Phosphorus adsorption in lowlands of Santa Catarina cultivated with rice and its relation with soil properties

Adsorção de fósforo em solos orizícolas catarinenses e sua relação com atributos do solo

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ABSTRACT - Soils have different capacities to retain phosphorus (P). In seasonal flooded soils iron (Fe) oxides and hydroxides of poor crystallinity, increase with time, and could be the most important constituent in P adsorption, during the time the soils remain unflooded. The present paper had the objective to determine the maximum adsorption capacity of P (MACP), collected from five selected soils in lowland rice areas in the Santa Catarina state, to search for soil individual parameters that best correlates with maximum adsorption capacity of P (MACP). The rates of P used to determine the MACP were calculated based on the concentration of indigenous P in the soil. The sorption of P and the P in solution data were then fitted to the Langmuir sorption isotherm equations. The results obtained for the parameters ‘a’ and ‘b’ (binding energy and MACP, respectively) were correlated with selected soil parameters. The Langmuir equations adequately described P adsorption in the soils. The maximum sorption of P varied widely, ranging from 0.419 to 1,450 mg g⁻¹, where the organic soil (OXs) presented very high MACP, which could lead to a less availability of the element to the plants. The coefficients of correlation showed a significant association between MACP and the following soil parameters: P indigenous, Fe oxides extracted with ammonium oxalate at pH 3.0 (Fe₃o) and pH 6.0 (Fe₆o), as well as the ratios Fe₃o/Fe₅ and Fe₆o/Fe₅, suggesting that these chemical parameters can be utilized to characterize the P adsorption in these soils.

Key words: Oryza sativa. Isotherm of Langmuir. Flooded soils.

RESUMO - Os solos têm capacidades diferentes de reter o fósforo (P). Em solos sazonalmente alagados, óxidos e hidróxidos de ferro (Fe) de baixa cristalinidade tornam-se predominantes com o passar do tempo, e poderão ser os componentes mais importantes na adsorção de P, durante o período em que o solo permanece drenado. Deste modo, o presente trabalho teve por objetivo avaliar a capacidade máxima de adsorção de P (CMAP) de cinco solos catarinenses, utilizados no cultivo de arroz irrigado e buscar atributos que estimem a CMAP. As doses para a determinação da CMAP foram calculadas com base no P remanescente (P-rem), sendo os dados de P sorvido e P solução ajustados pela equação de Langmuir. Os valores obtidos para os parâmetros energia de ligação (a) e CMAP (b) foram submetidos a partir da análise de correlação com alguns atributos dos solos. O modelo de Langmuir adequou-se aos valores de P adsorvidos pelos solos. A maioria dos solos estudados apresentou CMAP elevada, variando de 0.419 a 1,450 mg g⁻¹, onde o solo orgânico (OXS) apresentou CMAP muito alta, o que poderá acarretar em uma maior disponibilização do elemento para as plantas. Os coeficientes de correlação demonstraram haver associação significativa entre a CMAP e os parâmetros P-rem, óxidos de Fe extraído por oxalato de amônio a pH 3 (Fe₃o) e pH 6 (Fe₆o), bem como para as relações Fe₃o/Fe₅ e Fe₆o/Fe₅, revelando que esses atributos podem ser utilizados para caracterizar a adsorção de P dos solos avaliados.

INTRODUCTION

Adsorption of P by the soil is one of the main mechanisms that affect P availability to the plants. Studies involving P adsorption can be adequate to predict the behavior P adsorption in the soil as well as to manage fertilizer recommendation in terms of quantity, type, frequency and method of application in order to improve the efficiency of applied P (AFSAR; HOSSAIN, 2012).

Methods used to predict P availability in waterlogged soils are not as efficient as those used for aerated soils (CHANG, 1978). This is the result of the increase on solution P following waterlogging, which cause reduction of Fe³⁺ to Fe²⁺ due to a decrease on redox potential, increasing P availability to the plants (CHACON et al., 2006), and the magnitude of this phenomenon varies according to some soil characteristics, including mineralogical, chemical and electrochemical attributes (GONÇALVES et al., 2011).

Following alternates of wetting-drying cycles in the soil, poorly crystallized iron oxides and hydroxides, such as lepidocrocite and ferrihydrate, which have higher specific surface area and higher chemical reactivity than well crystallized fractions, become predominant over time (HERNÁNÉZ; MEURER, 2000) and they can be the most important soil compounds to adsorb P during the period of drying (RANNO et al., 2007). In addition, different soils will have variations on maximum adsorption capacity of P (MACP) and on binding energy between P compounds and soil colloids with consequences on the amount of labile P (CORRÊA; NASCIMENTO; ROCHA, 2011).

Some mathematical models have been used to describe P sorption in many soil types, and the Langmuir model is the most commonly used to describe P adsorption isotherms (GONÇALVES et al., 2011; MELO et al., 2015; RANNO et al., 2007). This model estimates two constants: the ‘a’ constant is related to the binding energy of P to the soil, and the ‘b’ constant is related to the MACP. Some authors (GONÇALVES et al., 2011; RANNO et al., 2007; SILVA NETO et al., 2015) found correlations between MACP and chemical, physical and mineralogical characteristics of many soils.

Thus, it is important to study the dynamics of P involving characterization and quantification of the parameters that affect its adsorption to the mineral components of the soil as well as the stability of the reactions in seasonally flooded soils with different source materials. In addition to improving the understanding of the adsorption process of P and its availability to plants, it will allow the use of these parameters in chemical methods of P quantification and its inclusion in the interpretation of P availability to improve phosphate fertilization for irrigated rice.

This study aimed to evaluate the MACP and its association with some soil attributes of five soils previously cropped with rice under the waterlogging system in the State of Santa Catarina, Southern of Brazil.

MATERIAL AND METHODS

This study was carried out in Lages, SC, Southern of Brazil, in 2015. Five soils were collected from fields usually cropped with rice in the wetting-drying system in the State of Santa Catarina. They included an Organossolo Háplico Sáprico típico, OXs, (Hasplosaprists) collected in the municipality of Jaguaruna (28º27’23” S, 49º00’18” W), a Gleissolo Háplico tê Distrófico típico, GXbd, (Endoaquents) collected in the municipalities of Gaspar (G) (26º57’47” S, 48º57’37” W) and Itajaí (I) (26º56’44” S, 48º45’29” W), a Cambissolo Háplico tê Distrófico típico, CXbd, (Dystrudepts), collected in the municipalities of Itajaí (I) (26º56’41” S, 48º45’48” W) and Pouso Redondo (PR) (27º14’34” S, 49º58’49” W).

All soils (150 kg each) were collected after rice harvest from the surface layer of 0-20 cm depth. Then, they were air-dried and passed through a 2.0 mm screen and analyzed. Chemical attributes were determined according to Tedesco et al. (1995) and physical attributes according to Embrapa (1997).

Crystalline iron oxides (Fe₃⁺) were extracted with dithionite-citrate-bicarbonate (DCB) method at 80 ºC (MEHRA; JACKSON, 1960), in two successive extractions, each with a 15 minutes shaking. A sample of 0.2 g of soil was placed in a 50 mL centrifuged bottle that received 40 mL of a solution containing 0.3 mol L⁻¹ sodium citrate and 1.0 mol L⁻¹ sodium bicarbonate at a 8:1 ratio. In each extraction, it was used 1.0 g of sodium dithionite, divided in three portions of 0.33 g each, and a shaking time of one minute.

After the addition of each sodium dithionite aliquot, the suspension was stirred for 1 minute, at a water bath temperature of 80 ºC. At the end of each extraction, the suspension was centrifuged at 3,000 rpm for 10 min and the extract completed to 50 mL with the citrate-bicarbonate solution.

Poorly crystallized iron oxides (Fe₂⁺) were extracted with ammonium oxalate [(NH₄)₂C₂O₄·H₂O] 0.2 mol L⁻¹ at pH 3.0 (Fe₃⁺) and pH 6.0 (Fe₂⁺), in the dark. The desired pH values were previously adjusted according to Schwertmann (1964). Ammonium oxalate (40 ml) was added to 0.2 g of soil in centrifuged tubes of 50 ml covered with aluminum paper. Tubes were shaken for 2 hours in the dark, following by 5 minutes of centrifugation. Then, the supernatant was transferred...
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The amounts of adsorbed P, obtained from the Langmuir equation, were compared to those obtained experimentally, in order to evaluate the ability of the model to fit the experimental data. Simple linear correlation analysis were performed between the “a” and “b” parameters and the soil attributes related to P adsorption, considering all soils or only the group of mineral soils. Statistical analysis was performed with the SAS® software.

RESULTS AND DISCUSSION

General characteristics of the soils

The original attributes of the five soils previously cropped with rice are presented on Table 1.

Phosphorus adsorption

The amount of P adsorbed by the soils increased with increases on P added (Figure 1). Initially, the adsorption occurred with high intensity and, in the highest rates, there was a tendency of stabilization, even in the soils containing high contents of oxides (Table 2), demonstrating a decrease on P adsorption as the saturation sites proceed like what was found by Oliveira et al. (2014). When P is added to the soil, there is a initial phase of P retention, which is rapid due to the electrostatic attraction, followed by a phase not too fast caused by P adsorption through ligand exchange, mainly OH⁻ and OH₂⁺ located in

to volumetric flasks of 50 ml and the volume completed with ammonium oxalate. In the supernatants extracted with dithionite and oxalate at pH 3.0 and 6.0, Fe contents were determined by atomic absorption spectroscopy, and the ratios Fe_o3/Fe_d and Fe_o6/Fe_d were calculated.

The concentrations of P used in the equilibrium solutions depended on the values of remaining P (rem-P) in the soils, obtained according to Alvarez et al. (2000). For the GXbd-G soil, which had rem-P between 30 and 44 mg L⁻¹, we used 0, 8, 12, 20, 30, 40, 50, 60, 70 and 80 mg L⁻¹ P; for the CXbd-I soil, which had rem-P between 19 and 30 mg L⁻¹, we used 0, 5, 10, 15, 25, 35, 50, 65, 80, 95 and 110 mg L⁻¹ P; for the other three soils, OXs, GXbd-I and CXbd-P, which had rem-P between 10 and 19 mg L⁻¹, we used 0, 7.5, 15, 30, 45, 60, 75, 90, 110, 130 and 150 mg L⁻¹ P. These P rates were added to triplicate soil samples, in a soil: solution ratio of 1:10. Then, tubes were shaken for 16 h, centrifuged, and subsequently P was quantified in the solution.

Following, the Langmuir sorption isotherm model was used to fit the experimental P adsorption data (adsorbed P and P in solution) according to the following Equation:

\[
\text{Adsorbed P} = \left( a \times b \times \text{solution P} \right) ÷ \left( 1 + a \times \text{solution P} \right),
\]

where Adsorbed P = amount of P adsorbed per unit of soil mass (mg g⁻¹); a = constant related to the binding energy (L mg⁻¹); b = maximum adsorption capacity of P (MACP) (mg g⁻¹); and solution P = concentration of P in the equilibrium solution (mg L⁻¹). Thus, the “a” and “b” parameters were estimated from the hyperbolic model.

Table 1 - Original attributes of the soil samples collected from the 0-20 cm depth in rice croplands in the Santa Catarina State

<table>
<thead>
<tr>
<th>Atributo</th>
<th>Soil¹</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>OXs</td>
</tr>
<tr>
<td>pH (H₂O)</td>
<td>5.6</td>
</tr>
<tr>
<td>OM (g kg⁻¹)</td>
<td>218</td>
</tr>
<tr>
<td>Rem-P (mg L⁻¹)²</td>
<td>13</td>
</tr>
<tr>
<td>P (mg dm⁻³)³</td>
<td>3.41</td>
</tr>
<tr>
<td>K (cmol_d dm⁻³)⁴</td>
<td>0.83</td>
</tr>
<tr>
<td>Ca (cmol_d dm⁻³)⁵</td>
<td>10.89</td>
</tr>
<tr>
<td>Mg (cmol_d dm⁻³)⁵</td>
<td>4.71</td>
</tr>
<tr>
<td>Al (cmol_d dm⁻³)⁵</td>
<td>0.00</td>
</tr>
<tr>
<td>H+Al (cmol_d dm⁻³)⁵</td>
<td>10.90</td>
</tr>
<tr>
<td>CTCpH7 (cmol_d dm⁻³)</td>
<td>27.33</td>
</tr>
<tr>
<td>Sand (g kg⁻¹)</td>
<td>746</td>
</tr>
<tr>
<td>Silt (g kg⁻¹)</td>
<td>73</td>
</tr>
<tr>
<td>Clay (g kg⁻¹)</td>
<td>181</td>
</tr>
</tbody>
</table>

¹OXs: Organossolo Háplico Sáprico típico (Haplosaprist)-Jaguaruna; GXbd-G: Gleissolo Háplico tb Distrófico típico (Endoaquents); GXbd-I: Gleissolo Háplico tb Distrófico típico (Endoaquents)-Itajaí; RCXbd-I: Cambissolo Háplico tb Distrófico típico (Dystrudepts)-Itajaí; CXbd-P: Cambissolo Háplico tb Distrófico típico (Dystrudepts)-Pouso Redondo. ²Remaining P. ³Extracted by Mehlich-1
the oxyhydroxide surfaces (NOVAIS; SMYTH; NUNES, 2007). As a result, P adsorption can decrease by frequent addition of this nutrient to the soil over time. The adsorption curves adjusted to the mathematical model of Langmuir were similar to those obtained using the experimental data (Figure 1). The determination

Figure 1 - Phosphorus adsorption as affected by the equilibrium concentration and curves obtained from the experimental data or from those estimated from the hyperbolic Langmuir model for the following soils: OXs= Organossolo Háplico Sáprico típico (Haplosapríst)-Jaguaruna; GXbd-G= Gleissolo Háplico tb Distrófico típico (Endoaquents); GXbd-I = Gleissolo Háplico tb Distrófico típico (Endoaquents)-Itajaí; CXbd-I = Cambissolo Háplico tb Distrófico típico (Dystrudepts)-Itajaí; CXbd-P = Cambissolo Háplico tb Distrófico típico (Dystrudepts)-Pouso Redondo.
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Table 2 - Adjustment parameters obtained from the Langmuir isotherms, Fe forms, and ratios of Fe oxides with different degrees of crystallinity on soil samples collected from the 0-20 cm depth in rice croplands in the Santa Catarina State

<table>
<thead>
<tr>
<th>Solo</th>
<th>Parameters</th>
<th>Iron Forms</th>
<th>Ratios</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CMAP (b)</td>
<td>a</td>
<td>Feď</td>
</tr>
<tr>
<td>OXs</td>
<td>1.450</td>
<td>0.430</td>
<td>11.83</td>
</tr>
<tr>
<td>GXbd-G</td>
<td>0.419</td>
<td>0.810</td>
<td>13.03</td>
</tr>
<tr>
<td>GXbd-I</td>
<td>0.849</td>
<td>0.669</td>
<td>13.51</td>
</tr>
<tr>
<td>CXbd-I</td>
<td>0.693</td>
<td>0.517</td>
<td>17.65</td>
</tr>
<tr>
<td>CXbd-P</td>
<td>0.823</td>
<td>0.796</td>
<td>15.63</td>
</tr>
</tbody>
</table>

OXs: Organossolo Háplico Sáprico típico (Haplusapr-Itajai; GXbd-G: Gleissolo Háplico tb Distrófico típico (Endoaquents); GXbd-I: Gleissolo úmido úmido típico (Endoaquents)-Itajaí; CXbd-I: Cambissolo Háplico tb Distrófico típico (Dystrudepts)-Pouso Redondo. 2Parameter from Langmuir isotherms, where MACP is the maximum adsorption capacity of P (‘b’ parameter) and “a” is a constant related to the binding energy of adsorption. 3Extracted with ammonium oxalate at pH 6. 4Extracted with ammonium oxalate at pH 3. 5Extracted with dithionite-citrate-bicarbonate

coefficients (R²) obtained from the Langmuir equation (Table 2) indicate that the mathematical model was efficient to predict P adsorption on the studied soils, as was previously observed by other authors (CORRÊA; NASCIMENTO; ROCHA, 2011; RANNO et al., 2007). The different slopes of the curves show, however, that the magnitude of P adsorption differed among soils.

Soils presented a broad variation on both MACP and binding energy (parameters “b” and “a” respectively of the Langmuir isotherm) (Table 2). The maximum amplitude for these two parameters occurred on soils GXbd-G and OXs; soil GXbd-G had the lowest value for MCPA (0.419 mg g⁻¹) and the highest binding energy (0.810 mg L⁻³), while soil OXs had the opposite, that is, the highest value for the MACP (1.450 mg g⁻¹) and the lowest value for the binding energy (0.430 mg L⁻³). Ranno et al. (2007) also found a broad variation of MCPA and binding energy of P on 16 lowland soils from the Rio Grande do Sul State, Southern of Brazil, previously cropped with rice. Similar results for the amplitude of these two parameters occurred on soils GXbd-G and OXs; soil GXbd-G had the lowest value for the MACP (1.450 mg g⁻¹) and the highest binding energy (0.810 mg L⁻³) (BROGGI et al., 2011) and the Pernambuco State (0.037 to 0.904 mg g⁻¹) (CORRÊA; NASCIMENTO; ROCHA, 2011). According to these authors, this large amplitude is mainly due to differences on the materials that originated the soils, which, in addition to the action of the weathering agents, produce soils with diverse chemical and physical characteristics that interact differently with P. This factor may also be the responsible for the variation of MCPA of the soils used in our study (Tables 1 and 2).

The highest MACP found for the OXs soil is probably due to the anionic character of the organic compounds, which through cations bridges with Al, Fe and Ca may adsorb P originating ternaries complexes (PAVINATO; ROSOLEM, 2008). In addition, the organic matter also contributes for the increment of phosphate adsorption, through the impediment of oxides crystallization (MEHMOOD et al., 2010), increasing the ratios of Feď/Feď and Feď/Feď (Table 2) and, thus, the adsorption surface (SILVA NETO et al., 2008).

According to the adsorption capacity classification of P of tropical soils proposed by Juo and Fox (1977), most of our soils (GXbd-I, CXbd-I and CXbd-P) are within the class with high MCPA (500 to 1,000 mg kg⁻¹); the OXs is in the very high MCPA class (> 1,000 mg kg⁻¹) and the GXbd-G is in the medium class. The predominance of soils with high MCPA is associated to the alternation in the soil oxidation conditions, which increases the reactivity of Fe oxides, phenomenon also found for seasonally waterlogged soils (GONÇALVES et al., 2011; RENNO et al., 2007). In our study, the soil with the lowest MCPA (GXbd-G) presented the lowest values for Feď, Feď, Feď/Fed and Feď/Feď, which may increase the availability of P to the plants relatively to the other soils, especially in relation to the OXs soil that had the highest MACP.

The Fe/Fed ratio is used as an index of the crystallinity of Fe oxides in the soil, where the highest values are related to the presence of crystallization inhibitors, which may make difficult the transformation of oxides of poor crystallinity into more crystallized forms (CURI et al., 2008). Overall, the values for this ratio were high in our soils (Table 2) because the alternation in the oxi-reduction conditions, inhibiting the formation of crystalline Fe oxides and favoring the formation of Fe oxides of poor crystallinity (GONÇALVES et al., 2011). The higher values for...
the Fe/Fed ratios presented by the OXs soil are also associated to the fact that the organic matter acts as inhibitor of the crystallinity of Fe oxides (SILVA NETO et al., 2015), resulting in higher levels of Fe (pH 3 and 6) and, consequently, higher values for the Fe/Fed ratio. Gonçalves et al. (2011) and Silva Neto et al. (2008) have shown the benefits of organic matter on formation of Fe oxides with poor crystallinity. Thus, the lower degrees of crystallinity of the Fe oxides, expressed by higher Fe/Fed and Feo/Fed ratios, resulted in higher reactivity of the oxides and, consequently, higher P adsorption, as can be observed from the MCPA values of the soils (Table 2).

The highest positive correlation indexes found in our study were between MCPA and the Fe values extracted from the soil by oxalate (Feox3 and Feox6) as well as with FeFedx/Fed and Feox6/Fed ratios (Table 3), which shows that the adsorption of P in these soils is mainly related to Fe oxides of poor crystallinity, which predominate in the colloidal phase of poorly drained soils (GONÇALVES et al., 2011). These constituents represent the most active adsorption sites of P in both aerated and waterlogged soils (GONÇALVES et al., 2012; GONÇALVES et al., 2011; MEHMOOD et al., 2010).

The importance of poor crystallinity Fe oxides on soil P availability to the plants was reported in previous studies carried out on rice waterlogged croplands in the States of Rio Grande do Sul (GONÇALVES et al., 2008) and Santa Catarina States of Rio Grande do Sul (GONÇALVES et al.). These studies carried out on rice waterlogged croplands in the Pernambuco State, which found rem-P values ranging from 12.8 to 57.8 mg L\(^{-1}\) and a high dependence relation with MCPA (r = -0.95**).  

Table 3 - Simple linear correlation coefficients (r) between parameters of the Langmuir isotherms and attributes of the five soils from rice croplands of the Santa Catarina State

<table>
<thead>
<tr>
<th>Attribute</th>
<th>Parameter</th>
<th>MACP (b)(^1)</th>
<th>(a)(^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Clay</td>
<td></td>
<td>-0.24*</td>
<td>0.45*</td>
</tr>
<tr>
<td>Organic matter</td>
<td></td>
<td>0.86*</td>
<td>0.55*</td>
</tr>
<tr>
<td>Rem-P(^3)</td>
<td></td>
<td>-0.84*</td>
<td>0.42*</td>
</tr>
<tr>
<td>Fe(_{ox3})(^5)</td>
<td></td>
<td>-0.43*</td>
<td>0.05*</td>
</tr>
<tr>
<td>Fe(_{ox6})(^6)</td>
<td></td>
<td>0.97*</td>
<td>-0.61*</td>
</tr>
<tr>
<td>Fe(<em>{ox3}/Fe</em>{ox6})</td>
<td></td>
<td>0.87*</td>
<td>-0.50*</td>
</tr>
<tr>
<td>Fe(<em>{ox6}/Fe</em>{dis})</td>
<td></td>
<td>0.90*</td>
<td>-0.61*</td>
</tr>
</tbody>
</table>

\(^1\)MACP: maximum adsorption capacity of P (parameter “b”). \(^2\)“a”: constant related to the binding energy of P. \(^3\)Rem-P: remaining P. \(^5\)Fe\(_{ox3}\): extracted with citrate-bicarbonate-dithionite. \(^6\)Fe\(_{ox6}\): extracted with ammonium oxalate at pH 3. \(^*\) and *: non-significant and significant at 5 % level, respectively (n = 5)

The remaining P (rem-P) is an important factor that affects adsorption of P in the soil. According to the criteria presented by Alvarez et al. (2000), the determination of rem-P may help the interpretation of P availability and its critical level in the soil. The values for rem-P in our study varied from 13 mg L\(^{-1}\) (in the OXs) to 34 mg L\(^{-1}\) (in the GXbd-G). According to the interpretation table presented by ALVAREZ et al. (2000), which considers the values of rem-P, all our soils (Table 1) are in the class classified with very low P availability.

The amount of P adsorbed estimated by rem-P showed a close and inverse relationship of dependence with MACP (r = -84**) (Table 3), confirming the importance of this parameter to understand the reaction of P in the soil (ALVAREZ et al., 2000). Similar results were obtained by Corrêa, Nascimento and Rocha (2011) in ten soils of the Pernambuco State, which found rem-P values ranging from 12.8 to 57.8 mg L\(^{-1}\) and a high dependence relation with MACP (r = -0.95**).

Soil clay content did not correlate with MCPA (b) (r = -0.24*, n = 5) when the entire soil group was considered. However, when only the mineral soils were included, a significant positive correlation between these two parameters was found (r = 0.71, n = 4), but the same did not occur for binding energy (r = 0.09*, n = 4). This is probably due to the predominance of Fe oxides in the efficiency of all chemical methods to evaluate the availability of P for rice plants. Thus, these parameters can be included in the methods used to evaluate availability of P in waterlogged soils and also used for improving the recommendation of phosphate fertilization in this production system.
The MACP (the ‘b’ parameter of the Langmuir model) was efficient to fit the experimental data for most soils; the MACP ranged from 0.419 to 1.450 mg g⁻¹ and the organic soil (OXs) presented the highest value, which could represent a great availability of P to the plants; showing that these attributes can be used to characterize P adsorption by the soils.

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REFERENCES


