



Phosphorus saturation and superficial fertilizer application as key parameters to assess the risk of diffuse phosphorus losses from agricultural soils in Brazil

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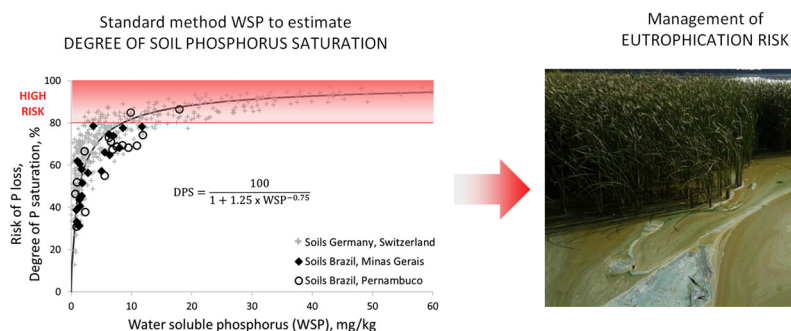
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HIGHLIGHTS

- Fast and simple P loss risk assessment established for Brazilian soils.
- Reaction of fertilizer P with Fe and Al hydroxides proven in Oxisols by FTIR analyses.
- Soil-fertilizer reaction probably decisive for P losses in surface runoff.
- Palygorskite and sepiolite occurrence indicated in some Entisols.
- Targeted P levels for plant production resulted in low P loss risks for major crops.

GRAPHICAL ABSTRACT



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ABSTRACT

In Brazil, a steady increase in phosphorus (P) fertilizer application and agricultural intensification has been reported for recent decades. The concomitant P accumulation in soils potentially threatens surface water bodies with eutrophication through diffuse P losses. Here, we demonstrated the applicability of a soil type-independent approach for estimating the degree of P saturation (DPS; a risk parameter of P loss) by a standard method of water-soluble phosphorus (WSP) for two major soil types (Oxisols, Entisols) of the São Francisco catchment in Brazil. Subsequently, soil Mehlich-1P (M1P) levels recommended by Brazilian agricultural institutions were transformed into DPS values. Recommended M1P values for optimal agronomic production corresponded to DPS values below critical thresholds of high risks of P losses (DPS = 80%) for major crops of the catchment. Higher risks of reaching critical DPS values due to P accumulation were found for Entisols due to their total sorption capacities being only half those of Oxisols. For complementary information on soil mineralogy and its influence on P sorption and P binding forms, Fourier transformation infrared (FTIR) spectroscopic analyses were executed. FTIR analyses suggested the occurrence of the clay minerals palygorskite and sepiolite in some of the analyzed Entisols and the formation of crandallite as the soil specific P binding form in the investigated Oxisols. Palygorskite and sepiolite can enhance P solubility and hence the risk of P losses. In contrast, the reshaping of superphosphate grains into crandallite may explain the chemical processes leading to previously observed low dissolved P concentrations in surface runoff from Oxisols. To prevent high risk of P losses, we recommend avoiding superficial fertilizer application and establishing environmental thresholds for soil M1P based on DPS. These measures could help to prevent eutrophication of naturally oligotrophic surface waters, and subsequent adverse effects on biodiversity and ecosystem function.

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1. Introduction

Brazil is a major player in the world food market, being e.g. one of the largest producers of soybean and sugarcane. Nowadays $220 \cdot 10^6$ ha (~25% of the country's total area) are in agricultural land use (Dias et al., 2016). Whereas increasing harvests were connected to the deforestation of natural Brazilian biomes in the past, a strong intensification trend (i.e., higher harvest amounts by same agricultural area) has been reported for recent years (Dias et al., 2016).

The development of Brazil to one of the breadbaskets of the world has been accompanied by an increase in P fertilizer consumption. In comparison to the early 1960s, the amount of P used in agriculture is nowadays ~30 times higher and a P accumulation in soils has taken place over recent decades (Martinelli et al., 2010; Roy et al., 2016). Brazil's agriculture nowadays applies about twice the inorganic P fertilizer per unit of cropland area than that in the U.S.A., which results in a P surplus of $5\text{--}18 \text{ kg P ha}^{-1} \text{ yr}^{-1}$ for the 11 Brazilian states with intensive agricultural production (Roy et al., 2016).

One biome that has been massively affected by agricultural expansion in recent decades is the Brazilian Cerrado (Marris, 2005). The intensive agricultural development of Brazil's second largest biome started in the 1960s (Lopes and Guilherme, 2016). It was triggered by major investments in the agricultural sector regarding research on adapted agriculture on soils of low fertility, building of infrastructure and financial support to farmers (Lopes and Guilherme, 2016). Nowadays about 50% of the original area of the Cerrado of $200 \cdot 10^6$ ha has been transformed into agricultural area (Monfreda et al., 2008; Lapola et al., 2014).

Agriculture in Brazil commonly takes place on highly weathered soils with very high P sorption capacities due to high Al and Fe contents, also referred to as "P fixing soils", accounting for about half of Brazil's cropland (Sanchez et al., 2003; Roy et al., 2016). The massive expansion of agriculture into the Cerrado was possible by putting its soils that were originally not considered adequate for agricultural production into agricultural use by special measures, e.g. liming and high applications of P fertilizer (Yamada, 2005; Lopes et al., 2012). In Brazil, agricultural soils being in production are evaluated regarding soil fertility by estimating plant available P by a modified Mehlich-1 soil test method (M1P, EMBRAPA, 1997) and the anion exchange resin method (van Raij et al., 1986; Bissani et al., 2002). Based on M1P, partly very high P applications are recommended to enhance soil fertility and to ensure optimal agricultural yields (Ribeiro et al., 1999; Cavalcanti et al., 2008). Moreover, superficial fertilizer application has been recommended for some crops and is apparently also used widely in order to save time in the agricultural production process (Cavalcanti et al., 2008; Bortolon et al., 2016).

Whereas a certain P level in soils is necessary to sustain an optimal agronomic production, P applied to agricultural soils in excess results in P accumulation, with concomitant P losses from agricultural areas, subjecting surface water resources to eutrophication processes (Carpenter et al., 1998; Kleinman et al., 2011; Sattari et al., 2012). In Brazil, elevated P concentrations in water bodies due to agricultural practices have been widely reported (Ghosh et al., 2011; Ribeiro et al., 2014; Santos et al., 2014). P losses from agricultural areas are of high importance due to highly nutrient-limited aquatic ecosystems being vulnerable to changes in ecosystem metabolism and eutrophication, e.g. in rural parts of the Cerrado and the Caatinga (Gücker et al., 2009; dos Santos Rosa et al., 2013; Hunke et al., 2015; Selge et al., 2016).

The degree of P saturation (DPS) of agricultural soils has been studied in many parts of the world, in order to define DPS threshold values above which there is a strong increase in the risk of P losses from soil to water (Nair, 2014). The DPS is well correlated with dissolved P concentrations in leakage and surface runoff (Sharpley, 1995; Maguire and Sims, 2002; Vadas et al., 2005). There are different approaches to determine DPS. As P sorption isotherms are time consuming and costly to measure, the DPS of a soil is commonly estimated relating oxalate extractable P to the extractable Fe and Al of acidic soils (Beauchemin and Simard, 1999; Nair, 2014). In calcareous soils, DPS is estimated relating

the extractable P to Ca and Mg (Ige et al., 2005; Xue et al., 2014). Consequently, these approaches are soil type-dependent. Instead of oxalate, other soil test methods such as Mehlich-1, Mehlich-3 or Olsen are also used (Ige et al., 2005; Nair, 2014; Bortolon et al., 2016). Different DPS approaches have been investigated for their applicability to Brazilian soils (e.g. Ghosh et al., 2011; Abdala et al., 2012; Alleoni et al., 2012; Bortolon et al., 2016). Furthermore, environmental thresholds for P loss have been suggested for Brazilian Oxisols by correlating DPS with the M1P method (Ghosh et al., 2011; Alleoni et al., 2014; Gatiboni et al., 2015). Generally, these studies confirmed the validity of the DPS approaches on Brazilian soils, and that M1P can be used as, or be integrated into environmental thresholds. However, these approaches are valid for certain soil types only.

The soil type-independent DPS approach introduced by Pöthig et al. (2010) for European soils has not been tested yet on tropical soils of Brazil. The DPS determined by sorption isotherms and total phosphorus (TP) was related to a standard extraction method of water-soluble phosphorus (WSP) in a soil type-independent correlation. Consequently, the rather complex, time consuming and expensive to determine parameter DPS can be estimated by the simple standard soil P test method of WSP. Thus, Pöthig et al. (2010) concluded that this approach can be used for a simple and fast risk assessment of P losses worldwide.

Critical soil DPS values are reached at different amounts of total accumulated P in different soil types, due to different P sorption capacities (e.g. Pöthig et al., 2010). P sorption and reaction with fertilizer phosphates and emerging P binding forms are a result of the chemical composition and physical properties of the soils (minerals, pH and surface properties). Combined with chemical analyses, Fourier transformation infrared (FTIR) spectra can serve as a fingerprint for mineral identification (Madejova and Komadel, 2001) and consequently deliver relevant insights into soil characteristics that are important for P sorption and reaction processes, and thus have an impact on the risk of P losses.

Superficial fertilizer application can result in high dissolved P concentrations in surface runoff, and is thus highly relevant to estimates of P loss risks (Shigaki et al., 2006; Mori et al., 2009; Bertol et al., 2010). For surface runoff studies on Brazilian Oxisols superficially fertilized with manure, high concentrations of dissolved P as high as 6 mg/L have been reported (Mori et al., 2009; Bertol et al., 2010). In contrast, Oxisols with inorganic superficial fertilizer applications exhibited relatively low dissolved P concentrations, rarely exceeding a concentration of 1 mg/L (Bertol et al., 2007; Bertol et al., 2010; Fischer et al., 2016).

In a former study (Fischer et al., 2016), we investigated the risk of P losses from agricultural soils in the Rio São Francisco (RSF) catchment by: 1) deriving DPS values from monitoring data of M1P through establishing a pedotransfer function between WSP and M1P and 2) assessing dissolved P concentrations in surface runoff of superficially fertilized Oxisols. In the current study, we complement this line of research by 1) testing the WSP-DPS correlation established on European soils (Pöthig et al., 2010) on two contrasting different tropical soil types and 2) investigating the effect of superficial fertilizer application on risk parameter of P losses, namely WSP and DPS. Furthermore we 3) performed FTIR analyses for acquiring complementary information regarding the influences of soil mineralogy on P sorption and P binding forms and 4) transformed recommended M1P levels in soils from agricultural institutions into DPS values using results of the former study in order to investigate the emerging P loss risk from soil P management in Brazil. With our study, we provide a comprehensive summary of a new approach for assessing current and future risks of P losses in the RSF catchment, which is also applicable to other parts of Brazil.

2. Material and methods

2.1. Study site and soil sampling

This study was carried out in the framework of the INNOVATE project (www.innovate.tu-berlin.de), which investigated the RSF catchment, and

in particular the catchment and water quality of the Itaparica reservoir in the lower-middle part of the RSF in Pernambuco. The RSF catchment covers an area of about 639,000 km², equaling 7.5% of Brazil's territory (ANA, 2013). According to the Köppen-Geiger climate classification (Kottek et al., 2006) the upper catchment is characterized by two climates, i.e. warm temperate climate with dry winters and hot summers (Cwa) and equatorial climate with dry winters (Aw; e.g. Belo Horizonte with an annual mean precipitation (AP) of 1460 mm and an annual mean temperature (AT) of 21 °C, INMET n.d.). The lower middle catchment is characterized by drier conditions than the upper catchment, with hot steppe climate BSh (Kottek et al., 2006) dominating (e.g. Petrolândia: AP = 470 mm; AT = 26 °C, INMET n.d.; APAC n.d.) and persistent water scarcity problems (ANA, 2013). The upper and the lower middle catchment are part of the Cerrado and Caatinga biomes, respectively (Fig. 1A). Cropland currently accounts for ca. 6.6% of the catchment area, and new irrigation projects are planned to increase agricultural production (Koch et al., 2015; CODEVASF n.d.). Future scenarios for the catchment range from a steady state concerning total cropland area to a more than doubling of cropland until 2035 (Koch et al., 2015, Fig. 1B). The most important crops covering >75% of the total arable land are soybeans, maize, beans and sugar cane (IBGE-SIDRA, 2015).

Two sites were chosen in order to account for the contrasting soils and climate conditions of the catchment: One dominated by Latossolos/Oxisols and representative of the upper catchment, the other one dominated by Neossolos/Entisols in the lower middle catchment (Fig. 1C, EMBRAPA, 2011, soil classification: Sistema brasileiro de classificação de Solos = SiBCS, EMBRAPA, 2006/USDA soil classification system, Soil Survey Staff, 1999). Oxisols and Entisols are major soil orders in the RSF catchment covering 63% of its area (Fig. 1C, see also Fischer et al., 2016). According to the classification system of the World Reference Base for Soil Resources (WRB, IUSS Working Group WRB, 2015), the dominating soil groups in the sampling sites were Ferralsols and Arenosols (Araújo Filho et al., 2013; EMBRAPA, 2011). The sampling sites were located at the irrigation schemes at the Itaparica reservoir, Pernambuco, namely Apolônia Sales and Icó Mandantes and in the region of São João del-Rei, Minas Gerais.

Soil samples were taken from a total of 35 cropland and pasture sites in 2013/2014 (Fig. 1C). The sampling strategy was to receive a wide range of P levels of the Oxisols and Entisols in order to be able to test the WSP-DPS correlation. This was accomplished by: i) sampling different agricultural fields of permanent and temporary crop types which

are known to receive different amounts of P fertilizer (Ribeiro et al., 1999; Cavalcanti et al., 2008), such as banana, tangerine, coconut, maize, sugar cane, beans, cabbage, bell pepper and melon and ii) support of local agricultural technicians providing knowledge about the history of P fertilizer application on the agricultural fields. Samples were taken as cores (height: 41 mm; diameter: 56 mm) from the top soil layer, which is considered to be the most important soil layer for surface runoff events (Sharpley, 1985).

Samples were divided into two groups: (a) samples without superficial fertilizer application, in which we investigated the correlation between WSP and DPS and (b) samples with superficial fertilizer grains, including samples that had been subjected to irrigation schemes, in which fertilizer had been added to the irrigation water (fertigation). Henceforth, these latter samples are also referred to as samples with excess fertilizer. Additionally, ten samples were taken from the 0–20 cm layer in both MG and PE (five samples in both regions). This depth range is usually sampled for deriving fertilizer recommendations based on M1P analyses (Ribeiro et al., 1999, Cavalcanti et al., 2008).

2.2. Soil analyses

Soil samples were air-dried and sieved (2 mm mesh size) prior to analysis. Soil pH values were determined with 0.01 M CaCl₂ in a 1:2.5 soil-CaCl₂ suspension. Soil densities were determined by weighing 50 cm³ of soil. The investigation of WSP, DPS ($DPS = (TP / (TP + SP_{max})) \times 100$), P sorption isotherms, SP_{max} and total phosphorus content (TP), Al, Fe, Ca and Mg were executed according to Pöthig et al. (2010). Instead of a temperature at 450 °C, calcination was performed at 990 °C to create optimal digestion conditions for determination of TP and the cations. Soil organic matter (SOM) was estimated from the determined cations by $SOM = \text{ignition loss} - \text{mass losses from the reactions of } CaCO_3, MgCO_3, Al \text{ and Fe hydroxides and kaolinites into their oxides}$.

Additionally, results of soil analyses from our previous study, i.e. soil densities, WSP, Fe, Al and DPS values were used (Fischer et al., 2016). In some samples of Oxisols, after filtrations of WSP extracts through 0.45 μm filters, a second filtration with 0.2 μm filters was necessary in order to obtain a clear solution for photometrical analyses. All P concentrations were measured photometrically (Murphy and Riley, 1962) with a UV-vis photometer (UV 2102, Shimadzu Corp.).

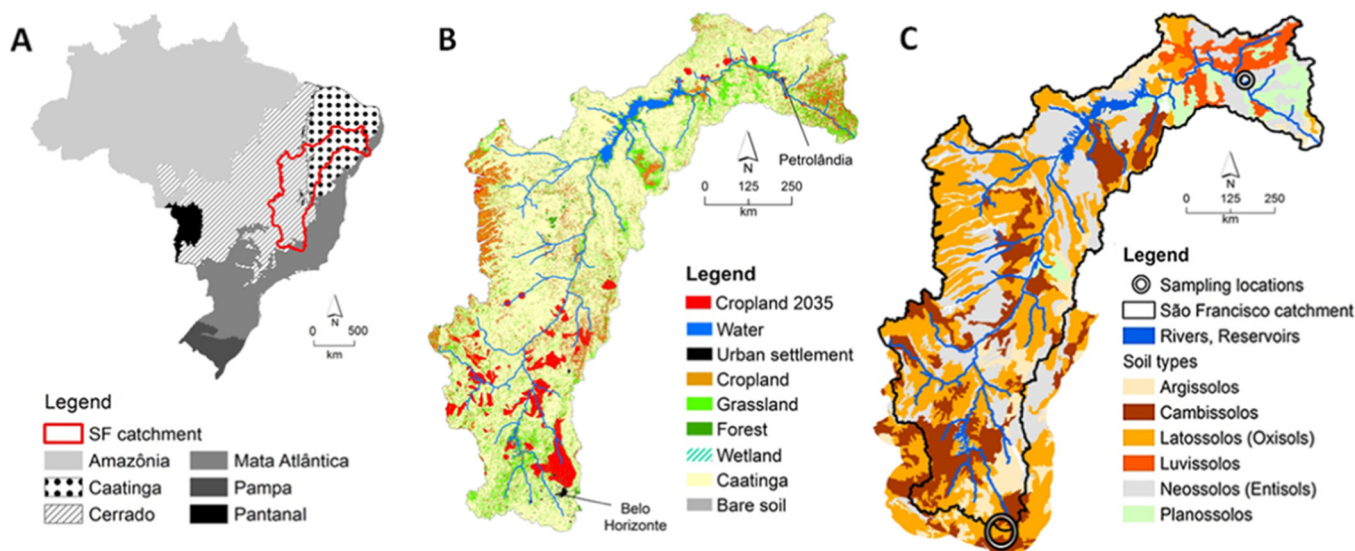


Fig. 1. The São Francisco catchment: (A) Location in Brazil and its biomes (IBGE, 2004), (B) current land use in the São Francisco catchment with predicted potential maximum expansion of crop area until 2035 according to Koch et al., 2015 (map: Koch et al., 2015, modified), and (C) sampling locations and soil types in the São Francisco catchment (Fischer et al., 2016, modified, source soil map: EMBRAPA, 2011).

Table 1
Characteristics of the investigated soils from Minas Gerais (MG; Oxisols) and Pernambuco (PE; Entisols): Parameters determined for testing the WSP-DPS approach are marked in grey. TP = total phosphorus, PSC = TP + SP_{max} (SP_{max} = remaining sorption capacity, PSC = phosphorus sorption capacity), DPS = degree of P saturation, WSP = water soluble phosphorus, n = number of samples. Results from this study and Fischer et al., 2016.

Sites	Soil type		pH	soil density g/cm ³	Ignition loss (900°C), %	Fe g/kg	Al g/kg	Ca g/kg	Mg g/kg	TP	PSC	DPS	WSP
										mg/kg	mg/kg	%	mg/kg
MG	Oxisols	n	12	30	26	22	22	8	8	26	26	26	26
		min	3.9	0.83	6.4	30.0	34.4	2.1	0.5	159.7	480.7	31.3	0.8
		max	6.5	1.17	20.3	84.0	134.3	7.1	1.4	1790.6	2308.6	78.5	19.8
		MEDIAN	4.8	1.00	12.6	45.0	71.9	4.3	1.1	471.7	749.7	62.6	4.3
PE	Entisols	n	12	51	28	33	33	32	32	28	28	28	28
		min	5.0	1.17	1.3	2.4	3.7	1.4	0.2	102.0	139.3	30.9	0.7
		max	6.6	1.56	8.7	22.3	28.8	59.2	9.1	932.1	1183.7	86.4	36.5
		MEDIAN	6.2	1.40	3.0	6.5	9.1	3.5	0.7	179.7	343.9	67.8	9.0

Soil samples (15 from MG, and 16 from PE) were analyzed by FTIR in order to characterize the mineralogical composition of the soils. Because of low P concentrations in soils (commonly <0.1%), the emerging P binding forms from reactions of fertilizer phosphates with soils are difficult to study directly on soil samples (Lindsay et al., 1989). Consequently, fertilizer grains separated from six soil samples of Oxisols in Minas Gerais were characterized by FTIR analyses in order to gain insights into the reaction of soils with fertilizer P. Samples were dried at room temperature and powdered. Subsequently, samples of 5–6 mg were ground mechanically with 800 mg dried KBr (105 °C) and pressed under vacuum conditions into disks with a diameter of 20 mm. FTIR spectra were recorded with a Fourier transform spectrometer (FTIR-8300, Shimadzu) over a range of 400–4000 cm⁻¹ at 4 cm⁻¹ resolution and 50 scans. Additionally, annealed samples (900 °C) were studied to gain complementary information by observing thermochemical reactions.

To study the effect of excess fertilizer on WSP, consecutive WSP extractions were performed on 21 soil samples including soil samples with and without excess fertilizers. After each extraction the supernatant was removed and analyzed for P, and the remaining soil sample was extracted again.

2.3. Transformation of recommended M1P levels in DPS

Recommended M1P levels for different crops in the RSF catchment were transformed into corresponding DPS values by using a M1P-WSP correlation determined on a set of soil samples of the same study area ($WSP = 0.1662 \times M1P$, $R^2 = 0.94$; Fischer et al., 2016). Subsequently DPS values were calculated as $DPS = 100/(1 + 1.25 \times WSP^{-0.75})$, following the approach by Pöthig et al. (2010).

2.4. Statistical analyses

We used the nls tool package of the statistical software R (R Core Team, 2015) to fit non-linear regressions to measured data of this and a former study (Pöthig et al., 2010) using the model $DPS = 100/(1 + a \times WSP^{-b})$. The parameter a was set to 1.25 according to Pöthig et al. (2010). 99% confidence intervals of the parameter b were determined using the function *confint* of the R package MASS to test whether DPS-WSP relationships of the Brazilian sites in this study differed from the previously published relationship (Pöthig et al., 2010). In the regression analyses, only WSP values ranging between 0 and 18 mg/kg from Pöthig et al. (2010) were considered in order to cover the same WSP concentration range as that of soil samples without excess fertilizer in the present study.

3. Results and discussion

3.1. Soil characterization

The soils of the investigated areas in MG were mainly Oxisols. These were characterized by low soil densities and exceptionally high contents of Fe and Al of up to 84 and 134 g/kg, respectively (Table 1; Fischer et al., 2016). Table 1 gives an overview of crucial soil variables for characterization of the potential P losses of investigated agricultural soils from Minas Gerais (MG, Oxisols) and Pernambuco (PE, Entisols) regarding P sorption (SP_{max}, DPS), P accumulation (TP), P saturation (DPS) and P desorption (WSP). The soil organic matter (SOM) in both soil types is considered inconsequential (values varying between 0.4 and 3%, arithmetic mean = 1.5%) in the context of investigation of P saturation and P loss of our investigated soils (for SOM values derived from ignition losses: see material and methods and appendix).

The FTIR spectra of the studied soil samples of MG showed the for Oxisols typical bands of gibbsite, goethite and kaolinite (Fig. 2A, for more detailed information: see appendix, Table app.1A). From the evaluation of the hydroxide bands of 15 soil samples we concluded that 7 were dominated by kaolinite and 8 by gibbsite. This knowledge is relevant for the P sorption properties of the studied soils: the soil P sorption capacity at pH values between 3.8 and 6, as occurring in Oxisols, has been reported to be considerably higher at Fe and Al hydroxides than at kaolinites (McLaughlin et al., 1981) or bentonites (Dimirkou et al., 2002).

In a previous surface runoff study on Oxisols with superficially applied P fertilizer in our study region in Minas Gerais, relatively low P concentrations in runoff water, but considerable particulate P export was found (Fischer et al., 2016). FTIR analyses of the fertilizer grains from soil samples of MG revealed more insights in the underlying processes of P sorption/fixation on Oxisol particles. Although raw phosphates (apatite) and thermophosphates are also used as mineral P fertilizer on acid tropical soils (Lopes et al., 2012), five of the six investigated fertilizer grains were of “superphosphate” and thus dominated by SO₄²⁻ bands from very well crystallized gypsum. Despite of the different appearance of the two spectra caused by the amount of gypsum with its dominant sulfate bands, these spectra showed the same frequencies but different intensities for the phosphate bands (Fig. 2B). No indications of Ca-phosphates originating from superphosphate or their aged products were identified by FTIR. Assuming that the reaction of P fertilizer with soils of similar composition and pH value resulted in only one phosphate phase, the best conformity was found with crandallite [CaAl₃(PO₄)₂(OH)₅·H₂O]. Our spectra were compared to published data of five crandallite spectra of four different sources including one pure

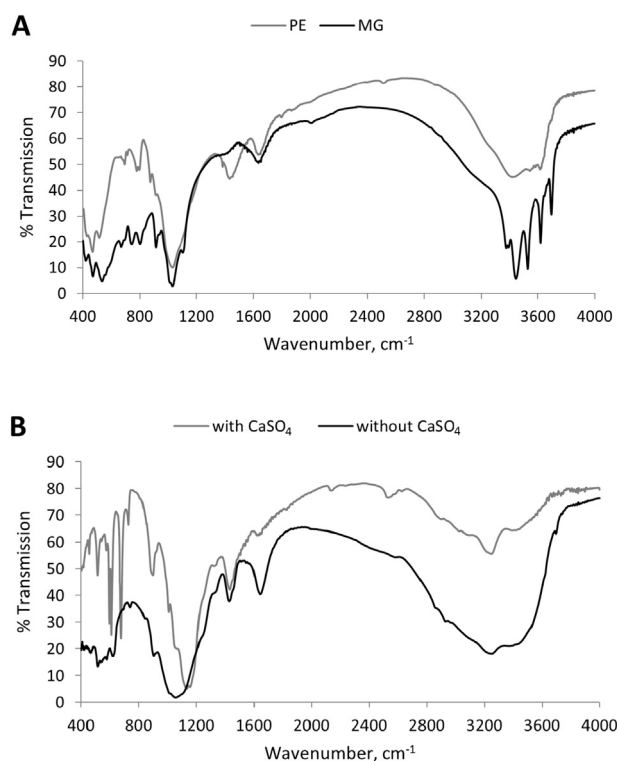


Fig. 2. FTIR spectra of A) soil samples from Minas Gerais (MG) and Pernambuco (PE) B) two fertilizer grains from Oxisols of Minas Gerais with CaSO_4 and without CaSO_4 .

synthetic and four natural crandallite minerals (for detailed discussion and observed wavenumbers of fertilizer grains with mineral identification: see appendix, Table app.2).

The formation of crandallite may happen by a reaction between the OH groups on the gibbsite surface and the H_2PO_4 groups of the fertilizer phosphate (see appendix: Fig. app. 1, Eq. app.2). The chemical conditions of the soils (i.e. low pH values and high Al contents, see Table 1) would well agree with the forming of crandallite as the main phosphate phase in the fertilizer grains. The poor degree of crystallinity may be caused by substitutions in the mineral structure. A final proof of the formation of crandallite would be possible by synchrotron-based high-energy X-ray diffraction (HEXD) or a long term study investigating the building of well crystallized soil specific P forms by FTIR and X-ray diffraction (XRD).

A reaction of fertilizer P with Oxisols, forming crandallite, would suggest that such reactions, or at least their first steps (i.e. chemisorption) also take place between dissolved phosphates from superficially applied P fertilizer and the very small Oxisol-particles during surface runoff events. Crandallite is yet more stable than ordinary Al phosphates and thus has a lower P solubility (Savenko et al., 2005).

The investigated Entisols were characterized by a higher soil density than the Oxisols (Table 1) and the presence of significant amounts of quartz and clay minerals (Fig. 2A, more detailed information: see appendix, Table app.1B). Fe, Al, Ca and Mg contents differed widely between samples (Table 1) and were comparable to European soils of Germany and Switzerland of a former study (Pöthig et al., 2010). Soil samples of two sites with Ca and Mg contents >4 g/kg showed the typical bands of CaCO_3 and MgCO_3 , as well as additional bands, which could be related by their characteristic frequencies to the minerals montmorillonite $(\text{Na,Ca})_{0.3}(\text{Al,Mg})_2\text{Si}_4\text{O}_{10}(\text{OH})_2 \cdot n\text{H}_2\text{O}$, palygorskite $(\text{Mg,Al})_2\text{Si}_4\text{O}_{10}(\text{OH}) \cdot 4\text{H}_2\text{O}$ and sepiolite $\text{Mg}_4\text{Si}_6\text{O}_{15}(\text{OH})_2 \cdot 6\text{H}_2\text{O}$ (Madejova and Komadel, 2001, Frost et al., 2001; for wavenumbers, mineral identification and more detailed information: see appendix, Table app.1B).

These three clay minerals occur together exclusively in xeric-, aridic- and semi-aridic soils as neoformed minerals and are associated with

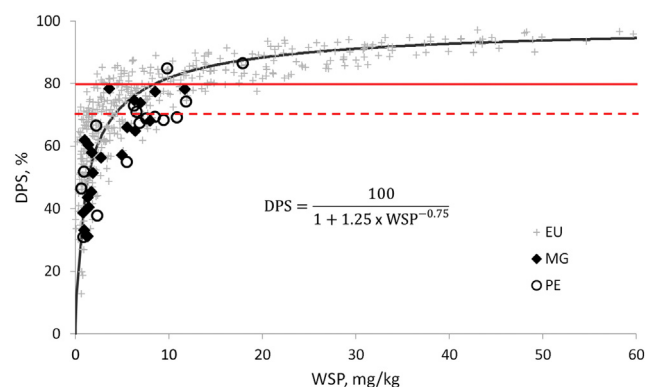


Fig. 3. Relationship between WSP and DPS for the investigated Brazilian soils (only samples without excess fertilizer): Dashed and solid red lines mark elevated and high risks of dissolved P losses, respectively. The black line is the soil type-independent function derived for European soils. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

carbonates as well as quartz. They are predominant in shallow shelf basins on passive margins or continental basins (Singer, 2002; Galán and Pozo, 2011). Even though these findings could not yet be confirmed by XRD analysis, the FTIR spectra and the above mentioned conditions, including the location of the samples in an area of the Jatobá Basin with shales and siltstones, calcareous sandstones and calcareous siltstones (Araújo Filho et al., 2013) suggest the existence of the three clay minerals in the studied soils. Furthermore, deposits of palygorskite also occur in other parts of semi-arid Brazil (Luz et al., 1988; Xavier et al., 2012).

This finding may also be an important factor for the P mobility in soils and the risk of P loss. Neaman and Singer (2004) reported that palygorskite and sepiolite release Mg^{2+} cations into the soil solution which decrease the aggregate stability of the soil clay fractions and improve the phosphorus availability in arid soils - thereby increasing the risk of P losses by drainage and surface runoff in irrigation agriculture and regions of heavy rainfall events.

3.2. Testing of the soil type-independent WSP-DPS correlation

The above outlined differences of the studied Brazilian soils from PE and MG resulted in P sorption capacities (PSC) of Oxisols on average twice as high as those from the investigated Entisols (Table 1). Despite the great differences between the investigated Oxisols and Entisols, both corresponded well with the soil type-independent correlation between WSP and DPS established on 429 European soil samples (Fig. 3, Table 2).

This finding was confirmed by statistical analyses, as 99% confidence intervals of the parameter b of the regression equation $\text{DPS} = 100 / (1 + 1.25 \times \text{WSP}^{-b})$ overlapped for all investigated soil groups (Table 2), and thus, the investigated Brazilian soils corresponded well with the regression previously determined for European soils (Pöthig et al., 2010), demonstrating its suitability for assessing the risk of P losses from agricultural areas in Brazil.

Table 2

Regression results for determinations of the parameter b, using the model $\text{DPS} = 100 / (1 + 1.25 \times \text{WSP}^{-b})$, and 99% confidence intervals of b; n = number of samples, MG = Minas Gerais, PE = Pernambuco, EU = Europe.

Soils	n	b	b, 99% confidence interval	
			Lower boundary	Upper boundary
MG	21	0.57	0.37	0.81
PE	16	0.53	0.37	0.71
EU	335	0.73	0.66	0.80

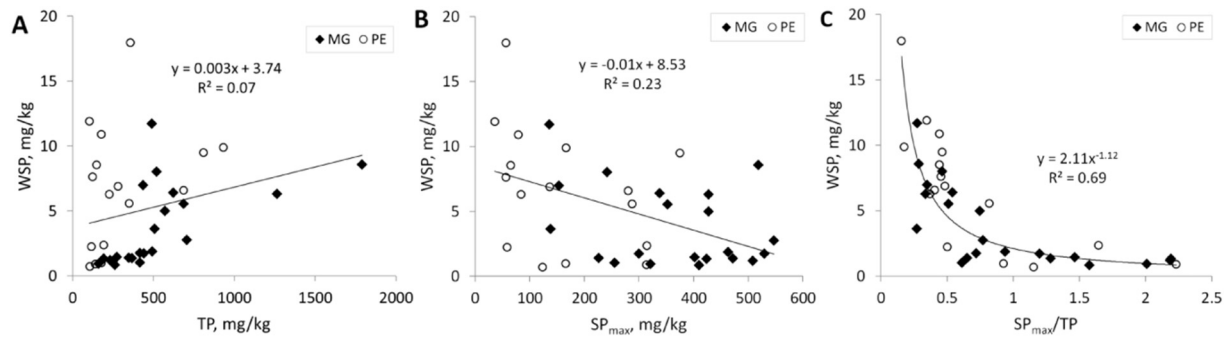


Fig. 4. Relationship between water-soluble phosphorus (WSP) and (A) total phosphorus (TP), (B) remaining sorption capacity (SP_{max}), and (C) the quotient of SP_{max} and TP: The SP_{max}/TP ratio is related to WSP in a soil type-independent correlation (see Pöthig et al., 2010).

The fitting of very different soil types in this correlation is explained by the fact that water reflects the natural P solubility of each soil according to its composition, the resultant pH value and soil specific P binding and sorption forms, and thus the degree of P saturation. These are the reasons for WSP being a function (f) of the ratio between the remaining sorption capacity (SP_{max}) and total phosphorus (TP): $f(WSP) = SP_{max}/TP$ (see Fig. 4C). Whereas SP_{max}/TP can be predicted by WSP and vice versa, TP or SP_{max} cannot be predicted by WSP alone, when the soil type is not considered (Fig. 4A, B). The ratio SP_{max}/TP takes into account the total accumulated P in relation to remaining sorption capacity of a soil. DPS is defined by $(TP/(TP + SP_{max})) \times 100$, which is equal to $DPS = 1/(1 + SP_{max}/TP)$. Replacing SP_{max}/TP by $f(WSP)$ results in the soil type-independent correlation between DPS and WSP: $DPS = 100/(1 + 1.25 \times WSP^{-0.75})$ reported by Pöthig et al. (2010). Consequently, the WSP-DPS approach is suitable for assessing the risk of P losses from agricultural areas in Brazil.

The fact that the WSP-DPS relationship formerly tested on sandy, loamy, calcareous and decomposed peat soils (Pöthig et al., 2010) is also valid for tropical soils with very different properties confirms the soil type-independency of the approach. From a chemical point of view the method has to be valid also on other soil types as a method using the water solubility should always reflect the given natural conditions in the soil. However, these conditions are altered when analyzing anoxic soils (e.g. soil horizons at groundwater level) as air-dried soils are used for the determination of WSP and DPS. The drying process changes the anoxic conditions, and accordingly the redox processes that affect P sorption and binding on Fe. Thus, the WSP-DPS approach probably cannot adequately assess the risk of P losses from these soils.

Both median values of measured DPS in MG and PE (62.6% and 67.8% respectively, Table 1) were low compared to a study of arable soils in Germany deriving DPS values from monitoring data (median DPS = 85% and 76% of monitoring data with DPS values >80%; Fischer et al., 2017). For the investigated Oxisols of MG, the low DPS values can be explained by exceptionally high P sorption capacities (Table 1). Even

though in some samples elevated risks of P losses (DPS > 70%) were determined, a high risk of P losses (DPS > 80%) was not found.

The investigated Entisols from PE were in agricultural use only since 1994, when the Icó Mandantes irrigation project started after the damming up of the Itaparica reservoir in 1988. Apparently, accumulated P has not yet resulted in high DPS values in the majority of the soils. However, in single samples DPS values higher than 80% were measured indicating a high risk of dissolved P losses.

In soils with low sorption capacities like sandy Entisols, high DPS and WSP values are reached at lower TP accumulations than in soils with high sorption capacities (e.g. Oxisols). This fact becomes apparent analyzing the average values of TP, PSC and DPS in Table 1: Entisols with only about half of the accumulated P (TP) and half the sorption capacity (PSC) of Oxisols reached a higher degree of P saturation (DPS) than Oxisols. Consequently, P accumulations in Entisols as high as those found in the studied Oxisols (i.e. 500 mg/kg) would result in DPS values >80%, leading to high risks of P losses. In the perspective of the ongoing agricultural intensification in Brazil, the indicated higher risk of P losses from Entisols should be considered in P fertilizer management to avoid unfavourable environmental impacts in the future.

3.3. Recommended M1P levels and concomitant risk of P losses

Relatively low P saturation values were also reported by a former study integrating monitoring data of M1P of Brazilian soils in the upper São Francisco catchment (mean of DPS and standard deviation: $54 \pm 22\%$, Fischer et al., 2016). However, in the previous study, a high spatial variability of estimated DPS values was found indicating a frequent occurrence of hot spots with high DPS values that should receive special attention regarding their potential impact on surface waters. Furthermore, future soil DPS values that submit surface waters to eutrophication processes have to be avoided. Such critical DPS values have e.g. been reported for central Europe (Schoumans and Chardon, 2015; Fischer et al., 2017).

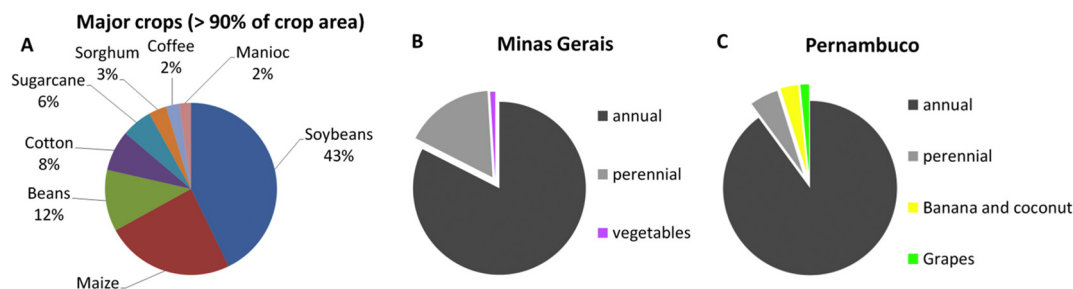


Fig. 5. Percentage of occupied agricultural crop area per crop (—type) in A) the São Francisco catchment B) Minas Gerais C) Pernambuco: The dominating crop type is annual crops in all 3 regions covering >90% of the total crop area.

Future risks of P losses were assessed by the evaluation of recommended P levels for agricultural soils to ensure an optimal agricultural production. Different M1P levels are recommended depending on the clay content of the soil and the type of crop planted. Highest M1P-levels are recommended for soils with lowest clay content, i.e. sandy soils, which are most vulnerable to P losses. In our evaluation, we focused on the fertilizer use manuals of the federal states of Minas Gerais and Pernambuco (Ribeiro et al., 1999; Cavalcanti et al., 2008; Cavalcanti et al., 2010).

The classification system of soil fertility in Minas Gerais is divided in 5 classes. Recommended P levels are defined by classes “good” and “very good”, which differ in dependence of the clay content of the soils. The DPS values resulting from recommended P level “good” for different crop types (Ribeiro et al., 1999) are given in Fig. 6. Recommended M1P levels for annual and perennial crops, i.e. major crops in Minas Gerais and the RSF catchment covering ≥90% of total crop area, corresponded to DPS values below high risk of P losses for sandy soils, as indicated by DPS values >80% (Figs. 5, 6). However, a conflict with environmental goals was identified in the recommendation for vegetables (Fig. 6) corresponding to DPS values up to 90%, which indicate exceptionally high risks of P losses. Although the overall share of vegetables on crops in Minas Gerais and in the RSF catchment is low (<1%), in single municipalities these crops cover up to 50% and more of total crop area (IBGE-SIDRA, 2015). The soil fertility class “good” on clayey soils corresponded to DPS values below the threshold value of high risks of P losses for all annual/perennial crops and vegetables (Fig. 6).

In Pernambuco, soil P fertility evaluation is based on 3 classes reaching from “low” to “high” (Cavalcanti et al., 2010). A low risk of P loss was identified for the lower threshold of soil fertility class “high” of M1P ≥ 30 mg/dm³ (Cavalcanti et al., 2010), which results in DPS values of ≥73% for annual crops (the problems arising from the non-existence of an upper limit of fertility classes are discussed below). Higher M1P levels are targeted for some irrigated perennial crops such as coconut and banana (M1P ≥ 40 mg/dm³ corresponding to DPS ≥ 77%), which cover about 4% of the crop area in Pernambuco (Fig. 5) and in some municipalities >35% of crop area (IBGE-SIDRA, 2015). Highest target M1P levels are given for irrigated grapes (on sandy soils: M1P > 80 mg/dm³ corresponding to a DPS of >85%), which are covering about 2% (Fig. 5) and up to 26% of total crop area in Pernambuco and in some municipalities, respectively. Just as in Minas Gerais, recommended P levels on clayey soils were below the DPS threshold value of high risks of P losses of 80%.

The relatively low risks of P losses for annual and perennial crops emerging from recommended M1P levels we found were in accordance with a study evaluating the risk of P losses by M1P in soils of Santa Catarina in southern Brazil, where critical P thresholds were found to be higher than critical levels for plant production (Gatiboni et al., 2015). In contrast, recommended P levels in German soils were

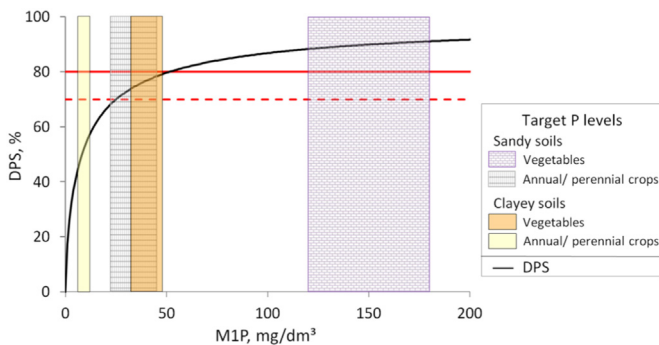


Fig. 6. Recommended P levels for sandy and clayey soils of Minas Gerais (Ribeiro et al., 1999) and resulting risks of P losses estimated by DPS: dashed and solid red line represent elevated and high risks of dissolved P losses, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

identified to be conflicting with environmental goals (DPS = 72–87%, Fischer et al., 2017). Whereas no conflict was identified for major crops of the RSF catchment, single crops that have substantial shares on total crop production in some municipalities showed a high risk of P losses. In these municipalities, more detailed research regarding the hydrological connectivity of agricultural areas to surface waters is recommended in order to identify regions, where best management practices such as buffer strips are necessary to prevent high nutrient inputs by surface runoff, which may cause eutrophication in these aquatic systems (Lemunyon and Gilbert 1993, Heathwaite et al. 2005, Taffarello et al. 2016).

In order to balance agronomic and environmental interests, we recommend considering an upper limit of M1P of 51 mg/dm³ in soils corresponding to average WSP and DPS values of 8.5 mg/kg and 80%, respectively, to avoid high risks of P losses in the future. However, in calcareous soils and soils fertilized with CaCO₃, Mehlich-1 was reported not adequate for assessing P availability (Kuo, 1996; Pierzynski, 2000; Arruda et al., 2015). In these soils more analyses are necessary to derive environmental thresholds by e.g. establishing a correction factor for M1P (Fischer et al., 2016) or by introducing methods which are not influenced by soil type such as WSP.

3.4. Superficial fertilizer application and its importance for dissolved P losses from Oxisols and Entisols

In soils with superficial fertilizer application/fertigation, the measured high WSP values caused by excess fertilizer in samples were not accompanied by elevated degrees of P saturation (Fig. 7A).

Whereas excess fertilizer in soil samples has an impact on WSP, the DPS determined with sorption isotherms remained nearly unaffected: the WSP analyses resulted in average P concentrations in the soil

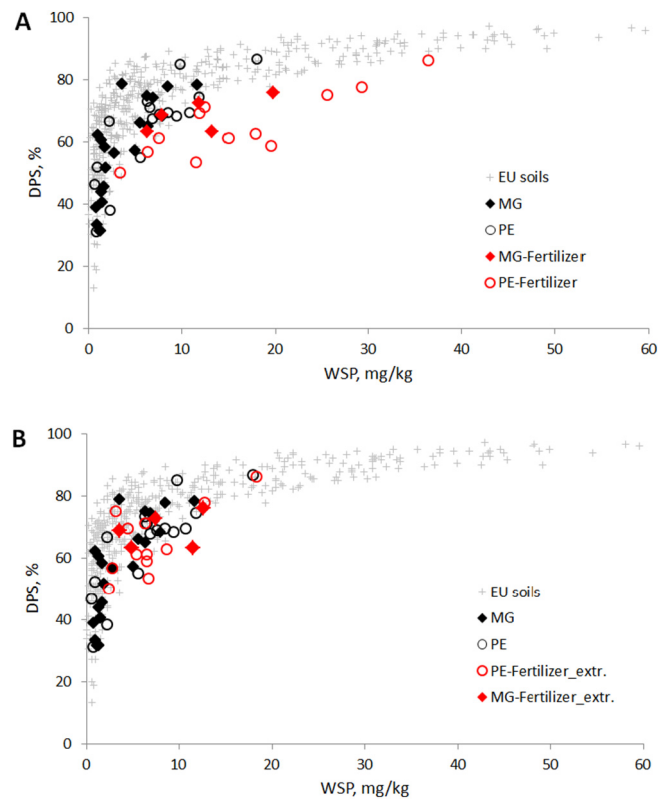


Fig. 7. Relationships between WSP and DPS for the investigated Brazilian soils with superficial fertilizer application from Minas Gerais (MG) and Pernambuco (PE), (A) considering superficial fertilizer grains/fertigation and (B) after removing excess fertilizer by consecutive WSP extractions: WSP values of the second extraction are shown. Data from European soils (EU soils) are shown for comparison (Pöthig et al., 2010).

extractants of 0.086 mg/L (4.3 mg/kg) for soils of MG and 0.180 mg/L (9.0 mg/kg) for soils of PE (Table 1). Soil samples with fertilizer particles produced maximum P concentrations of 0.396 mg/L (19.8 mg/kg) and 0.730 mg/L (36.5 mg/kg) for MG and PE, respectively. Though excess fertilizer has an impact on soil extractions with low P concentrations, such as occurring in WSP extractions, there was nearly no effect on P concentrations of sorption solutions in the range of 20 to 50 mg/L, which are used for the calculation of SP_{max} . The effect of excess P on the accumulated P (TP) was also low, particularly in Oxisols with higher TP values and sorption capacities than in Entisols. Consequently, our measured soil DPS values determined by TP and SP_{max} ($DPS = (TP / (TP + SP_{max})) \times 100$) remained virtually unaffected by the amount of water soluble excess fertilizer which had not reacted yet with the soil matrix to less water soluble soil specific P forms.

Because of the discrepancies between WSP and DPS in soil samples with and without excess fertilizer, we investigated the decline of WSP values in subsequent water extractions of soil samples in the two soil groups (Fig. 8).

In soils without presence of excess fertilizer, no sharp decrease in WSP between the first and second extraction was observed and the WSP decline was relatively constant between the 3 consecutive extraction steps (Fig. 8A). In contrast, the WSP extractions of soil samples from MG and PE with the presence of excess fertilizer (Fig. 8B and C, respectively) showed a sharp decrease in WSP after the first extraction, whereas the WSP declined relatively smoothly from the second to the third extraction step. Consequently, excess P fertilizer was largely extracted in the first extraction step.

Two consecutive P extractions of soil samples resulted in lower WSP values, converging to the WSP-DPS correlation determined for European soils in a former study and for Brazilian Oxisols and Entisols without excess fertilizer in this study (Fig. 7B, Fig. 3). The WSP extraction experiments indicate that WSP reacts very sensitive to excess fertilizer, and thus, shows the importance of superficial fertilizer application for dissolved P losses in surface runoff as reported in different studies (Shigaki et al., 2006; Bertol et al., 2010). However, calculating DPS values from WSP is problematic for soils with excess P fertilizer, because DPS can be overestimated. Similar effects can be expected for the Mehlich-1 extraction method used to estimate plant-available P. Some exceptionally high DPS values, and consequently high risks of P losses estimated for the municipality of Guanambi from monitoring data (Fischer et al., 2016) might be explained by superficial fertilizer grains in soil samples, resulting in an overestimation of M1P values of monitoring data and consequently also of the estimated WSP and DPS values. Therefore, for estimation of plant available P and DPS by standard soil extraction methods, such as M1P and WSP, it is of utmost importance to analyze soil samples without excess fertilizer.

In the previous surface runoff study on superficially fertilized Oxisols (Fischer et al., 2016), P was mainly exported in particulate form, and we supposed the sorption of dissolved P from fertilizer phosphates on Al and Fe hydroxides of transported soil particles in surface runoff. In the present study, further evidence was found supporting this hypothesis.

The FTIR spectroscopic investigation of fertilizer grains from Oxisol samples showed no bands of original fertilizer phosphate, and we hypothesize the formation of poorly crystalline crandallite [$CaAl_3(PO_4)_2(OH)_5 \cdot H_2O$] as the main phosphate phase. Such a reaction within a grain supports the assumption of similar reactions of dissolved $H_2PO_4^-$ and HPO_4^{2-} ions on surfaces of Al/Fe hydroxides in surface runoff events. Although the studied runoff events on Oxisol fields produced mainly particulate P loss, this does not mean that there is no risk of eutrophication for surface runoff receiving water bodies. When small soil particles with high P saturation reach surface waters with low P concentrations, such as reservoirs and streams, processes of P desorption and disintegration take place (Correll, 1998), which can trigger eutrophication effects in these systems.

In contrast, the sorption of dissolved P on the surface of Entisols of the sub middle catchment during surface runoff is most probably much lower, because of the overall lower PSCs of the soils as measured in our study. Consequently, high concentrations of dissolved P in surface runoff due to superficial fertilizer application are more probable at Entisol fields of Pernambuco. A surface runoff study on superficially fertilized Entisols would be necessary to confirm this assumption.

The importance of P losses from agriculture in the triggering of eutrophication processes in downstream water bodies is well known (Carpenter et al., 1998). Only recently, the implementation of soil P management measures resulting in more labile P in the surface relevant soil layers, such as superficial fertilizer application were discussed as a crucial factor for enhanced dissolved P loads to lake Erie leading to severe toxic algae blooms in recent years (Jarvie et al., 2017). Thus, from an environmental perspective, superficial fertilizer application has to be avoided in general, but especially prior to the rainy season to lower the risk of eutrophication of Brazilian water bodies, which are frequently used for drinking water use.

4. Conclusions

The soil type-independent approach by Pöthig et al. (2010) to estimate DPS by WSP, previously established on European soils, was proven to be suitable for tropical soils and is recommended for a simple and fast risk assessment of P losses in Brazil and worldwide. An implementation of environmental threshold values of Mehlich-1P could help to avoid future DPS levels in soils that endanger water bodies to eutrophication processes in the São Francisco catchment and Brazil. In the perspective of a trend to higher P application in parts of Brazil, special attention has to be paid on areas covered by soils with relatively low sorption capacities such as the investigated Entisols, which develop critical DPS values at low TP accumulations. The superficial application of P fertilizer can lead to high risks of P losses, despite overall relatively low DPS values below critical environmental thresholds. Especially in areas with a high hydrological connectivity of agricultural fields to surface waters (e.g. reservoirs and low order streams), avoiding superficial fertilizer application could contribute substantially to lower the risk of

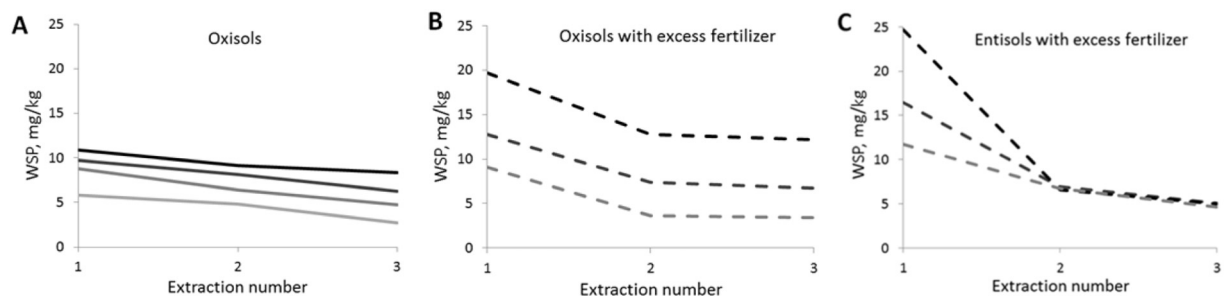


Fig. 8. The decline of WSP in samples without (A) and with excess fertilizer (B, C) in subsequent WSP extractions of Oxisols (A,B) and Entisols (C): Each line represents consecutive WSP extractions performed on one soil sample.

eutrophication processes that endanger safe water supply for local communities and livestock production, as well as aquatic biodiversity and ecosystem functioning.

Acknowledgements

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Appendix A. Investigation of Oxisols (MG), Entisols (PE) and fertilizer grains by FTIR spectroscopy

A.1. Oxisols

The mineralogy of Oxisols is dominated by kaolinite, gibbsite, goethite and hematite (Fontes, 1992). The FTIR spectra of our studied soil samples in the area of Minas Gerais ($n = 15$) showed all main bands of the above-mentioned minerals with the exception of hematite (Fig. 2A, Table app.1). Hematite has only two characteristic bands at about 470 cm^{-1} and 550 cm^{-1} (Rendon and Serna, 1981) overlapped by strong bands of kaolinite and gibbsite and was therefore not clearly detectable. Nevertheless its presence can be expected in our samples. Quartz was detected in only some of the Oxisols. In the OH-stretching region of the FTIR spectra, the bands of kaolinite and gibbsite are very specific. Kaolinite is characterized by four bands at $3696, 3669, 3653, 3620\text{ cm}^{-1}$ (Vaculikova et al., 2011) and gibbsite by bands at $3620, 3525, 3436$ and a double band at $3377/3394\text{ cm}^{-1}$ (Kloprogge et al., 2002). Differences in these band intensities were used to identify the dominant mineral in the soils: Gibbsite was considered to be dominant when the band at 3525 cm^{-1} was more intensive than the kaolinite bands.

A.2. Entisols

The characteristic double bands at around 800 cm^{-1} , which were found in all investigated Entisols, showed a significant amount of quartz. In addition to kaolinite, montmorillonite was identified as main clay mineral in some of the Entisols. Bands of humic acids at 2850 and 2925 cm^{-1} which are typically found in soils and sediments (Parikh et al., 2014) could be detected as very small bands in some of the Entisols, in the Oxisols their presence can only be suspected. This finding is in accordance to the estimated low SOM.

Table app.1A and B:

Band positions, band assignments and mineral identification of the studied Brazilian soil samples from Minas Gerais (MG) and Pernambuco (PE): Bands cited by Mönke (1962) and Elderfield & Hem (1973) were assigned by comparing them with reported assignments from Raman data (Ruan et al. 2001).

Wavenumber (cm^{-1})	Intensity	Band assignment	Minerals	References
Table app.1A: Minas Gerais				
405-410	sh-w	vFe-OH/Al-O-vib	Gt/Gb	Blanch et al. (2008)/ Elderfield & Hem (1973)
418-425	w	Al-O-/δSi-O-vib	Gb/K	Moenke (1962); Elderfield & Hem (1973)/ Vaculikova et al. (2011)
450	sh	Al-O-/Fe(3)-OH	Gb/Gt	Blanch et al. (2008)
468-470	vs	δSi-O-Si	K/Q	Vaculikova et al. (2011)/ Musić et al. (2011)
517-520	sh	Al-O-vib	Ds	Van der Marel & Beutelsbacher (1976)
535-540	s	δAl-O-Si/v(OH)	K/Gb	Vaculikova et al. (2011)/ Moenke (1962); Elderfield & Hem (1973)
560	sh	v(OH)	Gb	Van der Marel & Beutelsbacher (1976); Elderfield & Hem (1973)
630-635	sh	vFe-O	Gt	Blanch et al. (2008); Krehula et al. (2002)
667-670	w, br	v(OH)	Gb	Moenke (1962); Elderfield & Hem (1973)
698-700	w	Si-O perp/δSi-O	K/Q	Vaculikova et al. (2011)/ Hlavay et al. (1978)
742-754	m	Al-OH/Si-O perp	Gb/K	Elderfield & Hem (1973)/ Vaculikova et al. (2011)
798-803	m	δ(OH)/vSi-O-Si	Gb;Gt/Q	Elderfield & Hem (1973)/ Ruan et al. (2002)/ Musić et al. (2011)
911-914	s	δ(OH)	Gb/K	Kloprogge et al. (2002)/ Madejova and Komadel (2001)
936-938	sh-w	δ(OH)	K	Vaculikova et al. (2011)
966-968	sh	δ(OH)	Ds;Gb	Kloprogge et al. (2002)
1007-1010	vs	vSi-O	K	Vaculikova et al. (2011)
1020-1029	vs	δ(OH)/vSi-O	Gb/K	Elderfield & Hem (1973)/ Madejova and Komadel (2001)
1075-1080	sh	vSi-O	Q	Vaculikova and Plevova (2005); Hlavay et al. (1978)
1105-1110	w	Si-O perp	K	Madejova and Komadel (2001); Vaculikova et al. (2011)
1620-1630	m	δ(H-O-H)	K/Gb	Saikia & Parthasarathy (2010)/ Moenke (1962)
2000	sh-w	v(OH)	Ds	Van der Marel & Beutelsbacher (1976)
3180-3200	sh, br	v(OH)	Gt	Ruan et al. (2002)
3375-3377	w	v(OH)	Gb	Kloprogge et al. (2002)
3395-3397	w	v(OH)	Gb	Kloprogge et al. (2002)
3440-3446	vs	v(H-O-H)	Gb/K	Kloprogge et al. (2002)/ Madejova and Komadel (2001)
3524-3526	s-vs	v(OH)	Gb	Kloprogge et al. (2002)
3619-3620	s	v(OH)	Gb/K	Kloprogge et al. (2002)/ Madejova and Komadel (2001)
3648-3652	sh-w	v(OH)	K	Saikia & Parthasarathy (2010)/ Madejova and Komadel (2001)
3667-3668	vw	v(OH)	K	Vaculikova et al. (2011)/ Madejova and Komadel (2001)
3694-3696	s	v(OH)	K	Vaculikova et al. (2011)/ Madejova and Komadel (2001)
Table app.1B: Pernambuco				
418-419	sh-w	δO-Si-O	S	Frost et al. (2001)
425-430	sh	δO-Si-O	K/P	Madejova and Komadel (2001)/ Frost et al. (2001)
467-470	vs	δO-Si-O/δSi-O-Si	Q/M;K/P;S	Musić et al. (2011)/ Vaculikova and Plevova (2005)/ Frost et al. (2001)
515-525	sh-m	Al-O-Si/δO-Si-O	M/P;S;Q	Madejova and Komadel (2001)/ Frost et al. (2001); Hlavay et al. (1978)

(continued on next page)

Table app.1A and B: (continued)

Wavenumber (cm ⁻¹)	Intensity	Band assignment	Minerals	References
636-640	sh-vw	vSi-O	K;P	Madejova and Komadel (2001)
694-695	w-m	δSi-O/Si-O perp	Q/K	Hlavay et al. (1978)/ Vaculikova et al. (2011)
711-712	w-m	δCO ₃	Ca	Vaculikova and Plevova (2005); Huang & Kerr (1960)
778	w-s	vSi-O/δ(OH)	Q/S	Vaculikova and Plevova (2005)/ Frost et al. (2001)
798-800	w-s	vSi-O	Q	Vaculikova and Plevova (2005)
836-838	sh	δAlMgOH	M	Madejova and Komadel (2001)
873-874	sh-m	δCO ₃	Ca	Vaculikova and Plevova (2005)/ Huang & Kerr (1960)
908-915	w-m	δ(OH)/δAlAlOH	K/M;P	Madejova and Komadel (2001)
935-936	sh	δ(OH)	K	Vaculikova et al. (2011)
980-990	sh	vSi-O	P;S	Frost et al. (2001)
1005-1010	sh-w	vSi-O	K/S	Vaculikova et al. (2011)/ Frost et al. (2001)
1028-1035	vs	vSi-O	K;M;P	Madejova and Komadel (2001)
1075-1085	sh-m	vSi-O	Q/S	Hlavay et al. (1978)/ Frost et al. (2001)
1105-1115	sh	vSi-O	K;M	Madejova and Komadel (2001)
1164-1166	sh-w	vSi-O-Si	Q	Van der Marel & Beutelsbacher (1976)
1420-1460	w-m	vCO ₃	Ca	Vaculikova and Plevova (2005); Huang & Kerr (1960)
1620-1640	m, br	δ(H-O-H)	K/M;P;S	Saikia & Parthasarathy (2010)/ Madejova and Komadel (2001)
1795-1800	w	vCO ₃	Ca	Vaculikova and Plevova (2005)
2513	w	vCO ₃	Ca	Vaculikova and Plevova (2005)
3235-3250	sh	v(H-O-H)	P;S	Frost et al. (2001)
3400-3420	s, br	v(OH) H ₂ O	P	Frost et al. (2001)
3546-3550	w-m	v(OH) H ₂ O	P;S	Frost et al. (2001);
3612-3626	m	v(OH)/vMgOH	K;M;P;S	Madejova and Komadel (2001)/ Frost et al. (2001)
3665-3668	sh	v(OH)	K	Vaculikova et al. (2011)
3690-3695	sh-w	v(OH)/vMgOH	K/S	Vaculikova et al. (2011) /Frost et al. (2001)
3719-3720	sh-w	vSiOH	S	Vaculikova et al. (2011)

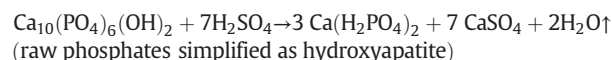
Shortcuts: s- strong, vs- very strong, m- medium, w- weak, vw- very weak, sh- shoulder, br- broad, v- stretching mode, δ- bending mode, vib- vibration, perp- perpendicular vibration

Minerals: Gb- Gibbsite, Gt- Goethite, Ds- Diaspore, Ca- Calcite, K- Kaolinite, Q- Quartz, M- Montmorillonite, P- Palygorskite, S- Sepiolite.

Band shoulders were identified by the second derivative of the spectra.

A.3. Fertilizer grains from Oxisols

FTIR analyses of five of the six fertilizer samples revealed enormous amounts of CaSO₄ (Fig. 2B, Table app.2) emerging from sulfuric acid treatment of raw phosphates that generates Ca(H₂PO₄)₂ as a water-soluble P fertilizer ("superphosphate"):



Eq. app.1

Consequently, FTIR spectra were dominated by SO₄²⁻ bands from very well crystallized CaSO₄·2H₂O (gypsum) at 595, 606, 676 and 1155 cm⁻¹ (Lane, 2007), partially overlying the less intensive phosphate bands, which were poorly dissolved, caused by the low degree of crystallization (Table app.2, Fig. 2B). Considering Oxisols dominated by gibbsite/goethite and soil pH values in the range from 4.4 to 5.8, reactions of the H₂PO₄⁻ and HPO₄²⁻ ions with the Al and Fe hydroxides are favored. Therefore, our investigation of FTIR spectra considered possible Al and Fe phosphates and hydroxy phosphates, also with mixed cations (Na⁺, K⁺, Ca²⁺, Mg²⁺, Mn²⁺, Al³⁺, Fe²⁺, Fe³⁺) and anions (PO₄³⁻, HPO₄²⁻, SO₄²⁻) by comparing them with published FTIR-mineral data. Best conformity was found with crandallite.

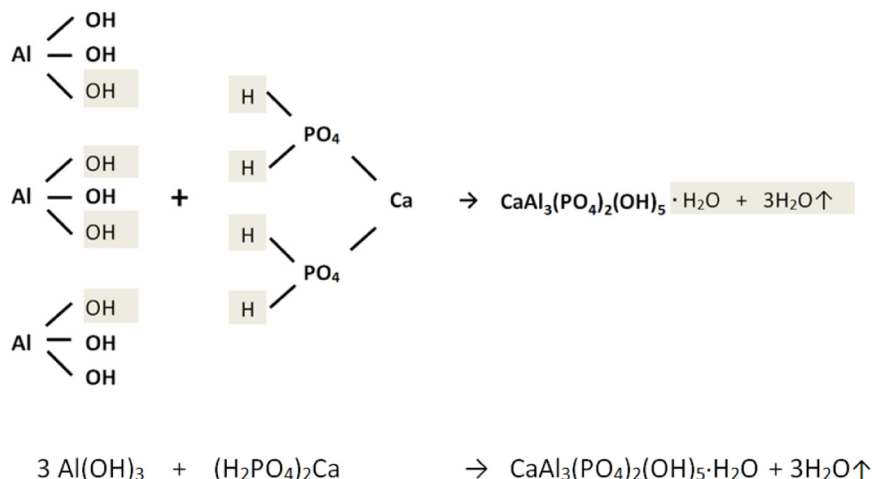


Fig. app.1, Eq. app.2. Proposed reaction of gibbsite with fertilizer phosphate forming crandallite in Oxisols.

Hypothesized formation of crandallite by a reaction between the OH groups on the gibbsite surface with the H₂PO₄ groups of the fertilizer phosphate: Crandallite crystallizes in the trigonal crystal system with PO₄³⁻ and HPO₄²⁻ groups in its structure (Frost et al., 2011). The FTIR spectra showed both, PO₄³⁻ and HPO₄²⁻ bands (Table app.2). The existence of HPO₄²⁻ units in our samples was also proven by the fact that the observed phosphate bands of the calcined (900 °C) samples were partly caused from vibrations of P₂O₇⁴⁻ ions due to the reaction:

**Table app.2**

Band positions, band assignments and mineral identification of the studied fertilizer grains of Oxisol soil samples from Minas Gerais: Band assignments were done by using reported data of crandallite (Frost et al., 2011); Gibbsite (Klopprogge et al., 2002; Ruan et al., 2001); Gypsum (Lane, 2007) and calcium carbonate (Andersen & Brecevic, 1991).

IR data of fertilizer grains of Minas Gerais				Published IR data for crandallite minerals				
Wavenumber (cm ⁻¹)	Intensity	Band assignment	Minerals	Frost et al. (2011)		Moenke (1962)	Sadler Research Laboratories (1982)**	Chukanov and Chervonnyi (2016)
				synthetic	natural			
418-425	vw	Al-O-vib	Gb					
455-457	sh	δs (PO ₄)	Cr	455-465		465	455	456
510-511	m	δs (PO ₄ /HPO ₄)	Cr	505-510		510	510	505
535-536	w	OH vib	Gb					
562-568	w	δs (PO ₄)/OH vib	Cr/Gb	562-565		562sh	565sh	
594-596	vs	δas (PO ₄)	Cr	580-595		595	580sh	590s
609-611	vs	δas (SO ₄ /PO ₄)	Gy/Cr					
630-631	sh-w	δas (PO ₄)	Cr	614-630		620	630	614
676-678	s	δas (SO ₄)	Gy					
725-728"	sh-w	δ(CO ₃)	Ca				735*	
805-810	sh-w	δ(OH)/OH vib	Cr/Gb	800-825		825	800-815	810
889-895	w-m	δ(OH)	Cr	882-895	895	871*	870*	882
912-914	sh	δ(OH)	Gb					
980-982	sh	vs (HPO ₄)	Cr	989	989	967		
1005-1008	m	vs (PO ₄)	Cr	1005-1015		1015	1005sh	1015sh
1043-1044	m-s	vs (PO ₄)	Cr	1034-1045	1045	1034	1040	1037s
1057-1061	sh	vas (PO ₄ /HPO ₄)/δ(OH)	Cr/Gb	1055-1066		1066	1055	
1070-1075	sh	vas (PO ₄ /HPO ₄)	Cr	1070-1078	1078			1074s
1100-1102	sh	vas (PO ₄ /HPO ₄)	Cr	1105-1113		1109		1113
1130-1132	vs	vas (SO ₄ /HPO ₄)	Cr	1120-1140	1133	1140	1120	
1156-1158	vs	vas (SO ₄)	Gy					
1163-1175	sh	vas (PO ₄ /HPO ₄)	Cr	1166-1172	1166		1175sh	1172sh
1184-1186	sh	vas (PO ₄ /HPO ₄)	Cr	1182		1182		
1220-1229	sh	vas (PO ₄ /HPO ₄)	Cr	1220-1227		1223	1225	1227
1320-1326	w	δ P-(OH)	Cr	1310-1330		1320	1330	1325
1418/1452	m	v (CO ₃)	Ca	1415-1492	1422/1492	1415/1452		1477
1616/1648	m	δ (H ₂ O)	Cr	1630-1660	1547/1656	1585/1649		1660
1825"	vw	v (CO ₃)	Ca		1760		2320	2360
2841-2850	sh-w	v P-OH	Cr	2853/2890	2853/2890			
2921-2922	sh	v P-OH	Cr	2921		2921sh		
3115/3150	sh	v H ₂ O	Cr	3115-3140		3124	3140	3115
3218-3240	s	v H ₂ O	Cr	3265	3265			3290
3290"		v (H ₂ O)	Cr	3300-3320		3314	3320	3315
3400-3440	s	v (H ₂ O)	Cr/Gb	3437-3450		3437sh		3450
3520-3546	m	v(OH)-Al/v(OH)	Cr/Gb	3544	3544			
3585"	sh	v(OH)-Al	Cr	3580			3580	
3610-3618*	sh	v(OH)-Al/v(OH)	Cr/Gb	3610	3610			

"") bands not occurring in all samples

735*, 870* and 871* may be due to carbonate

Shortcuts: s - strong, vs - very strong, m - medium, w - weak, vw - very weak, sh - shoulder, v - stretching modes, vs - symmetric stretching, vas - asymmetric stretching, δ - bending modes, δs - symmetric bending, δas - asymmetric bending, vib - vibration.

Minerals: Cr- Crandallite: CaAl₃(PO₄)₂(OH)₅·H₂O, Gy- Gypsum: CaSO₄·2H₂O, Gb- Gibbsite: Al(OH)₃, Ca- amorphous CaCO₃.

Band shoulders were identified by the second derivative of the spectra.

**) Sadler Research Laboratories (1982).

General remarks on Table app.1 and app.2:

The observed differences in the wavenumbers of the studied soil samples and fertilizer grains, shown as margins in Tables app.1 and app.2 are most likely caused by substitutions in the mineral structures: e.g. substitution of Fe³⁺ in goethite and hematite by Al³⁺ forming aluminous goethite and aluminous hematite (Fysh and Fredericks, 1983). In clay minerals Al³⁺ can be partly substituted by Fe³⁺ as has been shown for kaolinite (Premovic et al., 2009). These defects cause shifts in the IR frequencies of naturally occurring minerals.

Minor Al substitutions by Fe in the mineral structure of crandallite and differences in the technique of measurement of the IR spectra (ATR or KBr) probably also caused the differences in the FTIR spectra of our samples and in the reported frequencies of the four cited natural crandallite spectra in comparison to the synthetic one. Consequently the frequencies of the cited bands are also shown as margins (Table app. 2).

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