

Soil organic matter effects on plant available and water soluble phosphorus

Tsutomu Ohno · Bruce R. Hoskins · M. Susan Erich

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Abstract The degree of phosphorus saturation (DPS) has been shown to be a suitable initial indicator of P loss potential from agricultural soils to surface waters. In addition, several agronomic soil tests have been evaluated as environmental predictive tools. The objectives of this study were: (1) to evaluate the modified Morgan soil test, used on acid, high-aluminum soils of the northeastern United States, as a predictor of water-soluble P and (2) to determine the effect of soil organic matter (SOM) on the ability of both DPS and soil test P to predict water-soluble P. The soils were divided into three SOM classifications depending on their loss-on-ignition contents and analyzed for water-soluble P, modified Morgan soil test P, and oxalate-extractable P, Al, and Fe. The relationship between DPS and water-soluble P showed a change point at about 15% DPS, as did the relationship between DPS and modified Morgan soil test P. A DPS of 15% corresponded to about 14 mg kg⁻¹, a threshold above which water-soluble P could be expected to increase more rapidly with additional P loading. The slopes of the regression lines of water-soluble P as a function of soil test P were 0.050, 0.036, and 0.021 (mg water-soluble P kg⁻¹ soil/mg soil test P kg⁻¹) for the low, medium, and high SOM classification groups, respectively. SOM level had a less significant effect on the relationship between DPS and water-soluble P. Higher levels of SOM were associated with higher levels of oxalate-extractable Fe and Al and, therefore, higher P

sorption capacities and lower DPS values, resulting in less P in solution at all soil test levels.

Keywords Organic matter · Oxalate extraction · Water-soluble phosphorus · Water-soluble carbon · Modified Morgan soil test phosphorus

Introduction

Maintaining and building levels of soil organic matter to improve soil quality is a fundamental principle of sustainable agricultural systems (Magdoff and van Es 2000). Farmers are frequently advised to “build soils” by adding soil organic matter to improve microbial activity, nutrient cycling, and soil physical properties. Total soil C, particulate organic C, and soil microbial biomass C have been shown to be closely related to inputs of C (Griffin and Porter 2004). Among the many properties potentially affected by the level of soil organic matter, the quantity of water-soluble P in soils is of fundamental importance with respect to both crop production and environmental protection. Plant P uptake is very sensitive to P concentration in soil solution (Barber 1995); thus, the maintenance of an adequate concentration of P in soil solution is important for crop production. However, high soil solution P levels increase the risk of eutrophication if P is transported from agricultural soils to surface waters. Because soil test P is generally well correlated with water soluble P, it can be used both as an indicator of the potential to supply crop P needs and as an indicator of potential environmental risk.

Recently, the use of degree of phosphorus saturation (DPS) as a parameter for predicting water-soluble P has become common (Breeuwsma and Schoumans 1987). Use of DPS was first popularized in the Netherlands where it

T. Ohno (✉) · B. R. Hoskins · M. S. Erich
Department of Plant, Soil, and Environmental Sciences,
University of Maine,
5722 Deering Hall,
Orono, ME 04469-5722, USA
e-mail: ohno@maine.edu

was designed to assess soil P content relative to that soil's capacity to sorb P. Degree of P saturation has been shown to be well correlated to soluble P across a range of soils (Pautler and Sims 2000). Soils with >25–30% oxalate extract derived DPS values have been categorized as potential contributors to groundwater P pollution (Nair et al. 2004; Breeuwsma et al. 1995). Theoretically, DPS is a more robust indicator of the environmental risk associated with any particular level of extractable P than P level alone because it incorporates an estimate of P sorption capacity. Using oxalate-extractable P, Al, and Fe values has the disadvantage of being significantly more time and labor intensive to determine than routine soil test P. However, recent research has revealed good correlations between DPS (oxalate-extractable P, Al, and Fe values) and soil test P (Sims et al. 2002; Beck et al. 2004).

It is widely recognized that organic amendments added to soils may influence P solubility (Iyamuremye and Dick 1996; Easterwood and Sartain 1990). Organic amendments are a source of water-soluble C that can directly affect P solubility through three mechanisms. Organic molecules may: (1) specifically sorb to soil minerals, competing with P for sorption sites; (2) complex with surface-bound aluminum or iron to form soluble organic-metal compounds substituting for, and releasing, previously sorbed P; or (3) sorb to soil particles at nonspecific sorption sites, increasing the surface negative charge of the particle and resulting in reduced electrostatic attraction of P to the soil surface (Traina et al. 1986). These mechanisms have been investigated in a number of laboratory studies (Guppy et al. 2005). The relationships between water-soluble C and P have also been investigated in soils sampled from a variety of field studies. For example, in a study of soils from four cropping systems in Maine, a linear relationship was found between water-soluble C and water-soluble P concentrations (Ohno et al. 2005).

Soils with higher amounts of organic matter generally support higher levels of water-soluble C than soils with lower amounts of organic matter; for example, the organic horizons of forest soils are generally higher in both than agricultural soils (Chantigny 2003). In addition, organic amendments, such as animal manure, increase levels of water-soluble C (Zsolnay and Grolitz 1994), and soils which have received repeated additions of animal manure generally have relatively higher levels of soil organic matter (SOM) as well (Erich et al. 2002). Therefore, despite the complexity of the relationship between SOM and water-soluble C (Kalbitz et al. 2000; Chantigny 2003), it is reasonable to assume that a positive relationship exists between these two properties.

The Mehlich-1 and Mehlich-3 soil tests have been shown to be useful tools for assessing plant available P as well as possible environmental risks from high soil P levels (Pautler and Sims 2000; Nair et al. 2004; Beck et al. 2004). However, the modified Morgan soil test (McIntosh 1969), used in

Maine, Connecticut, and Vermont, is more appropriate for many of the acid, high-aluminum soils of the northeastern United States. Our first objective was to evaluate modified Morgan soil test P by determining its relationship to water-soluble P and DPS. Secondly, we examined the influence of SOM on the ability of both modified Morgan soil test P and DPS to predict water-soluble P. Because of the relationship between SOM and soluble C and the known effects of soluble C on water-soluble P, we hypothesized that SOM level would affect the ability of soil test P and DPS to predict water-soluble P. SOM level is commonly measured in soil testing laboratories, whereas water-soluble C is rarely measured. If SOM is found to improve the predictive ability of soil test P, this property could be incorporated into an environmental assessment of P status. We do not propose the use of water-soluble C as a routine soil testing parameter.

Materials and methods

Soils and soil test characterization

One hundred and six soils were randomly selected from soils submitted to the University of Maine Soil Testing Laboratory to obtain a range of soil characteristics representative of agricultural soils in the northeastern region of the United States. Soils were air-dried and sieved (<2 mm) before characterization using the standard methods of the Maine Soil Testing Service (Hoskins 1997). Soil pH was measured in distilled water at a 1:1 (weight to weight) ratio, using pH and reference half-cell electrodes. Soil test P was determined by weighing 5 cm³ of soil and extracting with 20 ml of modified Morgan solution (0.65 mol l⁻¹ NH₄OH + 1.25 mol l⁻¹ CH₃COOH buffered to pH 4.8). Extracts were shaken for 15 min, and filtered through Schleicher & Schuell 720 paper. The filtrate was analyzed for total P by inductively coupled plasma-atomic emission spectrometry (ICP-AES). Loss-on-ignition at 375°C for 2 h was used as a measure of SOM content.

The water-soluble P was obtained by adding 30 ml of DI-H₂O to 3 g soil in a 50-ml centrifuge tube. The tube was shaken on an orbital shaker for 1 h, then centrifuged at 900×g for 25 min. The supernatant was decanted and vacuum filtered through a Nucleopore polycarbonate 0.4-μm membrane filter (Whatman, Florham Park, NJ, USA). Total P concentration in the filtrate was determined by ICP-AES. Soil water-soluble C was extracted by adding 10 ml of DI-H₂O to 1 g of soil in a 15-ml centrifuge tube. The suspension was shaken on an orbital shaker for 30 min at room temperature, centrifuged at 900×g for 30 min, and filtered through 0.45 μm Gelman Acrodisc syringe filters (Pall, East Hills, NY, USA). The extraction period was selected to minimize microbial transformation during extraction (Zhou and Wong

2000). The C concentrations of the extracts were determined using a Shimadzu TOC 5000 analyzer (Shimadzu Scientific Instruments, Braintree, MA, USA).

Phosphorus saturation

Acid ammonium oxalate extraction was used to determine DPS (Iyengar et al. 1981). Twenty-five milliliter of 0.2 mol l⁻¹ ammonium oxalate adjusted to pH 3.5 was added to 0.5 g of soil in a 50-ml centrifuge tube and shaken for 4 h in the dark. The tube was then centrifuged, filtered through Nucleopore polycarbonate 0.4- μ m membrane filters (Whatman, Florham Park, NJ, USA), and analyzed for total P, Al, and Fe by ICP-AES. Percent DPS was calculated using the equation recommended by Beck et al. (2004):

$$\% \text{DPS}_{\text{OX}} = \left\{ \frac{\text{P}_{\text{OX}} (\text{mmol kg}^{-1})}{[\text{Al}_{\text{OX}} + \text{Fe}_{\text{OX}}] (\text{mmol kg}^{-1})} \right\} \times 100 \quad (1)$$

where P_{OX}, Al_{OX}, and Fe_{OX} are the oxalate-extractable content of the elements expressed on a molar basis. There are many different formulations of DPS equation used throughout the literature; many include the empirical parameter α , typically set at 0.50 or determined individually for each soil (van der Zee and van Riemsdijk 1988; Lookman et al. 1996). Use of this parameter is intended to normalize P sorption across a range of soils with different P sorption maxima. However, determination of α for each soil examined is unrealistic for routine soil or environmental testing purposes and use of a constant α factor overestimates DPS in most cases (Beck et al. 2004). Therefore, we have followed the suggestion of Beck et al. (2004) to eliminate α from the DPS equation.

Data analysis

The data were analyzed using ANOVA with Systat version 11 (Systat Software, Point Richmond, CA, USA) to determine the statistical significance of differences of chemical parameters between the SOM classifications groups. The differences were considered significant at the $p \leq 0.05$ level. Segmented regression lines were calculated using the Java™ applet Regrlines written by Andrew Ganse of the Applied Physics Laboratory, University of Washington, Seattle, WA, USA.

Results and discussion

Soil properties

The frequency histogram for the modified Morgan soil test P values of the 106 soils in this set is shown in Fig. 1a. The soil test P values ranged from 0.9 to 56.2 mg P kg⁻¹, with

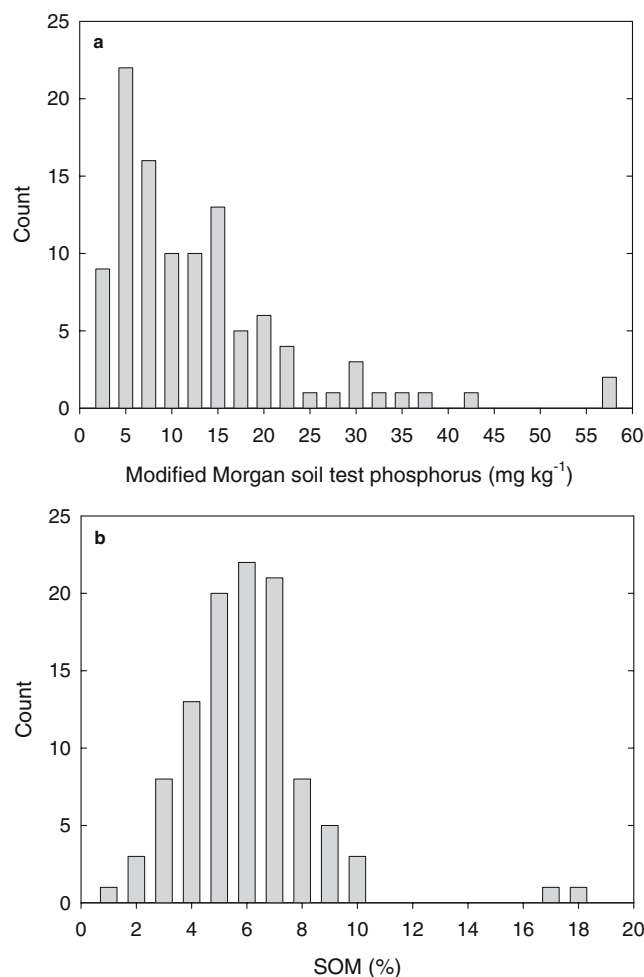


Fig. 1 Frequency histogram of **a** modified Morgan soil test phosphorus values and **b** loss-on-ignition values for the 105 soils used in this study

median and mean values of 9.3 and 11.5 mg P kg⁻¹, respectively. Although the specific P recommendations derived from the modified Morgan soil test P values are crop dependent, the general classifications of soil P status are: 0 to 2.5 mg kg⁻¹ P, low (9 of 106, 8.4%); 2.5 to 5.0 mg kg⁻¹ P, medium (22 of 106, 21%); 5.0 to 20.0 mg kg⁻¹ P, optimum (60 of 106, 57%); and greater than 20 mg kg⁻¹ P, above optimum (15 of 106, 14%) (Hoskins 1997). The SOM content, as measured by loss-on-ignition, ranged from 1.5 to 18.1% with a mean of 6.5% (Fig. 1b). To investigate the effects of SOM on soil P chemistry, the soils were divided into three arbitrarily chosen SOM groupings: low SOM (1.5 to 4.9%, $n=25$), medium SOM (5.0 to 7.5%, $n=55$), and high SOM (7.6 to 18.1%, $n=26$).

To ascertain that soils in the three SOM groupings were not distinct from each other with respect to soil chemical parameters which affect soil P behavior, the range and mean values of modified Morgan extractable K, Mg, Ca, and P and soil pH values are shown in Table 1. The

Table 1 Soil phosphorus, potassium, magnesium, and calcium content as determined by the modified Morgan soil test and the pH of the soils in the low, medium, and high soil organic matter (SOM) classification groups

Chemical parameter	Organic matter classification		
	Low OM Range (mean)	Medium OM	High OM
P soil test (mg kg ⁻¹)	0.9–27.8 (10.6)	2.3–56.2 (11.6)	0.9–55.3 (13.6)
K soil test (mg kg ⁻¹)	32–390 (157)	35–549 (165)	34–654 (172)
Mg soil test (mg kg ⁻¹)	14–166 (79)	13–324 (118)	18–551 (156)
Ca soil test (mg kg ⁻¹)	89–2,551 (881)	100–2,991 (1,202)	157–6,140 (1,882)
pH	4.6–6.9 (6.1)	4.9–7.4 (6.2)	4.8–7.4 (6.1)

modified Morgan soil test P values were not statistically different between the groups ($p=0.587$). Soil pH, which is a master variable for many soil reactions, was also not statistically different between the SOM groups ($p=0.728$). With the absence of significant differences in soil test P and pH among the SOM soil groupings, differences in P chemistry between the groups are likely to be a direct result of SOM level, rather than indirect effects caused by these two soil characteristics. Significant differences were found for the modified Morgan extractable Mg ($p=0.006$) and Ca ($p=0.001$) levels, but not for K ($p=0.920$) level of the soils in the three SOM classification groups (Table 1). Calcium and Mg levels were probably higher for soils containing higher levels of SOM because of the higher affinity of negatively charged functional groups present in SOM for divalent cations (Salmon 1964).

Interrelationships between DPS, soil test P, and water-soluble P

The water-soluble P as a function of DPS for all three SOM groups is shown in Fig. 2. A preliminary evaluation of the relationship between water-soluble P and DPS was con-

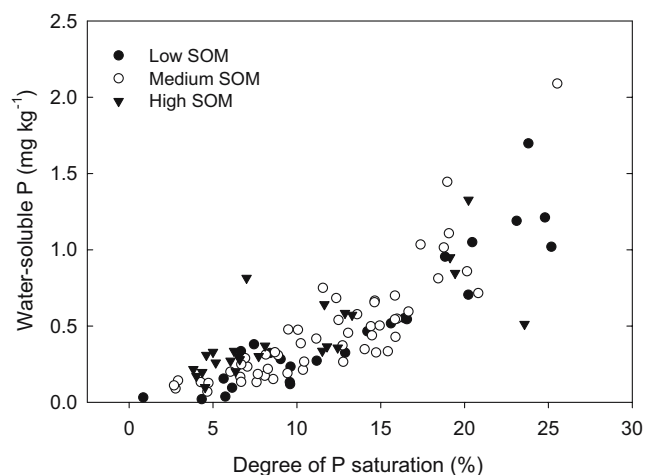


Fig. 2 Relationship between water-soluble phosphorus and oxalate-extraction based degree of phosphorus saturation for all 105 soils used in the study

ducted by fitting a linear regression to the relationship for each of the SOM groups. The 95% confidence intervals for the slope term of the linear regression of water-soluble P as a function of DPS for the low, medium, and high SOM classification groups were: 0.044 to 0.070 (mg P kg⁻¹ % DPS⁻¹), 0.049 to 0.070, and 0.024 to 0.051, respectively. The slope term for the combined pool was 0.052 mg P kg⁻¹ %DPS⁻¹. Because the combined pool slope was within the confidence interval band for the low and medium SOM classification groups, these two groups could be pooled, while the high SOM group would require separate analysis.

The concentration of water-soluble P has been shown to increase rapidly upon reaching a threshold level of DPS which has been termed the “change point” (Nair et al. 2004; Ilg et al. 2005; Maguire and Sims 2002; Breeuwsma et al. 1995). A change point of 15.4% DPS was determined a priori in the water-soluble P as a function of DPS for the low and medium SOM grouping pool, but no change point was observed for the high SOM group (Fig. 3). The slope above the “change point” was greater by a factor of 2.8 than the slope below the change point which supports previous research that a threshold point exists where the risk of increased water-soluble P increases substantially. The slope of the single water-soluble P vs DPS function of the high SOM group was identical to the slope of the initial (below the “change point”) phase of the water-soluble P vs DPS relationship of the low and medium SOM groupings. It is possible that higher levels of SOM inhibit the release of water-soluble P from higher DPS soils. However, there are only four high organic matter soils with DPS values greater than the change point, making it difficult to draw conclusions.

The oxalate-extractable DPS index was developed for acid soils and the presence of high pH soils in our sample set may affect the relationship between DPS and water-soluble P. Soils with pH values of 6.8 and higher, which accounted for 15 of the 106 soils in the set, were removed and the two-segment linear regression was recalculated. The new change point was 15.2% DPS and the two slopes were 0.036 and 0.105 mg P kg⁻¹ %DPS⁻¹ for the combined low and medium SOM pool with the high pH soils removed

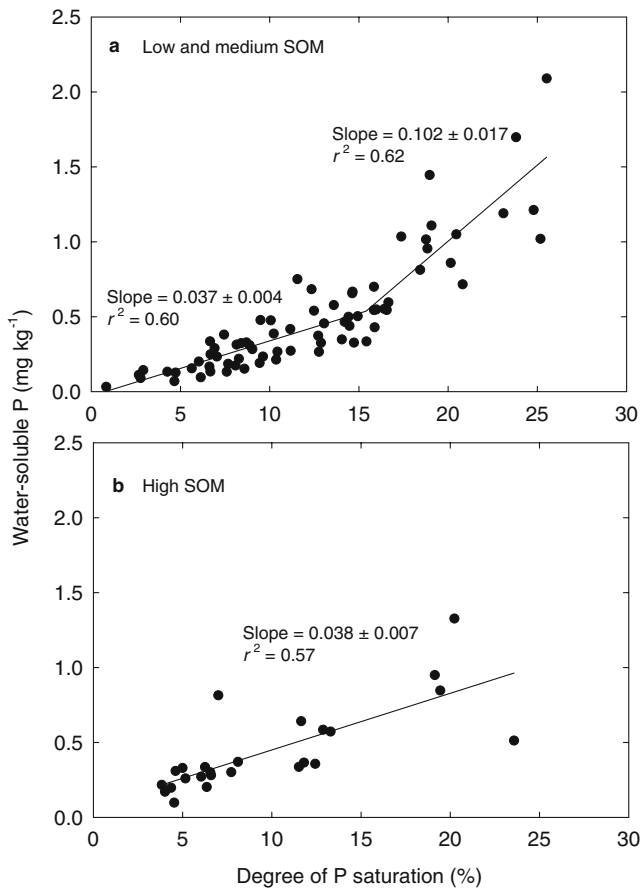


Fig. 3 Relationship between water-soluble phosphorus and oxalate-extraction based degree of phosphorus saturation for **a** combined low and medium soil organic matter groups and **b** for the high soil organic matter group

as compared to the change point of 15.4% and slopes of 0.037 and 0.102 mg P kg⁻¹ %DPS⁻¹ for the set which included the high pH soils. This indicates that the presence of higher pH soils did not affect the overall relationship. When the high pH soils were removed from the high SOM sample group, no change point was observed, and the slope was 0.040 mg P kg⁻¹ %DPS⁻¹, similar to the results found for high SOM soils that included the high pH soils.

Although oxalate extraction-based DPS values are generally well-correlated with water-soluble P, oxalate extractions are rarely used in routine soil testing. To evaluate whether the modified Morgan soil test P value could be used as a proxy for oxalate extractions, the relationship of the modified Morgan soil test P and DPS was investigated (Fig. 4). The modified Morgan extract removed an average of 60% of the P removed by oxalate across all three organic matter groupings (data not shown). The modified Morgan soil test P as a function of DPS also revealed a change point at 15% DPS. The change point corresponds to a soil test P value of 14 mg P kg⁻¹, which is toward the higher end of the optimum soil test P

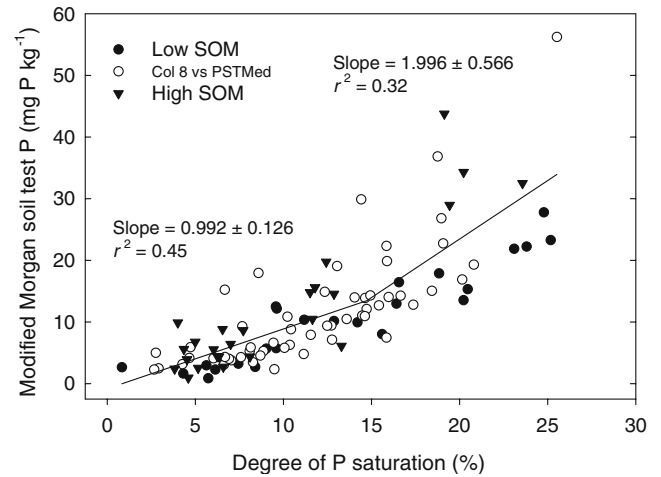


Fig. 4 Relationship between modified Morgan soil test phosphorus and oxalate-extraction based degree of phosphorus saturation for all 106 soils used in the study

classification group, with 34 of the 105 soils (32.4%) above this change point.

Unlike the DPS results, prediction of water-soluble P as a function of soil test P was best when the three SOM groups were considered separately (Fig. 5). The slopes of the linear regression lines decreased with increasing levels of SOM [0.050, 0.036, and 0.021 (mg water-soluble P kg⁻¹ soil/mg soil test P kg⁻¹) for the low, medium, and high SOM classification groups, respectively] This suggests that higher SOM levels decrease the amount of P in soil solution for a given amount of soil test P. Assuming that soils with higher SOM levels potentially support higher levels of water-soluble C than soils with lower SOM levels, this was an unexpected result. There is a significant amount of evidence in the literature suggesting that soluble organic molecules can inhibit the sorption (or precipitation) of soil P through direct competition with ligand exchange sites and the formation of soluble complexes with metals that would otherwise precipitate P (Iyamuremye and Dick 1996; Ohno and Crannell 1996).

SOM effects on water-soluble C and DPS

There is a positive relationship between SOM and water-soluble C in these soils (Fig. 6). The regression lines shown are for the low SOM and the high SOM groups; both were significant at the 5% level. The regression for the medium SOM soil data was not significant at the 5% level. The magnitude of the slope is significantly lower for the high SOM group than for the low SOM group, indicating less increase in soluble C with increasing organic matter content in the high SOM group. This may simply indicate a lesser degree of humification in higher organic matter soils. This may also be due to sorption of the organic ligands to the metal oxide surfaces in the high SOM soils. However,

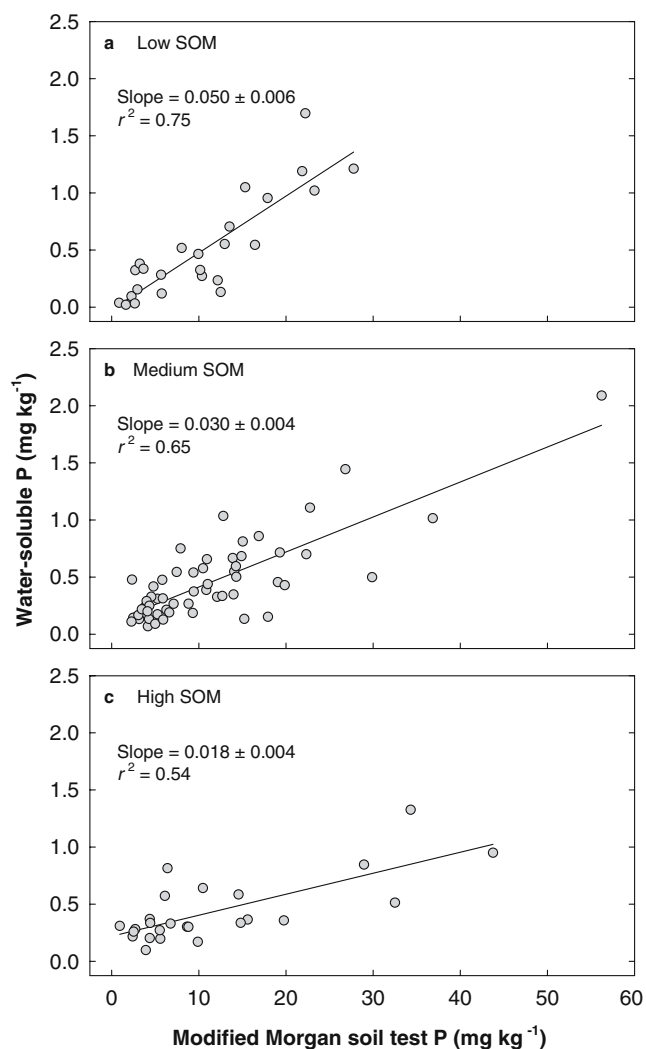


Fig. 5 Relationship between water-soluble phosphorus and modified Morgan soil test phosphorus for the **a** low soil organic matter group, **b** medium soil organic matter group, and **c** high soil organic matter group

many factors influence the level of soluble C found in these soils. These soils had been air dried and stored at room temperature for several months before determination of water extractable C. It is known that rewetting of dried soils produces a flush of soluble C due partly to the lysing of microbial cells and release of microbial biomass C. Mineralization of the C released upon rewetting forms the basis for one method of estimating soil microbial biomass (Franzleubbers et al. 2000). There is some evidence in the literature that the amount of C released upon rewetting dried soil may increase with increased storage time and storage temperature (Houba and Novozamsky 1998). Given the positive correlation between water-soluble C and SOM, it seems likely that rewetting releases some fraction of SOM in addition to microbial biomass C. The contribution of microbial biomass C to the level of soluble C may be proportionately larger in the lower SOM soils.

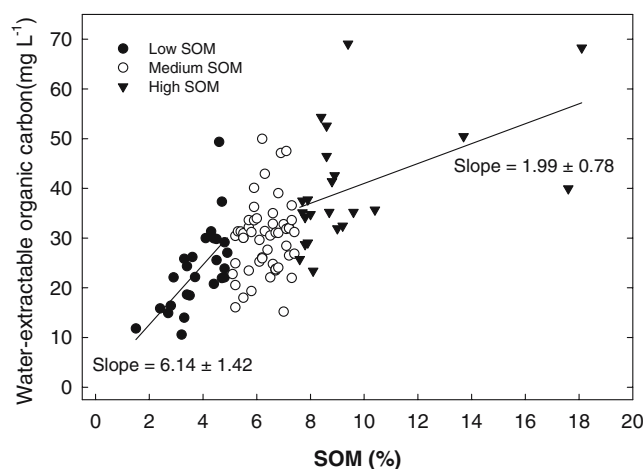


Fig. 6 Relationship between dissolved organic carbon content and loss-on-ignition for the three soil organic matter classification groups used in the study. The regression lines shown are for the low and high SOM groups which were significant at the 5% level

The median values of DPS were 7.0, 11.6, and 11.2 for the high, medium, and low SOM groups, respectively. The frequency distribution of DPS values for the high SOM group and the combined low and medium group is shown in Fig. 7. The frequency distribution visually shows that the soils in the high SOM group are distributed towards the lower DPS levels as compared to the pooled low and medium SOM grouping. Degree of P saturation may be lower in soils with higher levels of organic matter due to several factors. Soils with higher amounts of organic matter may have: (1) lower amounts of P sorbed than soils with lower levels of organic matter, (2) higher amounts of oxalate-extractable Al and Fe because they have higher

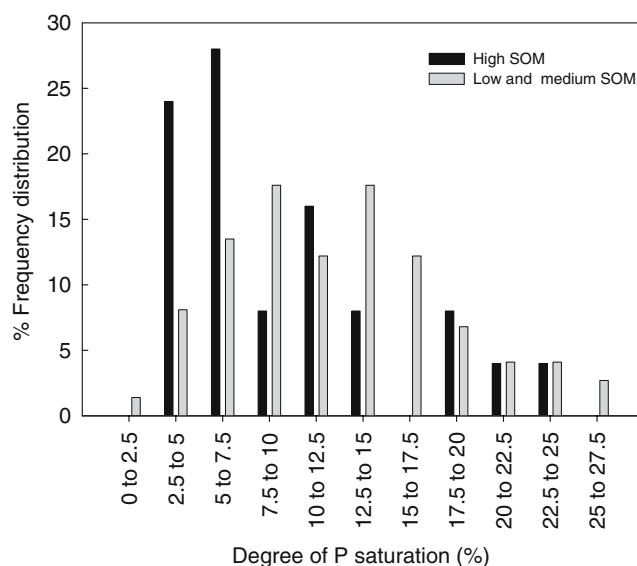


Fig. 7 Frequency histogram of degree of phosphorus saturation for the combined low and medium SOM soils and the high SOM soils used in this study

native amounts of metal oxides, or (3) higher amounts of oxalate-extractable Al and Fe due to higher amounts of organically complexed Al and Fe.

There is a significant ($p=0.001$) effect of the SOM classification groupings on the sum of oxalate-extractable Al and Fe content of the soils (data not shown). This suggests that one factor in the lower DPS values for the high SOM soil group is a greater sorptive capacity for P. Metal oxides have a preponderance of surface hydroxyl groups, i.e., Lewis acid sites (Sposito 1984). Metal oxides have been shown to contain high affinity sorption sites for dissolved organic matter (Baldock and Skjemstad 2000). Ligand exchange reactions involving carboxyl and hydroxyl groups of organic matter and surface hydroxyl groups of oxides have been reported to be the predominant mechanism for soluble C sorption onto metal oxides (Gu et al. 1994). Thus, metal oxide content is often correlated with the sequestering of soil organic C (Kaiser and Guggenberger 2000; Hughes 1982), and it is reasonable to postulate that higher levels of oxalate extractable Al and Fe in the higher organic matter soils indicate higher levels of metal oxides in these soils.

It is also likely that some of the oxalate-extractable Al and Fe in these soils may be derived from Al and Fe complexed by SOM (Schnitzer and Skinner 1964). Organically held Al and Fe have been shown to contribute to the P sorption capacity of a soil. Bloom (1981), using peat as a model for SOM, found that Al-substituted peat strongly adsorbed P, although H-saturated peat (pH 4.8) did not. Borggaard et al. (1990) found that removal of organic matter from soils with H_2O_2 decreased P sorption only when extractable Al and Fe also decreased. Zhang et al. (2005) used path analysis to partition direct and indirect effects of various soil properties on P sorption. They observed an indirect correlation between SOM and P sorption and suggested that this was the result of P sorbed by Al and Fe associated with organic matter.

Conclusion

The modified Morgan soil test P values were well correlated with both DPS and water-soluble P for all 106 soils examined, including some high pH soils. The relationship between DPS and water-soluble P showed a change point at about 15% DPS; above 15% DPS, water-soluble P increased more rapidly than below this value. The change point is similar to that observed in other studies (Nair et al. 2004; Maguire and Sims 2002; Breeuwsma et al. 1995). The relationship between DPS and modified Morgan soil test P also showed a change point at 15% DPS, a value which corresponds to 14 mg soil test P kg^{-1} . This level of modified Morgan soil test P represents a threshold above which water-soluble P is expected to increase more rapidly with additional P loading. Although SOM had a strong influence on the relationship

between soil test P and water-soluble P, the relationship between DPS and water-soluble P was less affected by SOM level. There was no evidence that P solubility was enhanced in soils with higher levels of organic matter; in fact, soils with higher levels of organic matter tended to have less P in solution at all levels of soil test P than soils with lower levels of organic matter. Higher SOM levels were associated with higher levels of oxalate-extractable Fe and Al and, therefore, higher P sorption capacities and lower DPS values.

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