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Degree of phosphate saturation in highly weathered tropical soils

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ABSTRACT

The degree of phosphate saturation (DPS) is an indicator for P-saturation, which is of assistance to the prediction of P losses and potential eutrophication of surface water. The scaling factor (α) estimates the adsorption capacity of the soil and is used to calculate the DPS. In soils from temperate regions, the value of α = 0.5 is widely used. However, using just a single value for α may fail to estimate the adsorption capacity correctly for all soils. In this study, the aims were (i) to calculate the scaling factor α and the DPS of highly weathered tropical soils with different chemical, physical and mineralogical properties in order to predict P losses; and (ii) to identify which soil properties are related to P adsorption. The scaling factor α and the DPS were calculated at 1, 3, 7, 21, 42 and 84 days (d), the highest one in recognition of the long-term kinetics of sorption. The values of α increased as the contact period increased. Lower DPS values were obtained in soils with high P adsorption capacity whereas the highest DPS values were obtained in soils with a lower adsorption capacity. Out of ten Oxisols studied, six of them had an α higher than 1. Contents of clay, organic carbon (C) and poorly crystalline (Al_{ox}) and crystalline ("free") Al oxides were the properties that best correlated with P adsorption. For the Oxisols, the clay content, poorly crystalline together with crystalline Fe and Al oxides represented the main components related to P adsorption. The highest DPS (31%) was found in Typic Udorthent. The content of poorly crystalline oxides was not suitable for the scaling factor α for most Oxisols, and only the Typic Udorthent exceeded the critical threshold of 23%, and is thus more susceptible to loss of P.

1. Introduction

The degree of phosphate saturation (DPS) is an indicator of the risk of loss of P from soil. Such losses are mainly a consequence of runoff and eventual leaching. The DPS has been used in countries such as the Netherlands (Van Der Zee and Van Riemsdijk, 1988), Germany, (Freese et al., 1992; Freese et al., 1995), Belgium (Lookman et al., 1995; Lookman et al., 1996), Ireland (Maguire et al., 2001), the United States (Paulter and Sims, 2000; Nair et al., 2004), and Canada (Ige et al., 2005). A major motivation for its use has been the risk of accumulation of P in surface waters in regions with relatively intensive animal husbandry. In contrast to temperate regions, humid tropical regions have highly weathered soils, high contents of Fe, Al and Mn hydroxides, and 1:1 aluminosilicates minerals with a strong tendency to adsorb P (Mesquita Filho and Torrent, 1993).

Because soils have a P critical saturation level, above which too much leaching may occur (Van Der Zee, 1988), the DPS becomes important as long as it is a potential indicator of contamination risk in the case of further P additions (Paulter and Sims, 2000). When determining the DPS level, the P content already present in the soil (P_{ox}) in relation to the maximum retention capacity has to be taken into consideration, principally when it correlates positively with the P dissolved in the runoff and the leached solutions (Liu et al., 2012; Wang et al., 2010).

The P sorption index (PSI) is a tool for assessing the potential of P to move from agricultural fields to surface water and indicates the current P adsorption capacity based on a single point from an adsorption isotherm (soil as sampled). The P sorption capacity (PSC) is a parameter which estimates the maximum amount of P that a given soil is able to adsorb. It is calculated by using the sum of the PSI and the content of P extracted by ammonium oxalate (P_{ox}). In this respect, the use of a saturation index, known as a scaling factor α is convenient as it directly relates the amount of P adequately sorbed to those soil properties that determine sorption. This factor is calculated as the molar ratio of the

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PSC ($mmol\,kg^{-1}$) over the sum of the poorly crystallized content ("amorphous") of Fe and Al extracted by an acid solution of ammonium oxalate (Fe_{ox} and Al_{ox} in $mmol\ kg^{-1}$), which can be regarded as a critical value of the DPS (Maguire et al., 2001). In this respect, the latter is based on the amount of P adsorbed to a soil at the moment that the soil is sampled, i.e., without further P adsorption in the lab. If oxalate extractable Fe and Al control P-sorption, the DPS relates P already adsorbed by a soil to its P adsorption capacity.

The value of $\alpha = 0.5$ has been widely used for soils found in temperate regions (Van Der Zee and Van Riemsdijk, 1988; Schoumans, 2009). The use of only a single α value, however, implies that all soils have a similar molar ratio ($PSC/(Fe_{ox} + Al_{ox})$). Beauchemin and Simard (1999) suggest that it is necessary to establish different values of α for groups or types of soils or even a separate value for each soil. In Brazil, DPS and saturation indexes have hardly been investigated, and it has not been established whether different soil types would be better characterized with different α values, in order to identify environmental risk. The scope of this paper is to determine α values for highly weathered tropical soils with different properties than those investigated so far and relate the scaling parameters with such properties. Consequently, by relating the DPS to certain of the soil properties in tropical humid regions, it may be possible to generalize the risk assessment to locations where soil map information is available, but where α has not been experimentally determined.

Our purpose was to calculate the parameterś scaling factor α, PSC and DPS for highly weathered tropical soils with different chemical, physical and mineralogical properties, and identify which soil properties are related to the DPS, PSC and P sorption index (PSI) by using the principal component analysis technique (PCA). We also selected those soils with high susceptibility to P losses and high potential for surface water eutrophication.

2. Materials and methods

A total of 29 soil samples from the topsoil layer (0–20 cm) with different chemical, physical and mineralogical properties were collected in forest, native and riparian forests and old reforestation in the state of Sao Paulo, Brazil, which had not been fertilized with either organic manure or commercial fertilizers. Soil samples were classified under the following soil types: Oxisols, Ultisols, Alfisols, Entisols, Inceptisols, Histosols and Mollisols (Soil Survey Staff, 1999).

Soil samples were chemically characterized using air-dried soil passed through a 2-mm sieve (10 mesh). Carbon content (C) was determined by a modified Walkley-Black method (Nelson and Sommer, 1982). Organic carbon content was measured in soil samples passed through a 100-mesh sieve after oxidation of organic matter in the soil with 0.167 M potassium dichromate solution ($K_2Cr_2O_7$) in the presence of concentrated sulfuric acid (Nelson and Sommer, 1982). Particle size analysis to determine the clay content was based on the hydrometer method (Gee and Or, 2002). The Fe and Al crystalline oxide contents were obtained by reacting the soil sample with a sodium dithionite-citrate-bicarbonate solution (Mehra and Jackson, 1960) and determined by atomic absorption spectrophotometry (AAS). The poorly crystallized forms of Fe, Al and P were extracted using 0.1 M oxalic acid solution + 0.2 M ammonium oxalate at pH = 3.0 (Schoumans, 2009) and determined by Inductively Coupled Plasma – Optical Emission Spectrometry (ICP-OES). In addition, the bioavailable P content was extracted by Mehlich 1 solution (0.0125 M H_2SO_4 + 0.05 M HCl) and water (Kuo, 1996).

2.1. Phosphorus sorption index

The PSI was calculated in order to determine the addition of a single amount of P (Bache and Williams, 1971). Therefore, 2.5 g of air-dried and 2-mm sieved soil samples were given 25 mL 0.01 M $CaCl_2$ (supporting electrolyte) with rates of P (KH_2PO_4) calculated from the maximum P adsorption capacity (S_{max}), previously measured by Langmuir isotherm (data not shown). The samples were divided into five groups, and the soils within each group received a concentration of P in proportion to their adsorption capacity (de Campos et al., 2016). The groups were divided as follows: I – Very high adsorption capacity ($S_{max} > 2000\,mg\,kg^{-1}$); II – High adsorption capacity (S_{max} between 1000 to $2000\,mg\,kg^{-1}$); III – Medium adsorption capacity (S_{max} between 500 and $1000\,mg\,kg^{-1}$); IV – Low adsorption capacity (S_{max} between 200 and $500\,mg\,kg^{-1}$); and V – very low adsorption capacity ($S_{max} < 200\,mg\,kg^{-1}$). The conversions into $mmol\,kg^{-1}$ of P and PO_4^{3-} are presented in the Appendix A.

The maximum contact period of samples in order to calculate the PSI was 84 d (12 weeks). During this period, P concentrations in solution were assessed at 1, 3, 7, 21, 42 and 84 d. The samples were analyzed in triplicate for each reaction period, and stirred daily for 2 h in a horizontal shaker at 150 osc min^{-1} after the first 24 h of stirring. After that, the samples were centrifuged at 1844 × g for 15 min, and an aliquot of the extract was taken to determine the P content by colorimetry (Murphy and Riley, 1962). The adsorbed P was calculated as the difference between the P added and the P remaining in the solution, and the PSI calculated using Eq. (1) as follows:

$$PSI\ (mmol\,kg^{-1}) = [X/(\log C)/(30.97)] \quad (1)$$

where: $X = P$ adsorbed $(mg\,kg^{-1}) = (P_i - P_f) \times (0.025\,L)/(0.0025\,kg$ soil); P_i = Initial P concentration ($mg\,L^{-1}$); P_f = Final concentration of P in the equilibrium solution ($mg\,L^{-1}$); C = Concentration of P at the reaction time when measured ($mg\,L^{-1}$); and 30.97 = phosphorus molar mass.

2.2. Scaling factor α and degree of phosphorus saturation

The scaling factor α was estimated by using the equation described in Van Der Zee and Van Riemsdijk (1988):

$$\alpha = (PSI_{84d} + P_{ox})/(Al_{ox} + Fe_{ox}) \quad (2)$$

where PSI_{84d} is the P sorption index at 84 d of reaction ($mmol\,kg^{-1}$), $Al_{ox} + Fe_{ox}$ correspond to the amount of poorly crystallized oxides of Fe and Al, and P_{ox} is the P content linked to oxides.

In the α calculation, the PSI_{84d} was adopted as the index of soil adsorption capacity in the long-term. The P_{ox} levels were deemed to estimate the P sorption capacity ($PSC = PSI_{84d} + P_{ox}$), where P_{ox} is the amount of P already adsorbed to the poorly crystalline structures. Thus, we followed an approach that was different from McGechan and Lewis (2002), who disregarded P already adsorbed by soil.

The DPS (%) was calculated as the ratio of the P_{ox} content already accumulated in the top soil (0.0–0.2 m) to the P sorption capacity given by $PSC = P_{ox} + PSI_{84d}$ (Van Der Zee and Van Riemsdijk, 1988), i.e.,

$$DPS\ (\%) = 100 * P_{ox}/PSC \quad (3)$$

2.3. Statistical analysis

The correlations between soil properties and DPS, PSI and PSC were evaluated by principal component and cluster analyses (PCA and Cluster, respectively) in order to identify the soil properties best correlated with the studied variables. PCA is a multivariate statistical method that aims to explain the major part of variations in data from a smaller number of components, which are linear combinations of the properties (Anderson, 2003). Multivariate analyses and multiple regressions were performed using the Statistica® software program (Statsoft, 2005). The criteria used to determine the factors followed the Kaiser Rule, taking into account eigenvalues ≥1 to explain over 85% of the total variance (Kaiser, 1958). Correlations had to be $\geq |0.70|$ to be considered (Manly, 1994).