Estimation of the degree of soil P saturation from Brazilian Mehlich-1 P data and field investigations on P losses from agricultural sites in Minas Gerais

P. Fischer, R. Pöthig, B. Gücker and M. Venohr

ABSTRACT

The degree of phosphorus saturation (DPS) of agricultural soils is studied worldwide for risk assessment of phosphorus (P) losses. In previous studies, DPS could be reliably estimated from water-soluble P (WSP) for European and Brazilian soils. In the present study, we correlated measured WSP and Mehlich-1 P (M1P) from soils of Minas Gerais (MG) and Pernambuco (PE) ($R^2 = 0.94, n = 59$) to create a DPS map from monitoring data. The resulting DPS map showed high spatial variability and low values of DPS (54 ± 22%, mean and standard deviation; $n = 1,827$). Measured soil DPS values amounted to 63 ± 14% and resulted in relatively low dissolved P concentrations measured in a surface runoff study in MG. However, fertilizer grains on the soil surface led to high WSP values (>30 mg/kg) indicating high risks of dissolved P losses. We suppose that small Oxisol particles with Fe and Al hydroxides sorbed most of the dissolved fertilizer P in runoff so that P was mainly exported in particulate form. In soils with lower contents of P sorption and binding partners, e.g. Entisols in PE, this effect may be less dominant. Consequently, superficial fertilizer effects have to be considered in addition to DPS in risk assessment of P losses from agricultural areas in Brazil.

Key words | diffuse P loss, nutrient management, P risk assessment, risk map, São Francisco, surface runoff P

INTRODUCTION

Phosphorus (P) loss from agricultural areas by surface runoff is an important pathway of nutrient emissions that contributes to the eutrophication of freshwater systems (Carpenter et al. 1998). To assess the risk of dissolved P losses in runoff, the degree of P saturation (DPS) is often reported as the best correlated parameter to dissolved P concentrations in runoff (Sharpley et al. 1996; Little et al. 2007). Standard soil extraction methods, such as water-soluble P (WSP) or Mehlich-3 P, which are simpler to determine than DPS, are also correlated to runoff P (Sharpley 1995; Vadas et al. 2005). However, of these extraction methods, WSP was shown to be the most suitable across different soil types (Pote et al. 1999; Penn et al. 2006). In order to allow for the use of standard extraction methods in P loss risk assessment, correlations between these methods and different DPS methods have been investigated (e.g. Beck et al. 2004; Xue et al. 2014). However, to our knowledge, an approach to estimate soil-independent DPS values from monitoring data has not been developed yet for Brazil.

Besides soil DPS, the type of fertilizer and its application as well as the intensity of rain events influence the dissolved P concentrations in runoff (Kleinman et al. 2002; Shigaki et al. 2006; Shigaki et al. 2007). For example, runoff from fields has lower dissolved P concentrations when the fertilizer is incorporated into the soils as opposed to soil surface applications (Kleinman et al. 2002).

In Brazil, a modified Mehlich-1 soil test method (Embrapa 1997) is used for analyses of plant-available P in soils. Based on extractable phosphorus by Mehlich-1 (M1P), fertilizer dosage recommendations are given by research institutions (e.g. CQFSRS/SC 2004). The fertilizer is commonly applied to the soil surface (Portuguese: adubação de cobertura), without incorporating it into the soil structure. The effects of superficially applied fertilizer have been the focus of surface runoff studies in Brazil (e.g. Mori et al. 2009; Bertol et al. 2010), where very high runoff dissolved P concentrations of up to 6 mg/L in runoff have been reported for some sites (Mori et al. 2009).
In another study, we showed that the correlation independent of soil type between WSP and DPS for risk assessment of P losses, established for European soils (Pöthig et al. 2010), can also be applied to Brazilian soils (Fischer et al. 2016a, in preparation). In the present study, we further developed this investigation by correlating measured WSP and M1P values of agricultural soils from the Brazilian federal states of Minas Gerais (MG) and Pernambuco (PE). DPS data were estimated and evaluated based on M1P monitoring data from MG and Brazilian federal state Bahia (BA). Furthermore, a runoff study was conducted at agricultural sites with Oxisols with extremely high amounts of Al and Fe, common in the southern part of MG, and superficially applied fertilizer. The aim of the runoff study was to assess dissolved P concentrations in runoff and to compare the results with estimated risk potentials via WSP and DPS.

**MATERIAL AND METHODS**

**Soil sampling and analyses**

Soil samples were taken in 2013/2014 as a part of the INNOVATE project (www.innovate.tu-berlin.de) which investigates the São Francisco catchment and, in particular, the catchment and water quality of the Itaparica reservoir. For assessing the potential P losses via runoff from agricultural soils within the catchment, two sampling sites were chosen (Figure 1). One, located in the region of São João del-Rei (MG), is representative for the conditions in the upper São Francisco catchment, i.e. warm temperate climate with dry winters and hot summers according to the Köppen climate classification (Kottek et al. 2006) and dominating Oxisols/Latossolos (EMBRAPA 2011) according to USDA soil classification system/Brazilian soil classification system (Sistema brasileiro de classificação de solos = SiBCS), respectively (Soil Survey Staff 1999; EMBRAPA 2006). The second study area is located at the Itaparica reservoir in the municipality of Petrolândia (PE) with hot steppe climate BSh (Kottek et al. 2006) and dominating Entisols/Neossolos according to USDA soil classification/SiBCS, respectively (EMBRAPA 2011).

All soil samples were taken as cores (height: 41 mm; diameter: 56 mm) from pastures and crop fields to retrieve the top soil layer (0–4 cm), which is considered to be most important for surface runoff events (e.g. Sharpley 1985). The soil samples were air-dried and sieved to <2 mm. The soil density was determined by the weight of 50 cm³ soil. For the runoff study, six soil samples were taken from the top to the slope toes of each field to consider soil heterogeneity within the fields prior to runoff events. Samples in and between the plant rows (with and without fertilizer on their surfaces) were taken to consider the influence of spatial heterogeneity on runoff P concentrations and WSP. Soil analyses of WSP, DPS, total P, Fe and Al were done according to Pöthig et al. (2010). The extraction to determine M1P was executed with a modified Mehlich-1 soil test method according to the EPAMIG (Empresa de Pesquisa Agropecuária de Minas Gerais) laboratory manual (personal communication; Embrapa 1997). Instead of a horizontal circular shaker, an overhead shaker was used. M1P was determined in mg/kg and transformed to mg/dm³ by multiplication with the corresponding soil densities. All P concentrations were measured photometrically (Murphy & Riley 1962) with a UV–vis photometer (UV 2102, Shimadzu Corp.).

**Water sampling and analyses**

Runoff water caused by heavy rainfall was sampled from two hill slopes with monocultures (cabbage, tangerine) and one with mixed cultures (cabbage, broccoli, carrot, etc.). All samples were taken at the slope toes of the fields in order to measure P concentrations in runoff leaving the fields. At the cabbage monoculture, two collectors (1 m inlet, used on 15 and 16 February 2014) on both lateral sides and one (4 m inlet, used on 23 January 2014) in the middle of the field were installed. All collectors were constructed similar
to Shigaki et al. (2007). The intensities of rain events were measured by rain gauges installed 1 m above the soil surface on the investigated fields. Samples were taken during or after heavy rainfall events (>15 mm/h).

At the tangerine and mixed cultures, field samples were taken by placing openings of plastic bottles against flow direction in runoff flows (ca. 3 cm water depth) on the field surface and in a temporary draining-ditch, respectively. Samples were taken at the beginning (for mixed cultures) or 10 min after the beginning (for Tangerine) of the event and subsequently in 10-minute intervals. Samples for analyses of dissolved P concentrations were put on ice after sampling and either filtered in the laboratory within 3 hours (mixed cultures) or frozen (tangerine, cabbage).

A digestion with potassium peroxydisulfate (K2S2O8), according to EN ISO 6878:2004, was executed on filtered (GF/F, 0.45 μm) and unfiltered samples prior to photometric P analyses (Murphy & Riley 1962) to determine total dissolved phosphorus (TDP) and total suspended phosphorus (TSP), respectively. A UV–vis NIR spectrometer (USB2000+, Ocean Optics Inc.) was used. Total suspended matter (TSM, mg/L) concentrations were determined by filtration of 150 to 500 mL of runoff samples through previously weighed GF/F filters and subsequent drying and weighing of the filters.

DPS risk map

M1P monitoring data (in mg/dm³) were obtained from the agricultural research organization EPAMIG for the year 2009 on a municipality level. These data were transformed into WSP according to correlations found in this study and subsequently DPS values were calculated (\(\text{DPS} = 100/(1 + 1.25 \times \text{WSP}^{-0.75})\), Pöthig et al. 2010). For the risk map, only municipalities having at least 10 individual values of M1P were included. For data visualization, municipality borders provided by IBGE were used. The ggplot2 package in the software R (R Core Team 2013) was used to create violin plots of DPS of selected municipalities in MG and BA.

RESULTS AND DISCUSSION

Regression equation to predict the DPS of Brazilian soils

Table 1 shows the two dominant soil types of the investigated areas in MG and PE, the average amount of applied fertilizer, the arithmetic means and ranges of WSP, M1P and DPS. Despite the differences in soil types and fertilizer application, the resulting WSP, M1P and DPS values for both regions were similar (see also Figure 2). This may be due to higher sorption and binding capacities of the Fe- and Al-rich soils of MG, which apparently were able to compensate for the higher fertilizer application (ANA 2013).

The correlation between measured WSP and M1P values (Figure 2) was highly significant (\(p < 0.01\)) and described by a single linear equation: \(\text{WSP} (\text{mg/kg}) = 0.1662 \times \text{M1P} (\text{mg/dm}^3)\). Subsequently DPS was calculated using the equation: \(\text{DPS} = 100/(1 + 1.25 \times \text{WSP}^{-0.75})\) (Pöthig et al. 2010). While this equation is independent of soil type, the relation between WSP and M1P may not be soil-independent, especially if calcareous soils are present. The soil samples showed no significant influence of soil type on the correlation between WSP and M1P (Figure 2). However, our investigated samples did not contain significant amounts of CaCO₃. The pH

<table>
<thead>
<tr>
<th>Sites</th>
<th>MG</th>
<th>PE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Soil type</td>
<td>Oxisols</td>
<td>Entisols</td>
</tr>
<tr>
<td>Fertilizer, kg/ha</td>
<td>310</td>
<td>60</td>
</tr>
<tr>
<td>Soil density, g/cm³</td>
<td>0.83; 1.17</td>
<td>1.17; 1.56</td>
</tr>
<tr>
<td>AM</td>
<td>1.38</td>
<td></td>
</tr>
<tr>
<td>WSP, mg/kg</td>
<td>min; max</td>
<td>0.3; 36.4</td>
</tr>
<tr>
<td>AM</td>
<td>9.4</td>
<td></td>
</tr>
<tr>
<td>M1P, mg/kg</td>
<td>min; max</td>
<td>1.6; 199.0</td>
</tr>
<tr>
<td>AM</td>
<td>56.2</td>
<td></td>
</tr>
<tr>
<td>DPS, %</td>
<td>min; max</td>
<td>31.3; 79.7</td>
</tr>
<tr>
<td>AM</td>
<td>60.2</td>
<td></td>
</tr>
<tr>
<td>Fe, g/kg</td>
<td>AM</td>
<td>52.8</td>
</tr>
<tr>
<td>Al, g/kg</td>
<td>AM</td>
<td>78.7</td>
</tr>
</tbody>
</table>
buffering of the acid in Mehlich-1 solution by soils containing CaCO₃ can lead to underestimations of M1P values. This requires the application of a correction factor, as used for other acid soil extraction solutions, such as calcium acetate lactate (VDLUFA 2002) before DPS data can be calculated in the above described way.

Nevertheless, the soil orders investigated here (Oxisols and Entisols) are major soil orders in the São Francisco catchment, MG (Figure 1) and Brazil, occupying 65%, 61% and 46% of the respective surface areas (EMBRAPA solos 2011). Therefore, the procedure to assess risk of dissolved P losses from agricultural areas presented here can also be transferred to soils containing no or low CaCO₃ contents in other Brazilian regions and states. However, more detailed investigations on other soil types and the development of a correction factor for M1P values measured on soils with CaCO₃ would definitely augment the accuracy of the prediction of DPS values.

**Risk map of DPS values and DPS data analyses**

A spatially differentiated map based on DPS arithmetic means of different municipalities in MG and BA (Figure 3(a)) showed high variability among locations. The highest average DPS value was calculated for Guanambi, a municipality in Bahia that is well-known for its intensive cotton production. However, both our measured (arithmetic mean: 65 ± 14%) and the estimated DPS (arithmetic mean: 54 ± 22%) values from M1P monitoring data are comparably low when compared to thresholds of elevated and high risks of dissolved P losses of 70 and 80%, respectively (Table 1, Figure 3). This confirms an overall low estimated risk of P loss with regard to DPS, e.g. when compared to agricultural areas of Germany (Fischer et al. 2016b, in preparation).

Arithmetic means and the distribution of DPS values for different municipalities as well as for the entire region were compared via violin plots (Figure 3(b)). The overall distribution of estimated DPS values, ranging from 8 to 96%, suggests that a high spatial resolution of M1P monitoring data is necessary to identify small-scale risk areas in the investigated region. Independent of the arithmetic mean, DPS values that indicate elevated risks of dissolved P losses were present in all municipalities. Single locations with agricultural soils of high risks were present even in municipalities with average DPS values far below the critical values for risk of P losses of <70–80% (Figure 3(b)). Consequently, we conclude that input data of high spatial resolution would be needed for an effective risk assessment which can promote fertilizer and emission management to reduce P losses from agricultural areas. Thus, the risk map elaborated in this study is a first step to characterize potential P losses in the studied region. More input data are needed to derive a detailed assessment of differences in risk of P losses among and within the different municipalities.

**Runoff study**

Our runoff study on Oxisols in MG showed generally low dissolved P concentrations in runoff. TDP concentrations were relatively low at all sites, with a maximum value of 0.40 mg/L observed at the cabbage plantation (Table 2).
TSP values ranged between 0.96 and 2.18 mg/L in the cabbage and mixed culture sites. TSP concentrations at the tangerine site were very low compared with the other fields. Temporal changes in TSP and TDP concentrations were relatively low during single rainfall events with temporally varying precipitation intensities, whereas the range of TSM concentrations was high in the tangerine and mixed culture site samples. At the cabbage site, TSM variations were low as only one average value per runoff event could be delivered from collector samplings (Table 2).

Soils of the runoff study showed a wide range in WSP values in all investigated fields, with some extremely high values (Table 2). Fertilizer grains in the planting rows led to exceptionally high values of WSP (>30 mg/kg) as compared to the samples taken between the planting rows (without visible fertilizer grains) which had values lower than the proposed threshold value of 5 mg/kg for identifying soils with elevated risks of dissolved P loss (Pöthig et al. 2010). The discrepancy between some extremely high WSP values and some observed low dissolved P concentrations in runoff was probably due to sorption of P on the Al and Fe hydroxides on the surfaces of the Oxisols (e.g. Börling 2003; Melo et al. 2015). Sorption processes of dissolved P to soil particles during the transport along the slope of a field can result in decreasing dissolved P concentrations in runoff (Sharpley et al. 1981). This effect seemed to be dominant in our study. Soils with high reactive surfaces and free adsorption places for P, e.g. the investigated Oxisols, can apparently compensate for the effect of a certain amount of inorganic fertilizer, and consequently P losses mainly occur in the particulate phase. In other Brazilian soils, as those studied from PE with Fe and Al contents lower by a factor of six (see Table 1), this effect may not occur to the same extent.

The very small particles present in our samples, which sorbed dissolved fertilizer P during the runoff process, can again easily release the absorbed P to waters of lower P concentrations, such as receiving reservoirs and rivers (e.g. Correll 1998). Consequently, the superficial fertilizer application can most probably contribute a substantial part to agriculture-driven eutrophication processes in Brazil’s water bodies.

**CONCLUSIONS**

A highly significant correlation between M1P and WSP suggests that the DPS of agricultural soils in Brazil with

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Table 2 | Results of water and soil analyses from the runoff study in Minas Gerais: n — number of samples per runoff event; RI — rainfall intensity; TSM — total suspended matter; TSP — total suspended P; TDP — total dissolved P; soil WSP — water-soluble P of the soil samples, values marked with F represent soil samples which contained fertilizer grains

<table>
<thead>
<tr>
<th>Agricultural field</th>
<th>Date 2014</th>
<th>n [-]</th>
<th>RI [mm/h]</th>
<th>TSM [g/L]</th>
<th>TSP [mg/L]</th>
<th>TDP [mg/L]</th>
<th>Soil WSP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tangerine</td>
<td>21.01.</td>
<td>3</td>
<td>19.2</td>
<td>0.8</td>
<td>min: 0.13</td>
<td>min: 0.08</td>
<td>min: 0.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>10.4</td>
<td>max: 0.19</td>
<td>max: 0.19</td>
<td>max: 47.9 (F)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>23.1</td>
<td>AM: 0.16</td>
<td>AM: 0.14</td>
<td></td>
</tr>
<tr>
<td>Cabbage</td>
<td>23.01.</td>
<td>1</td>
<td>21.6</td>
<td>10.4</td>
<td>1.94</td>
<td>0.40</td>
<td>min: 1.8</td>
</tr>
<tr>
<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>max: 30.5 (F)</td>
</tr>
<tr>
<td>Cabbage</td>
<td>15.02.</td>
<td>2</td>
<td>36.7</td>
<td>3.7</td>
<td>1.93</td>
<td>0.14</td>
<td>min: 1.8</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>9.6</td>
<td>1.68</td>
<td>0.10</td>
<td>max: 30.5 (F)</td>
</tr>
<tr>
<td>Cabbage</td>
<td>16.02.</td>
<td>2</td>
<td>no data</td>
<td>4.1</td>
<td>1.64</td>
<td>0.06</td>
<td>min: 1.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>6.1</td>
<td>1.65</td>
<td>0.07</td>
<td>max: 30.5 (F)</td>
</tr>
<tr>
<td>Mixed cultures</td>
<td>30.03.</td>
<td>3</td>
<td>13.5</td>
<td>2.1</td>
<td>min: 1.28</td>
<td>min: 0.08</td>
<td>min: 2.8</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>6.9</td>
<td>max: 1.81</td>
<td>max: 0.15</td>
<td>max: 33.6 (F)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>24.6</td>
<td>AM: 1.61</td>
<td>AM: 0.12</td>
<td></td>
</tr>
<tr>
<td>Mixed cultures</td>
<td>30.03.</td>
<td>1</td>
<td>36.0</td>
<td>9.2</td>
<td>2.03</td>
<td>0.13</td>
<td>min: 2.8</td>
</tr>
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<td></td>
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<td></td>
<td></td>
<td></td>
<td>max: 33.6 (F)</td>
</tr>
<tr>
<td>Mixed cultures</td>
<td>31.03.</td>
<td>6</td>
<td>24.0</td>
<td>min: 6.6</td>
<td>min: 0.96</td>
<td>min: 0.09</td>
<td>min: 2.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>max: 25.9</td>
<td>max: 2.18</td>
<td>max: 0.36</td>
<td>max: 33.6 (F)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>AM: 1.74</td>
<td>AM: 0.15</td>
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</table>
low or no CaCO₃ contents can be estimated by M1P monitoring data. The common agricultural practice of superficial application of fertilizer in Brazil (Portuguese: adubação de cobertura) is leading to a high potential of dissolved P losses by runoff. Superficial fertilizer application, however, does not necessarily result in high dissolved P concentrations in runoff in soils with high Al and Fe contents (e.g. Oxisols in southern part of MG). In regions with soils of lower contents of P sorption and binding partners, such as the studied Entisols from PE, this effect is probably less dominant and dissolved P losses may be substantially higher. Consequently, risk assessments of P losses in Brazil have to take into account the degree of soil P saturation, contents of P sorption and binding partners in soils and fertilization practices.

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