:10	1:10	1.33	19–140	18	0.94	Ketterings & Flock 2005
Various parent materials (pH < 7.3)	1:10	1:10	0.84–1.68	1–150	128	0.92	Hertlhy et al. 2006

<sup>a</sup>Slope: slope of the linear regression of Mehlich 3 vs. Bray 1; range: range of reported values of Bray 1 P; n: number of samples.

<sup>b</sup>Calculated weight/volume ratios (authors used volume/volume ratios), based on the assumption that 0.85 cm<sup>3</sup> of soil weighs 1 g.

Note. Extracted P was measured colorimetrically, with the exception of Mehlich 3 extracts in Gartley et al. (2002) where ICP-AES was used.

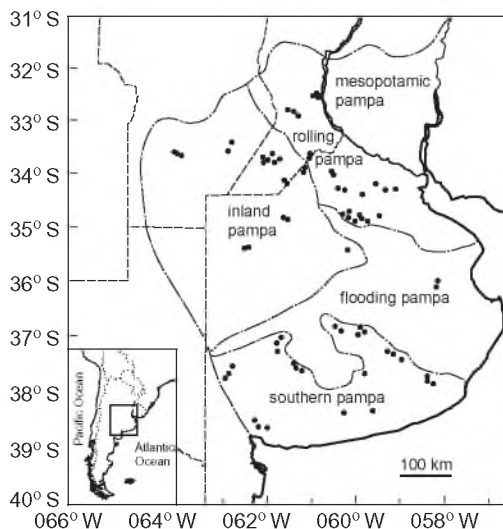
equivalent to 1:8.5 (wt/v, assuming that 1 g of soil has a volume of 0.85 cm<sup>3</sup>) (Brown 1998; Donohue 1992). In the Pampean region of Argentina, most soil-test laboratories used a soil/solution ratio of 1:8 (wt/v) for the Bray 1 method (Boschetti and Quintero 2005). Changing the soil/solution ratio may affect the amount of P removed by the extracting solution. However, little is known about the effect of changing the soil/solution ratio on the relationship between two soil-test methods. Other methodological variations among laboratories are the shaking time and the analytical technique used to measure P in the extract [colorimetry, inductively coupled plasma (ICP)]. These differences suggest that an observed relationship between soil-test methods in soils from one agricultural region should be used with caution in another region, even when both regions have similar soils.

The Pampean region is the most important agricultural area of Argentina. In this region, almost 70% of the soils are P deficient (Echeverría and García 2005), which is one of the major constraints to crop yield. Cropped soils of this region are relatively homogeneous in terms of taxonomy, mostly noncalcareous Mollisols (Soil Survey Staff 1999) developed from loess sediments under grassland, with prevailing udic and thermic water and temperature regimes (Hall et al. 1992), and have low P-buffering capacity (Mendoza 1986; Rubio, Cabello, and Gutierrez Boem 2008). Bray 1 has been calibrated as the soil P test for fertilizer recommendations in the main crops grown in the region. Only one study comparing Bray 1 and Mehlich 3 results was done with 25 soils from two counties from the southeast of this region. The authors reported that both methods removed similar amounts of P in 24 soils (Zamuner, Picone, and Echeverría 2006). Our objectives were to (a) determine the effect of soil/solution ratio on the amount of P removed by Bray 1 and Mehlich 3 methods, (b) compare the amounts of P removed by Bray 1 and Mehlich 3 in Mollisols from the Pampean region, and (c) determine whether soil/solution ratio affects the relationship between Bray 1 and Mehlich 3.

## Materials and Methods

Seventy-two soils from the Pampean region were chosen, mostly from the three ecological subregions where production of grain crops is the predominant soil use (Figure 1). Soil samples came from the southern Pampa (27 soils), rolling Pampa (25 soils), and inland Pampa (18 soils). The flooding Pampa is dominated by noncropped, hydromorphic, and alkaline soils, and only two soils were sampled there, representing the scarce highlands of this subregion (Hall et al. 1992). All selected soils were noncalcareous Mollisols (mostly Argiudolls and Hapludolls).

A composite sample from the top 20 cm of the soil was taken at each site. Soil samples were air dried, sieved to 2 mm, and analyzed for total organic carbon content by the Walkley–Black method and pH (1:2.5 soil/water). Soil P availability was determined with two extractants: Bray 1 [0.03 M ammonium fluoride (NH<sub>4</sub>F) + 0.025 M hydrochloric acid (HCl); Bray and Kurtz 1945] and Mehlich 3 [0.2 M acetic acid (CH<sub>3</sub>COOH) + 0.25 M ammonium nitrate (NH<sub>4</sub>NO<sub>3</sub>) + 0.013 M nitric acid (HNO<sub>3</sub>) + 0.015 M NH<sub>4</sub>F + 0.001 M ethylenediaminetetraacetic acid (EDTA); Mehlich 1984]. One g of soil was placed into a 50-mL tube (conical bottom, screw cap), and the extractant was added. Tubes were horizontally placed in a reciprocal shaker and were shaken for 5 min at 200 strokes per minute. Two soil/solution ratios were used: 1:10 and 1:8 (wt/v). After shaking, the soil suspension was filtered (Whatman no. 40) and the P concentration of the collected extract was determined colorimetrically by the ascorbic acid method (Kuo 1996). The four extracting methods (combination of two extractants and two soil/solution ratios) were denoted as follows: Bray 1<sub>1:8</sub>, Bray 1<sub>1:10</sub>, Mehlich 3<sub>1:8</sub>, and Mehlich 3<sub>1:10</sub>.



**Figure 1.** Location of the study area (the Pampas) and sampled soils (●). Region limits: - . - . , province limits: ---.

Results from the different methods were compared fitting a line representing the relationship between the amounts of P removed by two different methods. Lines were fitted using the standardized major axis method (also known as “reduced major axis”). This method has been pointed as more suitable than linear regression when the purpose of line-fitting is to summarize the relationship between two variables measured with error or to test if two methods of measurement agree (Warton et al. 2006; Webster 1997). In this method, departure of each data point from the fitted line in the Y and X directions is considered, as the fitted line minimizes the sum of triangular areas between the line and each data point. The permutation of variables Y and X does not affect the line fitted by this method, as it bisects the angle between the two regression lines (Y vs. X and X vs. Y). Lines were fitted with and without intercepts. Tests of whether slopes were different from 1 and intercepts were different from 0 were performed. The software SMATR was used for fitting the lines, testing the significance of their parameters, and comparing slopes of different lines (Falster, Warton, and Wright 2006).

## Results and Discussion

Table 2 shows the average and range of some soil characteristics and P removed by Bray 1 and Mehlich 3 methods in the soils used in this study. All soils had pH values lower than 7.5, which is consistent with the known fact that calcareous soils are scarce in the region. Most soils had medium to low values of extractable P (78% of soils had less than  $20 \mu\text{g g}^{-1}$  Bray  $1_{1:8}$ ). These levels of available soil P are very common in this region because of the low use of fertilizers, which has led to a progressive decrease of soil P levels (Gutiérrez Boem et al. 2008).

Even though there were differences in the amount of P removed by the four different extracting methods (combinations of extractants and soil/solution ratios), the whole set of

**Table 2**  
Mean, range, and variability of some soil characteristics and soil-test P for the 72 soils of the Pampas

Parameter	pH	SOC <sup>a</sup> (mg g <sup>-1</sup> )	Bray 1 (mg kg <sup>-1</sup> )		Mehlich 3 (mg kg <sup>-1</sup> )	
			1:8 <sup>b</sup>	1:10 <sup>b</sup>	1:8	1:10
Mean	6.1	38	16.3	19.9	17.9	20.6
Min	5.3	12	4.7	6.0	5.4	5.3
Max	7.5	22	83.0	99.2	82.2	106.0
SD	0.38	7.2	13.6	17.4	14.3	18.2

<sup>a</sup>SOC, soil organic carbon.

<sup>b</sup>Soil/solution ratio (wt/v).

comparisons showed high correlations between methods ( $r > 0.97$ , Table 3). High correlations between Bray 1 and Mehlich 3 were already observed in previous reports, especially when calcareous soils were excluded from the relationship (i.e., Mallarino 2003). In soils with pH greater than 7.4 (including calcareous soils), Mallarino (1997) observed a lack of relationship between Bray 1 and Mehlich 3 P, whereas both methods were closely related in soils with pH lower than 7.4 ( $r = 0.95$ ). Tran et al. (1990) observed that the relationship improved when calcareous soils were excluded (correlation coefficient changed from 0.96 to 0.98). Wendt (1995) reported that the relationship between both extractants improved when soils with high exchangeable Ca were excluded (regression  $r^2$  rose from 0.80 to 0.91). As soils used in our study were noncalcareous, we expected a high correlation between the P removed by Bray 1 and Mehlich 3 extracting solutions.

Soil/solution ratio affected the amount of P removed by both extractants (Table 3; Figure 2). At a ratio of 1:10 (wt/v), removed P was 20–24% greater than at a ratio of 1:8 (wt/v). This effect was observed in both extractants, but it was significantly greater in Bray 1 than in Mehlich 3 ( $P = 0.04$ ). These results were consistent with the known effect of increasing P removal by widening the soil/solution ratio (Fuhrman et al. 2005; Thomas and Peaslee 1973).

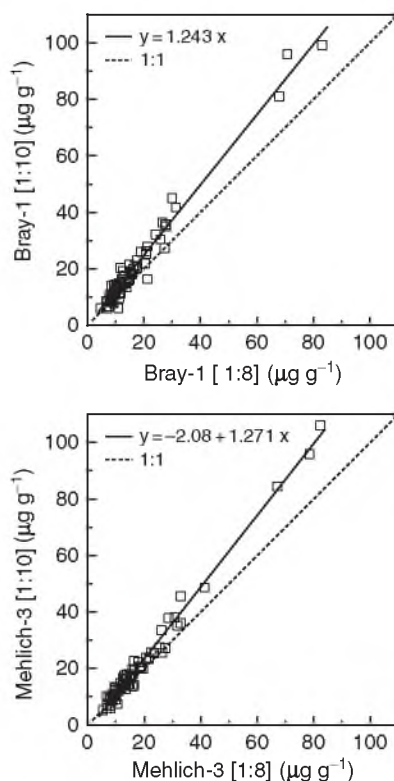
Both extractants removed different amounts of P. Comparisons at the same soil/solution ratios indicated that Mehlich 3 removed 4 to 8% more P than Bray 1 (Table 3, Figure 3). However, the particular soil/solution ratio used in the comparison affected the relationship between both extractants. The difference between extractants was slightly greater with a soil/solution ratio of 1:8 than of 1:10 (slope 1.078 > 1.041,  $P = 0.03$ ) (Table 3). This difference in the amount of P removed by Mehlich 3 and Bray 1 was similar to what was reported in some studies. In the original work where the Mehlich 3 method was described, it was reported that this extractant removed 3 to 4% more P than Bray 1 in 105 soils from the southern and mid-Atlantic states (Mehlich 1984). Michaelson, Ping, and Mitchell (1987) observed that Mehlich 3 removed an average of 12% more P than Bray 1 (range: 1 to 18%) in noncalcareous loess-derived soils. Mallarino and Blackmer (1992) reported that Mehlich 3 removed 6.4% more P than Bray 1 in 24 noncalcareous soils (mostly Molisolls) from Iowa. In the same soils and zone, but working with a larger dataset, Mallarino (1997, 2003) found that Mehlich 3 removed 11% more than Bray 1. Other studies showed larger differences between these two extractants, even using the same soil/solution ratio. Wendt (1995) observed that Mehlich 3 removed 37% more P than Bray 1 in 98 noncalcareous soils (primarily Alfisols, pH < 6.1). Similar results were

**Table 3**

Relationships between P extracted by different methods: Bray 1 and Mehlich 3 with two soil/solution ratios (subscripts), 1:8 and 1:10 (wt/v)

y	x	r	Intercept (a)	y = a + b x			y = b x		
				$p^a$ (a = 0)	Slope (b)	p (b = 1)	Slope (b)	p (b = 1)	
Same extracting solution, different soil/solution ratio									
Bray 1 <sub>1:10</sub>	Bray 1 <sub>1:8</sub>	0.98	-1.043	0.061	1.28	<0.001	1.243	<0.001	
Mehlich 3 <sub>1:10</sub>	Mehlich 3 <sub>1:8</sub>	0.99	-2.087	<0.001	1.271	<0.001	1.201	<0.001	
Different extracting solution, same soil/solution ratio									
Mehlich 3 <sub>1:8</sub>	Bray 1 <sub>1:8</sub>	0.98	0.6915	0.188	1.052	0.032	1.078	<0.001	
Mehlich 3 <sub>1:10</sub>	Bray 1 <sub>1:10</sub>	0.99	-0.1187	0.755	1.045	0.002	1.041	<0.001	
Different extracting solution and soil/solution ratio									
Mehlich 3 <sub>1:10</sub>	Bray 1 <sub>1:8</sub>	0.97	-1.208	0.086	1.337	<0.001	1.294	<0.001	

<sup>a</sup>p values of the test for intercepts (H0: a = 0) and slopes (H0: b = 1).



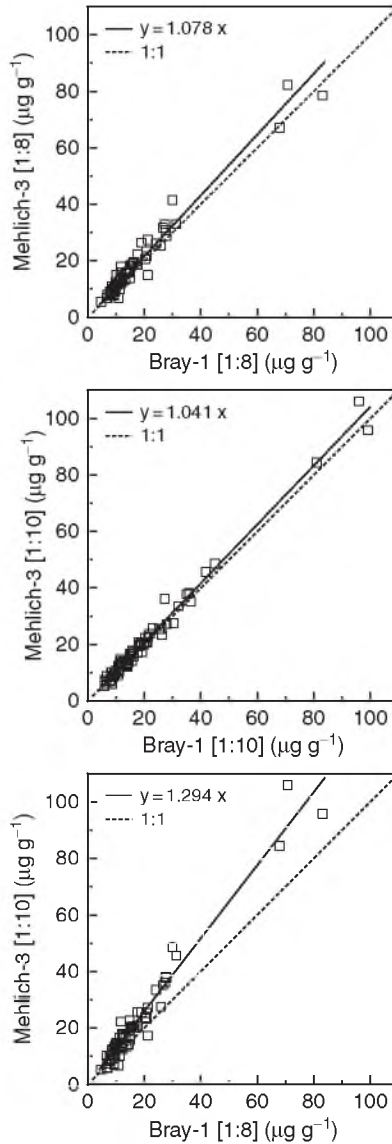
**Figure 2.** Effects of different soil/solution ratio (between square brackets) on phosphorus extracted by Bray 1 and Mehlich 3 extracting solutions. Slopes of fitted lines were significantly different from 1 ( $p < 0.001$ ).

observed in 18 noncalcareous, glacial till–derived soils ( $\text{pH} < 7.4$ ) (Ketterings and Flock 2005). Mehlich 3 extracted an average of 66% more P than Bray 1 in volcanic ash soils (Michaelson, Ping, and Mitchell 1987). Mehlich 3 removed an average of 28 to 57% more P than Bray 1 in noncalcareous soils formed under forest vegetation in glacial till (Eckert and Watson 1996).

When Mehlich 3<sub>1:10</sub> (the usual soil/solution ratio for this method in the Midwest) was compared to Bray 1<sub>1:8</sub> (commonly used in the Pampean region), the effects of changing both extracting solution and soil/solution ratio were added, and Mehlich 3<sub>1:10</sub> removed 29% more P than Bray 1<sub>1:8</sub> (Table 3, Figure 3).

## Conclusions

Our results stressed the importance of the standardization of methods within laboratories from the same region. Any change of the soil/solution ratio should be reported, as it has a big impact on test results. It should also be reported if the soil/solution ratio used is on a volume or weight basis, as using a 1:10 (v/v) is equivalent to 1:8.5 (wt/v), assuming that 1 g of sieved soil has a volume of 0.85 cm<sup>3</sup> (Peck 1998). Additionally, it is very important that all soil laboratories of the same region select the same protocol of the method that was



**Figure 3.** Relationships between phosphorus extracted by different extracting solution (Mehlich 3 and Bray 1) and different soil/solution ratio (wt/v, between square brackets). Slopes of fitted lines were significantly different from 1 ( $p < 0.001$ ).

used to develop the calibration database upon which the fertilization recommendations are based.

Even when using a standard method such as Bray 1 or Mehlich 3 methods, changes in the method procedures among laboratories from different regions may cause different soil-test results and differences in the relationship between extracted P by both methods. These differences should be taken into account when comparing soil P critical values for several crops reported in the literature from different agricultural regions of the world. In

general, differences in the relationships between Mehlich 3 and Bray 1 results reported in the literature could not be explained by specific soil characteristics. It should not be disregarded that they could be caused not only by soil differences but also by differences in method protocols among soil laboratories performing the comparisons. Therefore, reported relationships are only valid for the soils and region where they were developed and should not be extrapolated to other regions, even with similar soils.

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