Comissão 3.5 - Poluição, remediação do solo e recuperação de áreas degradadas

SOIL PHOSPHORUS_THRESHOLDS IN EVALUATING RISK OF ENVIRONMENTAL TRANSFER TO SURFACE WATERS IN SANTA CATARINA, BRAZIL

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ABSTRACT

The State of Santa Catarina, Brazil, has agricultural and livestock activities, such as pig farming, that are responsible for adding large amounts of phosphorus (P) to soils. However, a method is required to evaluate the environmental risk of these high soil P levels. One possible method for evaluating the environmental risk of P fertilization, whether organic or mineral, is to establish threshold levels of soil available P, measured by Mehlich-1 extractions, below which there is not a high risk of P transfer from the soil to surface waters. However, the Mehlich-1 extractant is sensitive to soil clay content, and that factor should be considered when establishing such P-thresholds. The objective of this study was to determine P-thresholds using the Mehlich-1 extractant for soils with different clay contents in the State of Santa Catarina, Brazil. Soil from the B-horizon of an Oxisol with 800 g kg⁻¹ clay was mixed with different amounts of sand to prepare artificial soils with 200, 400, 600, and 800 g kg⁻¹ clay. The artificial soils were incubated for 30 days with moisture content at 80% of field capacity to stabilize their physicochemical properties, followed by additional incubation for 30 days after liming to raise the pH(H₂O) to 6.0. Soil P sorption curves were produced, and the maximum sorption (Pmax) was determined using the Langmuir model for each soil texture evaluated. Based on the Pmax values, seven rates of P were added to four replicates of each soil, and incubated for 20 days more. Following incubation, available P contents (P-Mehlich-1) and P dissolved in the soil solution (P-water) were determined. A change-point value (the P-Mehlich-1 value above which P-water starts increasing sharply) was calculated through the use of
Introduction

The economy of the State of Santa Catarina in southern Brazil depends on agriculture, livestock farming, and the pork and poultry meat-processing industry. Approximately 14% of the state's gross domestic product (GDP) is estimated to be directly generated by these activities, and Santa Catarina is the largest pork-producer in the country (approximately 1.0 × 10^6 t yr^-1), accounting for 27% of national production (Embrapa, 2011; FIESC, 2012). Pig production is concentrated in two regions of Santa Catarina (Figure 1) and the large quantities of pig manure generated pose serious environmental issues. Region 1 accounts for over 70% of the pigs in the state and is characterized by clayey soils (Inceptisols and Entisols), which, however, are shallow and on steep slopes. Conversely, Region 2 contains approximately 10% of the pigs in the state, and its soils have sandy surface textures (Alfisols). Applications of high rates of swine manure to the soil surface without tillage are common in both regions, increasing P levels in the topsoil (Scherer et al., 2010) and promoting P transfer from soils to aquatic systems (Gatiboni et al., 2008; Guardini et al., 2012a,b).

Environmental impacts of pig production that significantly compromised the rivers in these regions led to intervention by the Federal Public Prosecutor's Office in the early 2000s, and establishment of state regulations restricting the application rate of liquid swine manure to 50 m^3 ha^-1 yr^-1 (FATMA, 2004). Although P is a major eutrophication agent, the regulations failed because levels of this nutrient in manures or the amount already present in soils was not considered, and P applications beyond...
soil retention capacities were also allowed. This generated an urgent need to develop a locally adapted tool enabling prediction of the maximum amount of P a soil may receive without high risk of environmental pollution. Recently, state regulations were revised (FATMA, 2014), and based on data shown in Gatiboni et al. (2014), P-thresholds were introduced as an environmental parameter to assess the risk of P transfer from soils to surface waters.

Heathwaite et al. (2005) describe P transfer from soil to surface waters as dependent on several parameters related to the source (soil), the transport process, and the receiving water body. The principal parameters related to the source include the content of soil labile P, type and rate of fertilizer and its frequency and mode of application, and the presence of crops or soil cover and management. Related to transport, the most important parameters are soil erosion rate, runoff, and subsurface drainage. Parameters related to the receiving water body are distance from the source and the width of buffer vegetation. Conversely, the P-threshold is only related to soil labile P, an important parameter because P is transferred in dangerous quantities if the soil is rich in labile P. Classification of potential P transfer from soils to aquatic environments using P-thresholds has methodological limitations, including variations in P-water with variations in the soil solution ratio (Koopmans et al., 2002). Furthermore, a major disadvantage comes from neglecting factors related to transport of water and sediment from the area (Sharpley et al., 2012). However, this method is a key tool for classification of soils by their environmental risks, as a result of the ease of establishing P-threshold values and their practical use.

Although the P-threshold method was used in the USA, most states have now developed a “P-index” model to evaluate the potential risk of soil P loss, which has also been proposed for some regions of Canada and Europe (Sharpley et al., 2012). Whereas P-thresholds consider only P levels in the soil, the P-index system, developed by Lemunyon and Gilbert (1993), considers data on soil type, soil P content, soil losses, and fertilizer use to estimate the risk of P transfer from a land area to surrounding water bodies. Few studies involving the use of a P-index have been published in Brazil (Lopes et al., 2007; Oliveira et al., 2010), making its calibration difficult. Nevertheless, as in any new method, immediate adoption is difficult because the system is composed of many variables that should be evaluated and tested in the field (SEARA17, 2013), and there is still no organized collection of such data in Brazil. Furthermore, there is less availability of large-scale topographic and soil maps or of locally adjusted data for estimation of soil erosion than in the USA. Given the environmental issues that have arisen in southern Brazil, an easily adopted method is needed for immediate use in the soils of Santa Catarina. From this perspective, the establishment of P-thresholds is a fast and readily applicable alternative whose results could possibly serve as the basis of a future P-index system.

Phosphorus thresholds are based on soil available P and assume that as P levels increase, a change-point occurs at which the soil begins to deliver large quantities of P to water bodies because of soil P saturation (Sharpley, 1995; McDowell et al., 2001; Nair et al., 2004; Casson et al., 2006). Since P-thresholds are dependent on soil sorption characteristics, soils with higher sorption capacity would raise the P-threshold values and take more P fertilization to reach the point when the soil starts to release P to water. One assessment of this phenomenon can be made by determination of the degree of P saturation (DPS), which is a measure that correlates the soil test P (STP) with the retention capacity of the sorption complex (Sharpley et al., 1996; McDowell et al., 2001; Koopmans et al., 2002; Bai et al., 2013). The most accepted assessment of the retention capacity of the soil sorption complex is evaluation of the maximum sorption capacity (Pmax) using isotherm procedures, although it is time-consuming and unfeasible in routine laboratory analysis. As an alternative to Pmax determination, Allen and Mallarino (2006) report that the soil DPS assessment, which is analogous to P-threshold, may be estimated using the ratio between P extracted by Mehlich-3 (STP) and the Fe and Al levels extracted by Mehlich-3 (as an estimate of soil sorption capacity). Using the same analogy, the P-threshold of a soil will depend on the clay content, which is a strong determinant of soil sorption capacity.

An initial approach to establishing an applicable P-threshold is to use current methods, which in Santa Catarina consists of soil P analyzed by the Mehlich-1 extractant (CQFS-RS/SC, 2004). This method is sensitive to soil retention capacity, extracting less P in clayey soils (Cajuste and Kussow, 1974). For that reason, the southern region of Brazil adopts four critical P levels, adjusted for increasing soil clay content (CQFS-RS/SC, 2004).
Taking advantage of information already available in soil test reports, the objective of the present study is to establish environmental P-thresholds for soils from Santa Catarina using Mehlich-1 as soil test P and the soil clay content as an estimator of soil sorption capacity.

**MATERIAL AND METHODS**

**Preparation and characterization of the soils used**

To avoid soils with different mineralogical compositions in the clay fraction, a single soil with high clay content was mixed with different amounts of sand to form soil samples with different textures of the same clay fraction. Following the mixtures, soil chemical properties were standardized by incubating moist soils with lime added to raise the pH to 6.0, following the procedures of CQFS-RS/SC (2004).

The soil selected for mixing with sand was an Oxisol (Almeida et al., 2003) collected at a depth of 150 to 220 cm (Bw horizon) in an area under natural pasture in the municipality of Campos Novos, Santa Catarina (27° 22' 27" S, 51° 04' 27" W). The soil was dried in a forced air oven at 65 °C, ground, and sieved to pass through a 2-mm mesh. Initial soil chemical analysis indicated the following characteristics: 800 g kg⁻¹ clay, 180 g kg⁻¹ silt, and 20 g kg⁻¹ sand, assessed using the pipette method (Embrapa, 1997), and 7.2 g kg⁻¹ organic matter, assessed using the wet oxidation method (Embrapa, 1997). Iron was 149 g kg⁻¹ by the citrate-bicarbonate-dithionite method (Mehra and Jackson, 1960) and 3.0 g kg⁻¹ by the ammonium oxalate method (Schwertmann, 1964). Soil cation exchange capacity (CEC) at pH 7.0 was 7.11 cmolc dm⁻³, pH(H₂O) was 5.2, and base saturation was 5 %, following procedures of Embrapa (1997).

To prepare the soils with ratios different clay contents, sand and soil were mixed at of 75 % sand + 25 % soil, 50 % sand + 50 % soil, 25 % sand + 75 % soil, and 0 % sand + 100 % soil; thus, the resulting mixtures contained 20, 40, 60, and 80 % clay, respectively (Table 1). Prior to mixing, the sand was passed through a system of sieves, and the particles sized from 0.5 to 1.0 mm were separated.

### Table 1. Soil physicochemical properties assessed following incubation for 30 days with water and another 30 days with lime in soils with ratios different clay contents

<table>
<thead>
<tr>
<th>Property</th>
<th>Sand:soil (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>75:25</td>
</tr>
<tr>
<td>Clay (%) (1)</td>
<td>20</td>
</tr>
<tr>
<td>Silt (%) (1)</td>
<td>5</td>
</tr>
<tr>
<td>Sand (%) (1)</td>
<td>75</td>
</tr>
<tr>
<td>Bulk density (kg dm⁻³)</td>
<td>1.25 a</td>
</tr>
<tr>
<td>OM (%) (2)</td>
<td>0.0 c</td>
</tr>
<tr>
<td>pH(H₂O) (1:1)</td>
<td>5.4 c</td>
</tr>
<tr>
<td>H⁺Al (cmolc dm⁻³) (3)</td>
<td>1.7 b</td>
</tr>
<tr>
<td>P (mg dm⁻³) (4)</td>
<td>1.7 a</td>
</tr>
<tr>
<td>K⁺ (mg dm⁻³) (4)</td>
<td>8 bc</td>
</tr>
<tr>
<td>Ca²⁺ (cmolc dm⁻³) (5)</td>
<td>0.1 d</td>
</tr>
<tr>
<td>Mg²⁺ (cmolc dm⁻³) (5)</td>
<td>0.1 d</td>
</tr>
<tr>
<td>Al³⁺ (cmolc dm⁻³) (5)</td>
<td>0.2 a</td>
</tr>
</tbody>
</table>

(1) Pipette method; (2) OM: organic matter, wet oxidation with H₂SO₄+K₂Cr₂O₇ (Embrapa, 1997); (3) H⁺Al estimated by SMP index, following Tedesco et al. (1995); (4) extracted by Mehlich-1, following Tedesco et al. (1995); (5) extracted by KCl 1.0 mol L⁻¹, following Tedesco et al. (1995). Means followed by the same letter in each line are not significantly different at the 0.05 level by the Tukey test.

Soil maximum P sorption capacity was assessed by adding 0.5 g soil to a centrifuge tube (with four replicates) and applying 15 mL of P solutions at concentrations of 0, 1, 2, 4, 6, 8, 16, 32, 64, 96, and 128 mg L⁻¹ P in a solution of 0.001 mol L⁻¹ CaCl₂.
These P treatments corresponded to 0; 30; 60; 120; 180; 240; 480; 960; 1,920; 2,880; and 3,840 mg kg⁻¹ P. The samples were stirred for 16 h in an end-over-end shaker at 30 rotations per minute (rpm). The solution was then separated from the soil through centrifugation at 5,000 rpm (approximately 2,000 g) for 14 min. The concentration of P in the soil solution was measured following Murphy and Riley (1962).

The experimental data for each soil were fit to the Langmuir mathematical model using version 9.1.3 of the Statistical Analysis System - SAS (SAS, 2006). The model used was

\[ \text{P}_{\text{sor}} = \frac{\text{k} \times \text{P}_{\text{max}} \times \text{P}_{\text{sol}}}{(1 + \text{k} \times \text{P}_{\text{sol}})} \]

where \( \text{P}_{\text{sor}} \): the amount of P sorbed, \( \text{k} \): a constant related to the binding energy, \( \text{P}_{\text{max}} \): the maximum P sorption capacity, and \( \text{P}_{\text{sol}} \): the amount of P in the equilibrium solution.

Soil incubation with P

The Langmuir model Pmax values were used to define the seven P rates (0 to 100 % Pmax) which were incubated with each soil of different clay content in four replicates for 20 days; during incubation, the samples were maintained at 80 % of FC. The amounts of water-soluble P (P-water) and the amounts of available P were assessed through use of the Mehlich-1 method (P-Mehlich-1). Water-soluble P was quantified by weighing the equivalent of 1 cm³ of soil derived from the incubation, adding 10 mL of distilled water, and stirring the samples for 1 h in an end-over-end shaker at 30 rpm. The samples were then centrifuged at 5,000 rpm (approximately 2,000 g) for 10 min, and the soil solution P was assessed following Murphy and Riley (1962). Phosphorus-Mehlich-1 was quantified following Tedesco et al. (1995) using 1 cm³ of soil and 10 mL of extraction solution. After 5 min of stirring in an orbital shaker, the samples were left decanting overnight and the solution P was assessed following Murphy and Riley (1962).

P-threshold assessment

The dependence of P-water on P-Mehlich-1 and clay content was tested using the data from the incubation of soils at varying P rates, conducting multiple regression analysis with SAS, version 9.1.3 (SAS, 2006), to assess the statistically significant parameters (p<0.01). A response surface methodology was used to display the data because the interaction between the two parameters was statistically significant.

Segmented functions relating P-Mehlich-1 and P-water for each soil clay content studied were fit using SAS (SAS, 2006) to determine the P-Mehlich-1 levels at which occurs the change-point and drastically increases the release of P into the water. A linear regression model with two segments was used for that purpose by applying the least squares method, and the optimum separation between the two segments was assessed by maximizing the coefficient of determination. The point of intersection between the two segments was termed the soil “P-limit”, and the soil P-threshold, which is the P-Mehlich-1 level, above which a high risk of P transfer from the soil to the water occurs, was arbitrarily set at 80 % of the P-limit.

Testing P-threshold efficacy in soil samples

Samples from the A horizon of 44 soils from several regions of Santa Catarina with a wide range of soil types from a survey conducted by Costa et al. (2013) were used for testing the efficacy of the proposed P-thresholds. In addition, 38 soil samples from two soil testing laboratories of the State of Santa Catarina were used. The samples were chosen to cover a wide range of soil textures and available P levels. Soil clay content, P-Mehlich-1, and P-water were assessed in the 82 soil samples, following the same methodologies described above. The soils were separated into two classes, below and above the P-threshold, and plotted on a graph relating P-Mehlich-1 and P-water.

RESULTS AND DISCUSSION

The P sorption curves shown in figure 2 and the results of fitting the respective Langmuir model show that the soil Pmax increased from 298 mg dm⁻³ in the 20 % clay soil to 2137 mg dm⁻³ P in the 80 % clay soil (Figure 2a). The Pmax value increased at a rate of 30.2 mg dm⁻³ for each percent of clay increase in the soil (Figure 2b).

The process of P sorption described by the Langmuir model considers at least two different phases. In the first phase, almost all the small quantities of added P are sorbed to the soil, and the high P retention capacity leaves little P in the solution. In contrast, in the second phase of sorption, with partially saturated sites, the amount of P exceeds the available binding sites leaving more P in the solution (Muljadi et al., 1966a,b). The P levels in the equilibrium solution are quite high when the soil P sorption reaches the Pmax value, and P transfer to the water would occur if fertilizer were added to soils at this magnitude. Thus, use of the Pmax value as an estimator of the upper limit of P rates to be applied to the soil would cause significant environmental impacts. Furthermore, the calculation of sorption isotherms is laborious and time consuming, and it is not a practical parameter for laboratory assessment in routine soil analysis, as emphasized by Allen and Mallarino (2006).
The values of P-water and P-Mehlich-1 determined after the incubation of soil samples for 20 days with different rates of P (Figure 3) showed that P-water were very close to zero with the application of low P rates (low P-Mehlich-1) to clayey soils that are not saturated with P, indicating that most of the added P sorbed to the soil with no significant increase of P in the water. However, an increase in P-water occurred with the addition of higher P rates (high P-Mehlich-1), occurring first in the more sandy soils and, subsequently, in the more clayey soils. Given their lower sorption capacity, sandy soils will deliver more P to the water in the event of additions of P, and at smaller amounts of P, than clayey soils will deliver.

Figure 3 confirms that clayey soils support greater P additions than sandy soils, without release of much P to the water, and confirm the hypothesis that the P-threshold assessed by Mehlich-1 should include soil clay content. These results are similar to those discussed by Sharpley et al. (1996), McDowell et al. (2001), Koopmans et al. (2002), and Bai et al. (2013). However, in figure 3 it is difficult to assess the change-point at which P-water begins to rapidly increase in response to P addition. Therefore, the use of segmented equations, as shown in figure 4, is a more accurate and widely used method in similar studies assessing change-points. For a soil with 20 % clay and P-Mehlich-1 values above 74 mg dm\(^{-3}\), P-water increased rapidly, thereby indicating that this value is the change-point of this soil. The change-point values of soils with 40, 60, and 80 % clay were 107, 126, and 147 mg dm\(^{-3}\), respectively (Figure 4).

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For safety reasons, it is recommended that the application of phosphate fertilizers or waste disposal should not be allowed after the change-point value of the soil is reached because this indicates high risk of soil P becoming a source of P pollution to surface waters. Therefore, we randomly set a value of 80% of the P-limit, designating that new value as the P-threshold. Thus, the P-thresholds of the soils studied would be 59, 86, 101, and 118 mg dm\(^{-3}\) from P-Mehlich-1 for soils with 20, 40, 60, and 80% clay, respectively. Sharpley et al. (2001) also chose P-limit percentage values to classify soils from the State of Pennsylvania, stipulating 75% of the P-limit to be the maximum value, beyond which measures restricting supplementation with P should be adopted.

Figure 5 shows the ratio between soil clay content and the Mehlich-1 values for P-limit and P-threshold. These P-Mehlich-1 values increased linearly with the clay content. As described above, the P-threshold was set at 80% of the change-point value and, therefore, the equation found is P-threshold = 43.5 + 0.95 Clay, where P-threshold is expressed as mg dm\(^{-3}\), and clay content is expressed as a percentage. A simplification of that equation is suggested because the slope was very close to 1.00 (0.95), resulting in the simplified model P-threshold = 40 + Clay, where P-threshold is expressed as mg dm\(^{-3}\), and the clay content is expressed as a percentage. The use of the simplified equation has the advantage of being an easily memorized and used equation, in which the user only

![Graph showing the relationship between soil clay content and Mehlich-1 values for P-limit and P-threshold.](image)

Figure 4. Phosphorus-water and P levels assessed by Mehlich-1 (M1) in soils with different percentages of clay following incubation for 20 days with varying P rates. The intersection of the equations is the change-point value.
needs to access a soil test report and add 40 to the percent clay content, thus calculating the maximum available P levels by Mehlich-1 (mg dm$^{-3}$) that may be present in the soil for low risk of P transfer to surface water bodies.

The efficacy of the model in separating soils with high and low risks of P transfer was tested in a set of 82 samples collected from several regions of Santa Catarina and with different textures and types of soils. The results showed that the model $P$-threshold = $40 +$ Clay was able to separate the samples into two classes, with low and high risk of P transfer, represented here by P-water values below and above 0.30 mg L$^{-1}$ (Figure 6), without outliers. Thus, the model was effective in identifying samples with higher potential for P transfer using only P-Mehlich-1 and soil clay content as inputs.

The Local Soil Fertility Committee (CQFS-RS/SC, 2004) has established critical levels (CLs) for plants that decrease with increasing clay content, given the sensitivity of the Mehlich-1 method to soil texture in southern Brazil (Figure 7). The CL of soils with clay content ranging from 0 to 20 % is 21.0 mg dm$^{-3}$ P. Conversely, the CL of soils with clay content ranging from 21 to 40 % CL is 12.0 mg dm$^{-3}$ P, and the CL of soils with clay content ranging from 41 to 60 % is 9.0 mg dm$^{-3}$ P. Finally, the CL of soils with clay content greater than 60 % is 6.0 mg dm$^{-3}$ P. The $P$-threshold value calculated using the model proposed for its calculation is always significantly greater than the CL, nearly double the CL in a 20 % clay soil, and 11 times greater in a 60 % clay soil. Thus, the risk of plant growth being limited by P deficiency does not occur when using the $P$-threshold model to limit the application of animal manure, for example. This enables the safe use of soil to discard manures when P levels by Mehlich-1 are between CL and $P$-threshold, as shown in figure 7.

To manage P additions to soil with the proposed model, a suggestion is to calculate the application rate of manure to be used (or any other phosphate

![Figure 5. Phosphorus levels assessed by Mehlich-1 extractant at which the P-water rapidly increases upon supplementation with P (change-point) and P levels, assessed by Mehlich-1, that are 80 % of the change-point (P-threshold). P-threshold simplified is the proposed simplified model to facilitate the calculation of the P-threshold.](image)

![Figure 6. Phosphorus-water and P-Mehlich-1 values in 82 soil samples from the State of Santa Catarina, Brazil. The samples were previously classified using the model $P$-threshold = $40 +$ Clay as below (white circles) or above (black triangles) the $P$-threshold.](image)

![Figure 7. Phosphorus critical levels, assessed by extraction with Mehlich-1, depending on the soil clay content, according to the Local Soil fertility committee (CQFS-RS/SC, 2004), with the $P$-threshold calculated using the $P$-threshold = $40 +$ Clay model.](image)
materials) based on the nitrogen needs of the plants used in the area as long as the soil remains below the P-threshold. Conversely, the application rate of manure to be used should only be based on the P needs of cultivated plants if the soil has P levels above the P-threshold, but below the change-point value. Finally, if the P levels are above the change-point, the application of P should be suspended until the levels decrease below the change-point value.

As discussed before, P-thresholds have methodological limitations, but this method is a key tool for classification of soils by their environmental risks, because of the ease of establishing P-threshold values and their practical use. In the future, local data generated regarding P transport may be incorporated into the model proposed here to generate a more complex model, similar to the P-index.

CONCLUSION

Soil may be classified by its risk of P transfer to surface waters based on the level of P extracted by the Mehlich-1 solution and soil clay content. The model proposed for calculating the P-threshold (in mg L\(^{-1}\), by Mehlich-1) for soils from the State of Santa Catarina, Brazil, is P-threshold = 40 + clay, where Clay is the percentage of soil clay.

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