The degree of phosphorus saturation of agricultural soils in Brazil and Germany: New approaches for risk assessment of diffuse phosphorus losses and soil phosphorus management

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Dipl. Geoökol. Peter Fischer

Präsidentin der Humboldt-Universität zu Berlin
Prof. Dr.-Ing. Dr. Sabine Kunst
Dekan der Mathematisch-Naturwissenschaftlichen Fakultät
Prof. Dr. Elmar Kulke

Gutachter: 1. Prof. Dr. Gunnar Nützmann

                2. Prof. Dr. Michael Rode

                3. Prof. Dr. Hans Estrup Andersen

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Abstract

The efficient use of phosphorus (P) as fertilizer in agriculture has a pivotal role in the supply of humankind with food. However, phosphorus (P) applied in excess to agricultural soils leads to P accumulations that threaten water bodies with eutrophication processes through diffuse P losses. The degree of P saturation (DPS) is an established parameter for assessing the risk of P losses from agricultural soils.

A soil type-independent approach that allows estimating DPS by a simple standard extraction method of water-soluble phosphorus (WSP) has so far only been applied to central European soils. In this thesis, the soil type-independency of the approach was confirmed on tropical Brazilian soils.

In Brazil, fertilization is customarily carried out by inorganic superficial fertilizer application and has to be considered in the risk assessment of P losses. The effect of superficial fertilizer application on P losses was investigated in a combination of different laboratory analyses and field studies. For the first time, temporal variations of P concentrations in single surface runoff events on superficially fertilized Brazilian Oxisols were analyzed, whereby: i) the range of dissolved P concentrations in surface runoff could be estimated by WSP analyses; ii) the chemical reaction of fertilizer grains with soils was identified, which could explain the observed low dissolved P concentrations in this and former reported surface runoff studies.

For assessing the risk of diffuse P losses through DPS from: i) monitoring data, and ii) recommended P levels in soils by agricultural institutions, pedotransfer functions were derived between WSP and standard soil methods, estimating plant-available P in Brazil (Mehlich-1) and Germany (Calcium-acetate-lactate = CAL). First DPS maps showed relatively small risks for the investigated region in Brazil and high risks for Germany, which were partly explainable by the different P levels recommended in the two countries.

The identified soil type-dependency of the CAL method limited the prediction accuracy of DPS. Moreover, the prediction of soil parameter equilibrium phosphorus concentration (EPC0), which is crucial for estimating plant-available P, was limited across different soil types. The correction of measured P values by the pH value of the CAL extraction solution strengthened the discrepancies between different soil types, and thus augments the probability of misinterpretation of soil P levels determined by the CAL method in the German fertilizer recommendation system.

Defining adequate soil P levels that address both optimized agricultural production and the protection of surface water from diffuse P losses is a challenge for many countries. In order to address both aspects with a simple and cost-effective method, standard soil test methods of water and $CaCl_2$ to estimate plant-available P were combined with the WSP-DPS approach. This approach could help to solve the challenges humanity faces in the coming decades: An efficient use of the limited resource P and the protection of surface waters from diffuse P losses.

German abstract

Eine effiziente Nutzung von Phosphor (P) als Düngemittel in der Landwirtschaft ist von entscheidender Bedeutung für die Versorgung der Menschheit mit Nahrungsmitteln. Zu hohe P-Düngermengen führen jedoch zu P-Akkumulationen in landwirtschaftlichen Böden und können zu diffusen P-Austrägen sowie Eutrophierungsprozessen in Oberflächengewässern führen. Der Phosphorsättigungsgrad (engl. degree of P saturation = DPS) ist ein etablierter Parameter, um das Risiko von P-Austrägen aus landwirtschaftlichen Böden zu erfassen.

Ein bodentypunabhängiger Ansatz, der den DPS anhand einer einfachen Standardmethode zur Ermittlung wasserlöslichen Phosphors (engl. water-soluble phosphorus = WSP) abschätzt (WSP-DPS-Ansatz), wurde bisher nur auf mitteleuropäische Böden angewendet. In der vorliegenden Arbeit wurde die Bodentypunabhängigkeit dieses Ansatzes für tropische brasilianische Böden bestätigt.

Die in Brasilien häufig praktizierte oberflächliche Aufbringung anorganischen Düngers muss in der Risikoabschätzung von P-Austrägen berücksichtigt werden. Der Effekt der Oberflächendüngung auf das P-Austragsrisiko wurde in einer Kombination verschiedener Labortechniken und Feldstudien untersucht. Erstmals wurde die zeitliche Variabilität der P-Austräge innerhalb einzelner Oberflächenabflussereignisse oberflächlich gedüngter brasilianischer Oxisols erfasst, wobei die Spannbreite gemessener gelöster P-Konzentrationen durch WSP abgeschätzt werden konnte. Des Weiteren wurde die chemische Reaktion der Düngemittel mit den Böden identifiziert, die zur Erklärung der in dieser Arbeit gemessenen und in der Literatur berichteten relativ geringen gelösten P-Konzentrationen im Oberflächenabfluss beitragen kann.

Um eine Abschätzung der DPS aus: i) Monitoringdaten und ii) von landwirtschaftlichen Institutionen empfohlener Boden-P-Gehalte zu ermöglichen, wurden Pedotransferfunktionen zwischen WSP und den Standardmethoden, die zur Abschätzung des pflanzenverfügbaren Phosphors in Brasilien (Mehlich-1) und Deutschland (Calcium-Acetat-Lactat = CAL) verwendet werden, bestimmt. Erstmals erstellte DPS-Karten beider Länder zeigten relativ geringe Austragsrisiken für das Untersuchungsgebiet in Brasilien und hohe Austragsrisiken für Deutschland; teilweise erklärbar durch die unterschiedlichen empfohlenen P-Gehalte in beiden Ländern.

Die in dieser Arbeit festgestellte Bodentypabhängigkeit der CAL-Methode limitierte die Genauigkeit der DPS-Abschätzung. Sie limitierte außerdem die Vorhersage der P-Gleichgewichtskonzentration in der Bodenlösung (engl. equilibrium phosphorus concentration = EPC0) verschiedener Bodentypen, die entscheidend für die Pflanzenverfügbarkeit von P ist. Die Korrektur gemessener P-Werte anhand der pH-Wert-Veränderung in der CAL-Extraktionslösung verstärkte die Unterschiede zwischen verschiedenen Bodentypen und erhöht die Wahrscheinlichkeit einer Fehlinterpretation gemessener P-Werte mit der CAL-Methode im derzeitigen deutschen Düngeempfehlungssystem.

Eine exakte Definition von P-Gehalten im Boden, die sowohl eine optimale Pflanzenproduktion als auch möglichst geringe diffuse P-Austräge gewährleistet, ist eine Herausforderung für viele Länder. Um mit einer einfachen und kosteneffizienten Methode beider Belange gerecht zu werden, wurden die Wasser- und CaCl$_2$-Methode zur Abschätzung von pflanzenverfügbarem P mit dem WSP-DPS-Ansatz kombiniert. Dieser Ansatz könnte helfen die Herausforderungen zu lösen mit denen die Menschheit in den nächsten Jahrzehnten konfrontiert sein wird: Einer effizienten Nutzung der limitierten Ressource P und dem Schutz der Oberflächengewässer vor diffusen P-Einträgen.

Contents

1 Introduction

1.1 Phosphorus: Limited resource, fertilizer and threat to surface water quality

Rock phosphate is a limited resource. Over the last decades, the awareness of the limitation of the resource P and its importance for humankind has increased. As summarized in a recent review by Chowdhury et al. (2017), estimates of the lifetime of phosphate rock reserves have differed widely in recent years, ranging from 70 to 100 years (Smil 2000, Fixen 2009) to 370 years (Cooper et al. 2011, Scholz and Wellmer 2013) or even 1000 years (Fixen and Johnston 2012, Sutton et al. 2013). Morocco and Western Sahara possess more than 70% of global rock phosphate reserves (USGS 2017). Many parts of the world, such as Europe, have very limited resources of rock phosphates and depend on fertilizer imports (Ott and Rechberger 2012, Withers et al. 2015). In 2014 the European Union included rock phosphate in the list of critical raw materials (European Commission 2014: IP/14/599 26/05/2014).

The major part of rock phosphate is used as fertilizer in agriculture (Liu et al. 2008, Chowdhury et al. 2014, Reijnders 2014). Phosphorus is a necessary element for plant growth that can limit agricultural production (e.g. Cleveland et al. 2013). As most soils are naturally poor in P in relation to P levels necessary for an intensive agricultural production, P is given as fertilizer to soils to enhance agricultural productivity. The role of P in sustaining agricultural production is unique. The safe supply of soils and plants with P has been described as a bottleneck of world food security (e.g. Blume et al. 2009). This is particularly a problem where soils are P deficient due to too low applications of P, such as in Sub-Saharan Africa (e.g. Buresh et al. 1997, Margenot et al. 2016). In contrast, industrial countries in Northern America and Europe have been applying more P to soils than was extracted by harvests over decades, which resulted in an accumulation of P in the soils (e.g. Sattari et al. 2012). This P accumulation, also referred to as residual soil P, is a danger to surface water quality due to the transport of soil P to water bodies by so called diffuse P losses (e.g. Novotny 1999, Sattari et al. 2012, Sharpley et al. 2013).

1.2 Diffuse P losses and eutrophication

Diffuse P losses from agriculture are a major driver for eutrophication processes in freshwater systems and coastal oceans (Carpenter et al. 1998, Correll 1998). The consequences of eutrophication processes in water bodies are manifold, including the loss of biodiversity, mass development of algae, building of anoxic conditions, fish kills and dangers to safe drinking water supply (e.g. Lawton and Codd 1991, Correll 1998, Smith 1998, Bennett et al. 2001 and references therein). Eutrophication processes that are driven by increasing organic and inorganic nutrient loads have been reported in freshwater and coastal marine systems, e.g. the spreading of bottom anoxia in the Baltic sea (Diaz and Rosenberg 2008, Carstensen et al. 2014, Kauranne and Kemppainen 2016), the "dead zone" in the Gulf of Mexico (Downing et al. 1999) or the mass development of algae in European lakes (e.g. Csathó et al. 2007, Ulén et al. 2007, Withers and Haygarth 2007).

In regions where water bodies like reservoirs are used for drinking water supply the avoidance of eutrophication processes is of utmost importance, as cyanobacteria blooms with concomitant toxin productions potentially lead to health risks, including cases of death of humans and cattle (e.g. Falconer 1989). One of the most severe outbreaks of gastro-enteritis attributed to a cyanobacterial bloom is reported for the Itaparica reservoir located in the dry northeastern region of Brazil (Chorus and Bartram 1999). After flooding of the dam in 1988, an epidemic resulted in 2,000 affected persons, including 88 deaths, mainly among children (Teixeira et al. 1993).

1.3 Planetary boundary P

The triggering of eutrophication processes of freshwater and coastal ecosystems through nutrient inputs from point and diffuse sources is considered a global problem (Smith 2003). The modification of the natural phosphorus cycle by anthropogenic activities leads to increased P nutrient emissions from land to surface water bodies, and puts both oceans and freshwaters at risk of eutrophication processes (Carpenter and Bennett 2011). In fact, these P emissions modify the natural biochemical flow of P in such a way that they have been identified as one of the major concerns for threatening the integrity of the Earth system as a safe operating space for humanity (see concept of planetary boundaries: Rockstrom et al. 2009, Steffen et al. 2015). The biochemical flow of P is considered to have crossed its critical threshold, i.e. its planetary boundary and consequently has to receive special attention (Fig. 1.1, Steffen et al. 2015).
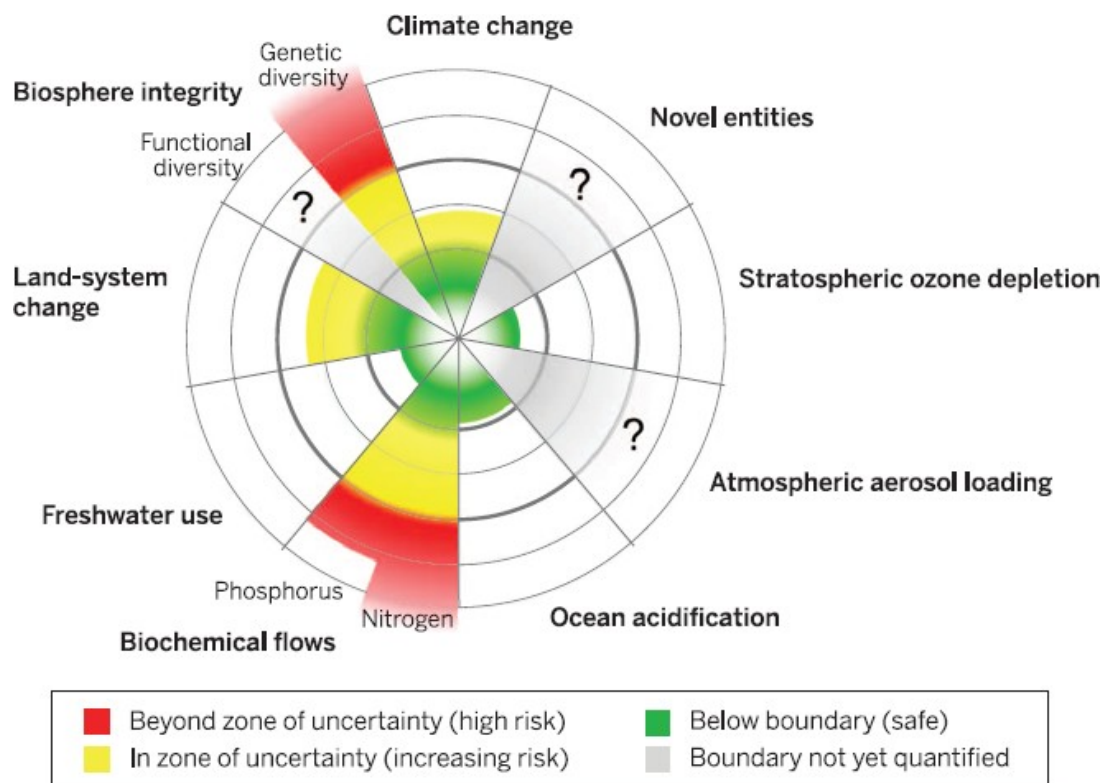

Figure 1.1: Planetary boundaries for a safe operating space of humankind: Biochemical flow of phosphorus has exceeded the planetary boundary regarding freshwater eutrophication (see Carpenter and Bennett 2011, figure from Steffen et al. 2015, reprinted with permission from AAAS).

1.4 Phosphorus emission pathways from agricultural areas to water bodies

P emissions from agricultural areas to water bodies happen mainly via surface runoff and subsurface flow. P is also lost from agricultural soils by wind erosion and gets into the atmosphere through dust and sea spray (e.g. Richey 1983, Li et al. 2008, Mahowald et al. 2008). However, P emissions to freshwater bodies by means of P deposition are so small in comparison to the huge amounts transported with waters from land to water bodies that they are normally not considered in the assessment of P emissions from agricultural areas to water bodies (e.g. Schlesinger 1991, Li et al. 2008, Pärn et al. 2012).

Surface runoff is normally the main diffuse pathway for P to reach the water bodies (e.g. Kronvang et al. 2007, Pärn et al. 2012). P is transported via surface runoff in particulate and dissolved form, whereby the major part (>75%) of P is normally transported in particulate form (e.g. Schuman et al. 1973, Sharpley et al. 1987, Hart et al. 2004).

Particulate P is generally considered as the fraction of a water sample not passing a filtration with 0.45 µm. The bioavailability of particulate P to primary production was reported to vary between 10% and 90% (DePinto et al. 1981, Dorich et al. 1985, Sharpley et al. 1992). When suspended particles enter water bodies, a re-equilibration between the particulate and the dissolved phase of P takes place, which among others depends on the dissolved P concentration of the receiving water body (e.g. Froelich 1988, Correll 1998). Thus, the potential of particulate P of surface runoff to contribute to eutrophication processes also depends on the characteristics of the receiving water body.

The dissolved P is generally classified as the fraction passing a filter with 0.45 µm (e.g. Haygarth and Sharpley 2000). Dissolved P measured by the method of Murphy and Riley (1962) was reported to be almost completely available for growth of algae (Lee et al. 1980, Ekholm 1998, Reynolds and Davies 2001). Colloidal P with a diameter of approximately 1nm to 1 µm (e.g. Ilg 2007) and dissolved organic P are also parts of the dissolved fraction, and are not entirely immediately bioavailable (Rigler 1968, Lean 1973). At the beginning of the 1990s, research in USA and Europe led to the conclusion that the role of dissolved P losses in surface runoff and its impact on eutrophication processes is of high importance (e.g. Kristensen and Hansen 1994, Sharpley et al. 1994).

Different measures can be implemented to hinder surface runoff from entering water bodies. In order to avoid particulate P entering surface waters, erosion prevention measures such as contour-ploughing, no tillage, intercropping and keeping a soil coverage with e.g. plant residues or wood chips (mulching) are recommended (Sims and Kleinman 2005, Schoumans et al. 2014). Buffer strips along rivers and lakes are also commonly applied measures to prevent the entrance of particulate P into water bodies (COST Action 869: Fact sheets 17 and 22). In contrast to particulate P, hindering dissolved P from entering water bodies is more difficult. Recommended measures are the reduction of the volume of surface runoff that enters surface water bodies, by e.g. establishing ponding systems (Fact sheet 53, COST Action 869) or the use of chemical amendments on soils to bind the soluble P (e.g. COST Action 869, Factsheets 5, 79). The most effective measure is the reduction of P fertilization to a level at which P mobility and P concentrations in surface runoff are reduced to a minimum.

P emissions from tile drainages have often been quantified as small in comparison to emissions by surface runoff and groundwater, e.g. in Europe and Germany (Kronvang et

al. 2007, Holsten et al. 2016). However, in certain areas such as lowland rivers with intensive agricultural use, where tile drainages contribute major water volumes to the total river discharge (e.g. Koch et al. 2013), a higher share of P emissions from tile drainages can be expected. P accumulation in soils and the concomitant increases in the degree of P saturation is the decisive factor for leaching processes from soils to drainages as regards the soil chemistry (e.g. Nair and Graetz 2002). Behrendt and Boekhold (1993) discussed the importance of the gradual saturation of soils and the concomitant increases of P losses by leakage in total P emissions from agricultural areas. Hereby they alerted that P losses by leakage from agricultural areas are a "chemical time bomb" (Stigliani et al. 1991) that has already exploded locally, and has a high potential to significantly alter overall P emissions in the future.

1.5 Estimation of the risk of dissolved P losses from soils

1.5.1   Degree of P saturation

The degree of P saturation (DPS) has been investigated in many parts of the world to assess the risk of dissolved P losses (e.g. Leinweber et al. 1997, Kleinman et al. 1999, Abdala et al. 2012, Xue et al. 2014). Different studies have shown DPS to correlate well with dissolved P concentrations in surface runoff and drainage (Sharpley 1995, Maguire and Sims 2002, Vadas et al. 2005). The DPS relates the extractable P of a soil to the maximum P sorption capacity of the soil (e.g. Van der Zee et al. 1987, Van der Zee et al. 1990, Breeuwsma and Silva 1992). It is commonly used to identify a critical percentage of occupied sorption sites, above which the risk of P loss from soil to water rises disproportionally (e.g. Nair et al. 2004, Xue et al. 2014). Mostly approaches are used that only consider a part of the sorption sites of a soil and correlate soil extractable P to e.g. Fe and Al on sandy, acidic soils (e.g. Börling et al. 2004, Nair et al. 2004, Ghosh et al. 2011) or Mg and Ca on calcareous soils (Ige et al. 2005, Xue et al. 2014). Consequently, these approaches are dependent on soil type. One of the most commonly used DPS approaches is given in equation 1.1 (e.g. Beauchemin and Simard 1999, Nair 2014).

$$(1.1) \quad \text{DPS} = \frac{\text{Oxalate}-\text{extractable P}}{\alpha \, \text{Oxalate}-\text{extractable [Fe+Al]}} \times 100$$

α is an empirical factor that varies according to the investigated soil type, and relates to the share of Fe_{ox} and Al_{ox} responsible for P sorption (e.g. Van der Zee and van Riemsdijk 1988). In many studies the value of 0.5 has been used for α (e.g. Van der Zee et al. 1990, Breeuwsma and Silva 1992, Maguire et al. 2001), however values of 0.1 and 0.68 have also been reported, and sometimes α is completely excluded from the equation (Hooda et al. 2000, Pautler and Sims 2000, Uusitalo and Tuhkanen 2000). Instead of using ammonium oxalate for the determination of extractable P, Fe and Al, other chemical extractants such as Mehlich-1 (Mehlich 1953) or Mehlich-3 (Mehlich 1984) are also used (e.g. Nair et al. 2004, Bortolon et al. 2016). The calculation of DPS by methods such as Mehlich-1, Mehlich-3 and Olsen (Olsen 1954), which are already in use for estimating plant-available P (e.g. Jordan-Meille et al. 2012, Schick et al. 2013) is often preferred, since no other additional methods have to be implemented. The maximum P sorption capacity is sometimes also estimated with the single sorption index by Bache and Williams (1971) or determined by sorption isotherms (e.g.

Sharpley 1995, Kleinman and Sharpley 2002, Jalali and Jalali 2016, Zhou et al. 2016).

A soil type-independent approach for estimating the DPS is based on a study on sorption isotherms, total phosphorus contents and water-soluble phosphorus of more than 400 samples in Germany and Switzerland (Pöthig et al. 2010). This study analyzed DPS for different soil types, including sandy, loamy, calcareous and decomposed peat soils. The DPS was determined as follows:

$$(1.2) \qquad \text{DPS} = \frac{\text{TP}}{\text{PSC}} \times 100 = \frac{\text{TP}}{\text{TP+SP}} \times 100 = \frac{1}{1+\text{SP/TP}} \times 100$$

where TP is total phosphorus determined by aqua regia digestion and SP is the remaining sorption capacity of the soil determined by the linearization of the Langmuir sorption isotherm. The sum of TP and SP is the total sorption capacity of a soil (PSC). The higher the total accumulated P of a soil (TP) the lower the remaining sorption capacity (SP) and vice versa. Pöthig et al. (2010) showed that the ratio between SP and TP is correlated to the standard extraction methodology water-soluble phosphorus (WSP) in a soil type-independent correlation (equation 1.3). Consequently, the time-consuming and costly to determine parameter DPS based on TP and sorption isotherms can be estimated by the fast and cheap to determine standard extraction method of WSP. The functional relation between DPS and WSP was found to be best described by the following empirical equation (marked in grey, Pöthig et al. 2010):

$$(1.3)\ \text{DPS} = \frac{1}{1+\text{SP/TP}} \times 100 = \frac{1}{1+\text{f(WSP)}} \times 100 = \frac{1}{1+1.25 \times \text{WSP}^{-0.75}} \times 100 \ , \text{R}^2 = 0.71$$

WSP values above 5 mg/kg were identified to signalize a DPS between 70 and 80% and thus correspond to high P loss risks from soil to water (Pöthig et al. 2010). In the thesis DPS values of 70% and 80% were defined as critical, indicating elevated and high risks of dissolved P losses, respectively. As the correlation between WSP and DPS is soil type- independent, the approach was recommended as a fast and simple risk assessment of P losses worldwide (Pöthig et al. 2010).

Pöthig et al. (2010) derived the first soil type-independent estimation of DPS by a simple and cheap to determine parameter (WSP), closing a big gap in the risk assessment of P losses from agricultural areas. WSP has been suggested and used as a suitable indicator for predicting environmental risks and plant-available P by different authors (e.g. van der Paauw 1971, Pote et al. 1996, Self-Davis et al. 2000, Vanderdeelen 2002). In this thesis, the WSP- DPS approach is the base for developing new knowledge regarding diffuse P losses and soil P management in Brazil, Germany and Europe.

1.5.2   Direct fertilizer effects

Besides critical DPS values due to accumulation of P in soils, direct fertilizer effects have been identified to have a major impact on dissolved P concentrations in surface runoff (e.g. Kleinman et al. 2002, Shigaki et al. 2006b). Organic (e.g. manure) and inorganic fertilizers (e.g. superphosphate) applied to the surface of soils, without any subsequent incorporation

into the soil matrix (i.e. ploughing), have been shown to result in high dissolved and particulate P concentrations in surface runoff (e.g. Shigaki et al. 2006b, Mori et al. 2009, Bertol et al. 2010). Hence, P losses from agricultural fields with superficial fertilizer application increase the probability of high nutrient emissions into adjacent water bodies. Consequently, the type of fertilizer application has to be taken into account in the assessment of the risk of P losses from agricultural areas.

1.6 Estimation of the risk of P losses by monitoring data: Plant-available P, critical source areas and nutrient emission models

When assessing the risk of P losses on larger scales, it has to be taken into account that data of soil parameters such as DPS or WSP are normally only available for single locations or for limited time periods. On a sub-catchment to river catchment level, the only available measured P data of soils with a high spatial and temporal resolution is determined by methods used to estimate plant-available P, e.g. Olsen, Mehlich-1, Mehlich-3 or Calcium-acetate-lactate (CAL, Schüller 1969). Although originally not developed for estimating the risk of P losses from soil to water, these methods have been correlated to risk parameter of P losses such as DPS, WSP or $CaCl_2$ (Scheinost 1995, Kleinman et al. 1999, Houben et al. 2011) by so-called pedotransfer functions (PTF) (Bouma 1989). "Mild extractants" such as WSP and $CaCl_2$ better reflect interactions of water with soil P in comparison to other methods used to estimate plant-available P, which are either basic or acid in pH (e.g. Calcium-acetate-lactate: pH = 4.1, Olsen: pH = 8.1, Mehlich: pH = 1.1) and thus extract larger amounts of soil P than under natural soil conditions and preferably dissolve either Ca- Mg- bound or Fe- and Al- bound phosphates (Lindsay 1979, Lindsay et al. 1989). In addition, methods to use plant-available P often contain chelating agents, such as Ethylenediaminetetraacetic acid (EDTA) in Mehlich-3, which increase the solubility of Fe, Al and Ca associated P (e.g. Kamprath and Watson 1980). The "mild extractants" H_2O and $CaCl_2$ have repeatedly been described as good estimators of immediately available P (e.g. Sissingh 1971, Neyroud and Lischer 2003) and are used in two European states as standard methodologies for estimating plant-available P (Jordan-Meille et al. 2012): Netherlands ($CaCl_2$ and distilled H_2O) and Switzerland (CO_2 saturated water).

High risks of P losses do not automatically result in significantly increased P emissions to surface waters, as the agricultural P that reaches water bodies is determined by the hydrological connectivity of adjacent areas to the surface waters. Consequently, the identification of so-called critical source areas (CSAs) is important, as only a small percentage of river catchments (ca. 20%, with a strong spatial variability) has been reported to produce the major part (ca. 80%) of P emissions, when considering both point and diffuse P emissions (Sharpley et al. 2009). Based on the same concept as CSAs also P indexes have been defined for different countries (Lemunyon and Gilbert 1993, Heathwaite et al. 2003, Andersen and Kronvang 2006). Two sets of factors are decisive for the definition of CSAs and P indexes; they are often referred to as transport factors and source factors (e.g. Gburek et al. 2000, Strauss et al. 2007). Transport factors determine the hydraulic connectivity of agricultural areas to surface waters through surface runoff (erosion and overflow) and subsurface flow (interflow and groundwater). Source factors characterize the risk of P losses from agricultural

areas emerging from e.g. DPS values of soils, or management related factors such as superficial fertilizer application, intercropping, erosion control etc.

Nutrient emission models play a decisive role in the identification of CSAs and estimation of P emissions from agricultural areas on river catchment scales (Overview and comparison of different models e.g. in Kronvang et al. 2009, Schoumans et al. 2009). These models efficiently combine source and transport factors. They commonly include plant-available P data (e.g. EPIC (Jones et al. 1984), CREAMS (Knisel 1980)) and are useful tools for quantification of diffuse nutrient emissions as well as for identification of hot spot regions of diffuse P emissions (e.g. Venohr et al. 2005, Shore et al. 2014, Yli-Halla et al. 2016). Furthermore, such models have also been used to set target values for coastal zones by defining natural background concentration, e.g. for the Baltic Sea catchment (Hirt et al. 2014) and consequently play a crucial role in environmental evaluations and regulations such as the Water Framework Directive (WFD, Directive 2000/60/EC) .

1.7 Important factors influencing the risk of P losses from arable soils in Brazil and Germany

In the thesis the risk of P losses from soils in Brazil (investigation area Rio São Francisco (RSF) catchment, hereinafter also referred to as São Francisco catchment (Fig. 1.2) and Germany was analyzed by an interdisciplinary approach (see 1.8). The following sections provide a short comparative overview of the most important agricultural facts in Brazil and Germany, focusing on the risk assessment of P losses.
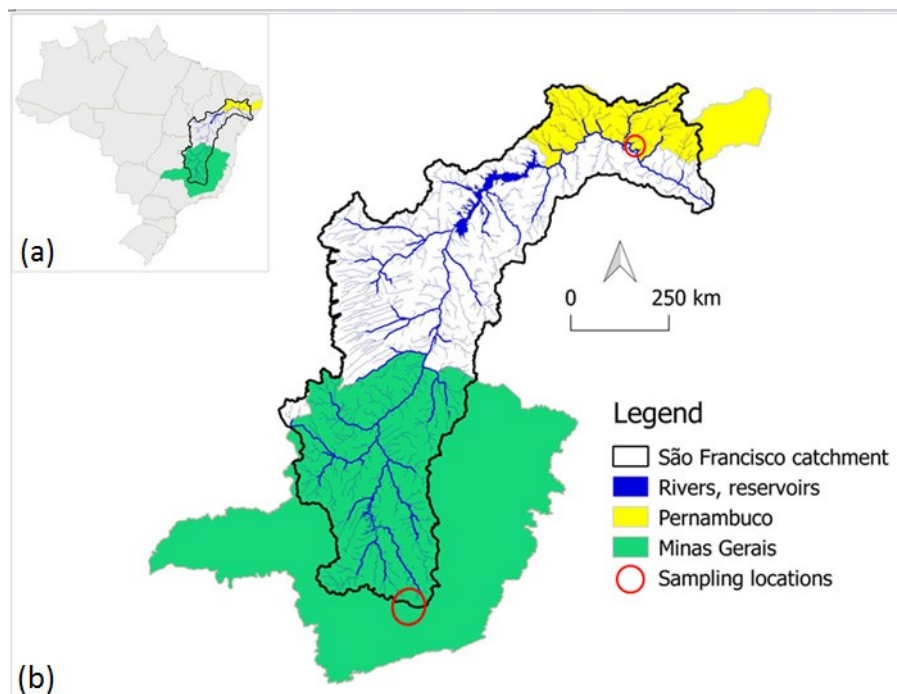

Figure 1.2: The location of the Brazilian investigation area: (a) in Brazil (b) in the Rio São Francisco catchment: Sampling sites in federal states of Minas Gerais and Pernambuco are marked with circles. Map sources: São Francisco river net and catchment: IBAMA-SISCOM, administrative data: GADM database of global administrative areas (Hijmans et al. 2009).

1.7.1   P application, P surplus, and P accumulation

The annual P surplus on soils can be calculated with agri-statistical data, i.e. P import to agricultural soils by fertilizer application minus P exported by harvests. The P accumulation in soils is the sum of annual P surpluses. Both the absolute level of P accumulation and trends in P surpluses differ between Brazil and Germany.

In Brazil, annual P surpluses have been reported to be highly variable (range: -2 to 18 kg ha^{-1} yr^{-1}) for the period 2005-2010 (Roy et al. 2016): for example, annual surpluses were 16 kg ha^{-1} yr^{-1} for Minas Gerais in southeastern Brazil and 1 kg ha^{-1} yr^{-1} for Pernambuco in the northeastern part of the country. An overall increase in P application is reported for recent years (Fig. 1.3, FAOSTAT) which can be expected to continue in the next years, considering the reported intensification trend in Brazilian agriculture (Dias et al. 2016), also leading to increasing P accumulations.
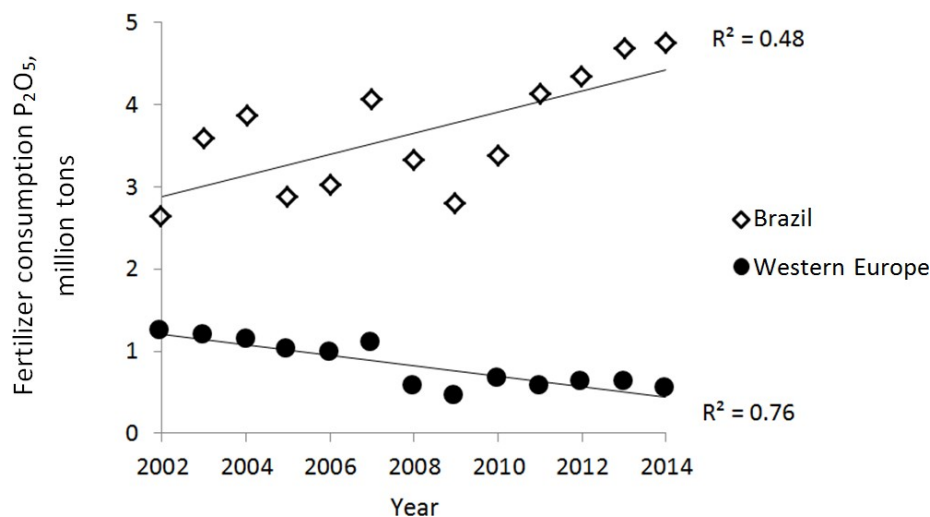

Figure 1.3: Fertilizer consumption in Brazil and Western Europe from 2002-2014: In Brazil an overall increase in fertilizer consumption can be observed, in contrast to western Europe where fertilizer consumption is decreasing; data source: fertilizer consumption per year by FAOSTAT (http://www.fao.org/faostat/en, accessed 17.03.2017).

In Germany, annual P surpluses reached their maximum in the 1970s and 80s with about 30 kg ha^{-1} yr^{-1} and have been reported to decline since then. The P accumulation was reported to be 800 kg/ha in the new federal states and 1200 kg/ha in the old federal states of Germany in 2005 (Nieder et al. 2010). A general declining trend in fertilizer consumption as observed in Germany during recent decades was also observed in other Western European countries (Fig. 1.3).

1.7.2   Soils and associated risks of P losses

The ability to sorb P is limited in all soils. Tropical soils as well as temperate soils consist of many soil types with vastly varying properties relating to mineralogy and pedogeochemistry, texture, organic matter and natural P contents (Tiessen et al. 1994, Agbenin and Tiessen 1995, Schucknecht et al. 2012). Often "typical" tropical soils are referred to as highly weathered Oxisols, with high contents of Fe and Al, Al-toxicity due to low pH values and P deficiency (Sanchez et al. 2003, Palm et al. 2007). Due to the high sorption capacities of these soils and the low immediate P availability for plants, these soils are also described as P fixing

soils (Sanchez et al. 2003, Palm et al. 2007). Around 50% of Brazilian cropland is located on such typical soils (Fritz et al. 2015, Roy et al. 2016). Whereas for decades the main interest for research was the agricultural usage of Brazilian soils (e.g. Lopes 1996), in recent years diffuse P losses from agricultural soils have also gained more attention (e.g. Shigaki et al. 2006a, ANA 2013, Abdala et al. 2012, Bortolon et al. 2016). Despite the high sorption capacity of "typical" tropical soils, their capacity to sorb P is not unlimited, and P losses from diffuse P losses are reported to contribute to elevated P concentrations in Brazilian surface water bodies (e.g. Ghosh et al. 2011, Ribeiro et al. 2014, Santos et al. 2014). Especially in regions with high livestock densities, where manure is applied to the soils as a cheap measure of waste disposal, negative effects of diffuse P losses on the water quality of surface waters are probable. This is of particular interest, as a strong increase in animal-based agriculture has taken place (Shigaki et al. 2006a). In addition, the fact that only ca. 55% of Brazilian cropland lies on P fixing soils (Roy et al. 2016) demands attention; moreover, research on the other Brazilian soils is crucial, as they are more vulnerable to reaching critical DPS values due to lower P sorption capacities.

In areas of intensive agriculture in temperate regions (e.g. in central Europe), soils have often been classified as having reached critical P levels, i.e. high DPS values (Leinweber et al. 1997, Rubaek et al. 2013, Schoumans and Chardon 2015). Soils with lower sorption capacities, such as sandy soils, reach critical P levels earlier than soils with high sorption capacities, such as clayey soils (e.g. Pöthig et al. 2010). This leads to a higher risk of P leaching and thus P losses to drainages in sandy soils (King et al. 2015). However, clayey soils have also been reported to significantly lose P to drainages, e.g. through preferential flow paths (e.g. Djodjic et al. 2004, King et al. 2015).

1.7.3   Management of soil P in Brazil and Germany

In Brazil, fertilizer recommendations are based on a modified Mehlich-1 P extraction analysis (Mehlich 1953, EMBRAPA 1997) and the anion exchange resin method (van Raij et al. 1986, Bissani et al. 2002). This thesis focuses on the most commonly applied M1P methodology in the investigation area of the São Francisco catchment. Different soil P levels are recommended for different crops and different regions of Brazil (e.g. Ribeiro et al. 1999, Cavalcanti et al. 2008). Often the clay content of the soils is considered and the target M1P level adapted accordingly. Upper limits of soil P levels, at which P surplus should be zero or negative, do often not exist in the recommendation systems (e.g. Cavalcanti et al. 2008). An example of soil fertility classes for annual crops in Minas Gerais, the federal state that covers the major part of the upper São Francisco catchment, is shown in Table 1. Depending on the crop type, target M1P levels are partly four times higher than in annual crops (see Chapter 2). Superficial fertilizer application is commonly applied in Brazilian agriculture (e.g. Cavalcanti et al. 2008, Bortolon et al. 2016). Superficial fertilizers as such already induce elevated P loss risks. Additionally, their application recommendations seem to require some adaptation, as they advise superficial fertilizer application before the rainy season (Calvacanti et al. 2008), leading to further increased risks of dissolved P losses in surface runoff (e.g. Shigaki et al. 2006b).

Table 1.1: Soil P fertility classes for annual crops in Minas Gerais, Brazil: Target P levels (marked in green) vary according to the clay content of the soil, an upper limit of Mehlich-1P where a stop of fertilizer application is recommended is not included (Table translated and modified from Ribeiro et al. 1999).

Brazil	Classification of soil fertility status				
	very low	low	medium	good	very good
Clay content, %	M1P, mg/dm³				
60-100	≤ 2.7	2.8 - 5.4	5.5 - 8.0	8.1 - 12.0	≥ 12.0
35-60	≤ 4.0	4.1 - 8.0	8.1 - 12.0	12.1 - 18.0	≥ 18.0
15-35	≤ 6.6	6.7 - 12.0	12.1 - 20.0	20.1 - 30.0	≥ 30.0
0-15	≤ 10.0	10.1 - 20.0	20.1 - 30.0	30.1 - 45.0	≥ 45.0

In Germany, P extraction methods of CAL (PCAL) and double lactate (PDL) are used to estimate plant-available soil P (VDLUFA 1991, 2002). Based on the PCAL/PDL levels, fertilizer recommendations are provided for agriculturally used soils (Table 1.1, Fig. 1.4). Class C is defined as target P level in soils, and P fertilizer recommendations are given accordingly to reach this target P level (e.g. Kerschberger et al. 1997).

Table 1.2: Soil P fertility classes for German soils: Target P levels (marked in yellow and green) have recently been reduced to lower levels (*in regions with annual precipitation < ~550 mm the recommended upper value is 75 mg/kg); at high P levels corresponding to class D and E, a reduction of P levels is recommended (Kerschberger et al. 1997, Taube et al. 2015).

Germany	Classification of soil fertility status				
	A	B	C	D	E
	(very low)	(low)	(correct)	(high)	(excessive)
Manual	PCAL, mg/kg				
Kerschberger et al. (1997)	≤ 20	20 - 45	45 - 90	90 - 150	≥ 150
Taube et al. (2015)	≤ 15	15 - 30	30 - 60*	60 - 120	≥ 120

P levels corresponding to class C have been reduced several times over the last decades (Übelhör and Hartwig 2012). Only recently the recommended PCAL values of class C were corrected once more to lower values (Taube et al. 2015). In order to reduce direct P losses from agricultural fields with surface runoff to surface water bodies, it is recommended to incorporate fertilizers shortly after application (BMEL, 2017). This indicates the contradictory agricultural practices in Germany and Brazil.
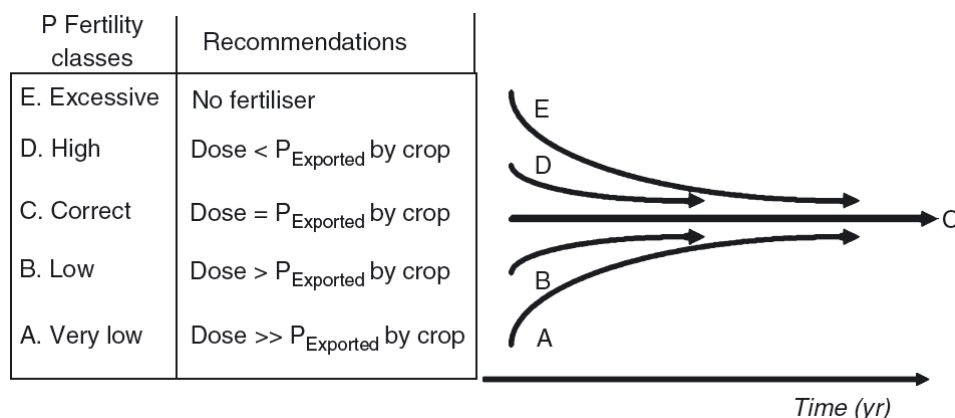

Figure 1.4: Soil fertility classes for German soils: P fertilizer recommendations are given according to the comparison of actual P levels in the soils with the target level defined by class C (figure from Jordan-Meille et al. (2012) based on Kerschberger et al. (1997), reprinted with permission from John Wiley and Sons).

1.8 Objectives, methodology and outline

1.8.1   Objectives

This thesis investigates the risk of P losses from agricultural areas in a multi-scale approach considering laboratory analyses, field studies, official monitoring data and input data for nutrient emission models. For the first time a soil type-independent DPS approach established on central European soils was: 1) tested on Brazilian soils, and 2) used for assessing the risk of P losses by monitoring data of plant-available P. Furthermore, the thesis provides an analysis of the emerging risk of dissolved P losses from 1) soil P management in agricultural soils of Brazil and Germany regarding recommended soil P levels from agricultural institutions and 2) superficial inorganic fertilizer application in Brazil. A surface runoff study was carried out in order to investigate the overall effect of DPS and superficial fertilizer application on dissolved P losses in Brazil. For complementary information on the risk of P losses from tropical soils in Brazil, soil mineralogy and its influence on P binding forms and P sorption were examined by means of Fourier transformation infrared (FTIR) spectroscopic analyses. Thus, central topics regarding diffuse P losses from agricultural soils in Brazil and Germany were addressed, i.e.:

- Soil mineralogy and its effects on risk of P losses (Brazil)

- Resulting risk of P losses by superficial fertilizer application (Brazil)

- P losses in surface runoff (Brazil)

- Integration of monitoring data in DPS risk assessment (Brazil, Germany)

- Interpretation of recommended P levels in agricultural soils with regard to environmental goals (Brazil, Germany)

1.8.2   Methodology

The thesis focuses on laboratory soil analyses. In Chapter 2, the investigation of sorption characteristics in order to test the soil type-independent WSP-DPS correlation of Pöthig et al. (2010) on tropical soils of Brazil is a central objective. FTIR analyses of soils and fertilizer grains were used to study soil mineralogy and soil specific P binding forms, respectively. In addition to soil analyses, water samples of surface runoff events in Brazil were also investigated (see Chapter 3). This was done in order to assess in how far risks of P losses, as determined by soil analyses, are reflected in P losses in surface runoff.

In Chapter 3 and 4, extraction methodologies for estimating plant-available P (Brazil: Mehlich-1, Germany: Calcium-acetate-lactate) are correlated to risk parameters of P losses WSP/DPS. For this analysis, soil samples were collected from Brazil and Germany and analyzed with the respective methods of estimating plant-available P as well as WSP. Linear regression equations between the extraction methodologies to estimate plant-available P and WSP were determined and used as pedotransfer functions (PTFs). Monitoring data on plant-available P and recommended P levels in soils from agricultural institutions were analyzed in order to assess the corresponding risk of P losses. For data visualization geographic information system ArcGIS 10.1 software (ESRI©) was used.

1.8.3   Outline and central research questions

The results of the thesis are presented in three manuscripts (Chapter 2-4) which are either published or are currently under review. Citation styles of the manuscripts were harmonized for better legibility. Chapter 2 and 3 are complementary, and address Brazil. In the final part of the thesis (see appendix) a poster is presented that summarizes important results of both chapters. Chapter 4 relates to Germany and Europe. Additional results are presented in the discussion part of the thesis. In the following a short overview of the different chapters and central research questions is provided.

Chapter 2: P saturation and superficial fertilizer application as key parameters to assess the risk of diffuse P losses from agricultural soils in Brazil

(submitted to Science of the Total Environment on 30th of October 2017)[1]

This chapter introduces the investigation area of the São Francisco catchment in Brazil and the soil chemistry of major soil types. A combination of different analytical methods was used to gain insights into soil mineralogy and sorption behavior of contrasting soil types and regions in the São Francisco catchment and their consequences for the risk of P losses. The following research questions are addressed:

1.) What differences in P sorption and mineralogy have to be considered in the risk assessment of dissolved P losses from contrasting soil types in Brazil?
2.) Is the soil type-independent approach to estimate the degree of P saturation (DPS) by water-soluble phosphorus established (WSP) on European soils (Pöthig et al. 2010) also valid for tropical soils of Brazil?
3.) Do recommended P levels determined by the Mehlich-1 method for agricultural soils meet requirements to avoid high risks of dissolved P losses?

Chapter 3: 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

(Published in Water Science and Technology: DOI: 10.2166/wst.2016.169)

Chapter 3 focuses on whether the intensified Brazilian agriculture in recent decades has already led to P accumulations in soils that result in critical DPS values above environmental thresholds. As M1P cannot be used straightforward to estimate the risk of P losses, a PTF was developed between soil P determined by the modified Mehlich-1 method used in Brazil and WSP. Monitoring data of M1P were transformed into WSP by the derived PTF, and DPS values were calculated by the WSP-DPS correlation of Pöthig et al. (2010). Furthermore, the effect of superficial fertilizer application on dissolved P losses in surface runoff on Oxisols was assessed by a surface runoff study. The following questions are addressed:

1.) What is the current risk of dissolved P losses in the upper RSF catchment derived from M1P monitoring data?

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[1] Manusript was accepted for publication in revised form on 2nd of February 2018, doi: https://doi.org/10.1016/j.scitotenv.2018.02.070

2.) What is the overall effect of soil DPS values in combination with superficial fertilizer application on dissolved P concentrations in surface runoff?

3.) Can dissolved P concentrations in surface runoff be estimated by soil analyses of WSP (see discussion)?

For the first time, a surface runoff study on Brazilian Oxisols with superficial fertilizer application reports the time course of dissolved and particulate P concentrations in surface runoff events, instead of reporting average values of a whole event. Thus, Chapter 5.1.3 presents a more detailed analysis and discussion of the results of the surface runoff study.

Chapter 4: The degree of phosphorus saturation of agricultural soils in Germany: Current and future risk of diffuse P loss and implications for soil P management in Europe

(Published in Science of the Total Environment: DOI: 10.1016/j.scitotenv.2017.03.143)

In Chapter 4, a PTF is determined between PCAL and WSP and a first DPS map of Germany based on PCAL monitoring data is established. The application of the CAL method on different soil types is discussed critically and an approach is developed that allows for a definition of P levels in soils that considers both agronomic and environmental needs. The central research questions of Chapter 4 are:

1.) What is the current risk of dissolved P losses from German arable soils derived from PCAL monitoring data?
2.) Do recommended PCAL levels for agricultural soils meet requirements to protect surface waters from diffuse P emissions?

Further results concerning the current practice in German soil P management to correct measured PCAL values on $CaCO_3$ containing soils are revealed in the discussion part. Furthermore, a PTF between WSP and soil phosphorus determined by the $CaCl_2$ method is presented in the discussion part in order to allow for an integration of the $CaCl_2$ method in the new approach of defining P levels in European soils, which considers both an agronomic production and a protection of surface water bodies from diffuse P pollution.

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

Fischer, P.[1,2]*, Pöthig, R.[3], Gücker, B.[4], Venohr, M.[5]

[1,3,5] Leibniz-Institute of Freshwater Ecology and Inland Fisheries (IGB), Department of Ecohydrology, Justus von Liebig Straße 7, 12489 Berlin, Germany
[2] Humboldt-University Berlin, Geography Department, Unter den Linden 6, 10099 Berlin, Germany
[4] Federal University of São João del-Rei, Department of Geosciences, Campus Tancredo Neves, 36301-360 São João del-Rei, MG, Brazil

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 M1P levels for plant production resulted in low P loss risks for major crops
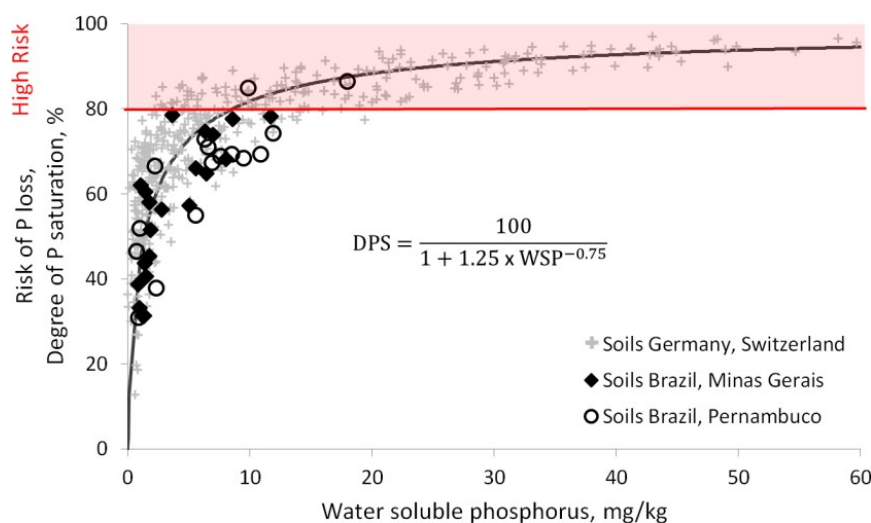

Graphical Abstract

Figure 2.1: Graphical Abstract.

Abstract

In Brazil, a steady increase in phosphorus (P) fertilizer application and agricultural intensification has been reported for recent decades, potentially threatening surface water bodies by diffuse P losses leading to eutrophication. Here, we tested a soil type-independent approach for estimating the degree of P saturation (DPS; a risk parameter of P loss) by water-soluble phosphorus (WSP) for major soil types (Oxisols, Entisols) of the São Francisco catchment in Brazil. WSP and DPS were strongly correlated, and thus the WSP-DPS approach proven to be valid for the studied Brazilian soils. We then transformed soil Mehlich-1P (M1P) levels recommended by Brazilian agricultural institutions 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 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.

Keywords: FTIR spectroscopy, palygorskite, soil specific P forms, DPS, eutrophication, Mehlich-1, soil fertility classes

2.1 Introduction

Brazil is a major player in the world food market, being e.g. one of the largest producers of soybean and sugarcane. Nowadays 220×10^6 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 area than that in the U.S.A., which results in a P surplus of 5-18 kg ha^{-1} yr^{-1} for the 11 Brazilian states with intensive agricultural production (Roy et al. 2016).

The biome that has been most affected by agricultural expansion in recent years is the Brazilian Cerrado (Marris 2005). The intensive agricultural development of the Cerrado started in the 1960s (Lopes and Guilherme 2016). Major investments in the agricultural sector concerning research on adapted agriculture on soils of low fertility, infrastructure and financial support of farmers by e.g. cheap loans, triggered the agricultural expansion into Brazil's second largest biome (Lopes and Guilherme 2016). Nowadays about 50% of the original area of the Cerrado of 200×10^6 ha has been transformed into agricultural area (Monfreda et al. 2008, Lapola et al. 2014 citing IBGE 2012).

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 optimum 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 optimum agronomic production, P applied to agricultural soils in excess can result 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 processes, 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).

To assess the risk of P losses from agricultural areas, the degree of P saturation (DPS) of 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 (Nair 2014). The DPS is well correlated with dissolved P losses from soil to water 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/or 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).

A soil type-independent approach to estimate DPS was introduced by Pöthig et al. (2010). Here, the DPS is defined as $(TP/(TP+SP_{max})) \times 100$, where TP is the total P content of a soil determined by *aqua regia* digestion and SP_{max} is the remaining sorption capacity of a soil determined by the linearization of the Langmuir sorption isotherm, which considers all sorption sites of a soil. The DPS was related to a standard extraction method of water-soluble phosphorus (WSP) in a soil type-independent correlation: $DPS = (1/(1+1.25 \times WSP^{-0.75})) \times 100$, $R^2 = 0.71$ (Pöthig et al. 2010). Consequently, the rather complex parameter DPS can be estimated by the standard soil P test method of WSP. Thereby, the determination of sorption isotherms can be avoided. Pöthig et al. (2010) concluded that this approach can be used for a simple and fast risk assessment of P losses worldwide, in which WSP values between 5 and 10 mg/kg soil correspond to average DPS values between 70 and 80%, indicating high risk of P loss. In subsequent studies, a DPS of 70% and 80% was used to classify soils as having elevated and high risks of P loss, respectively (Fischer et al. 2016, Fischer et al. 2017).

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, the soil type-independent method estimating DPS values by a simple and fast assessment of WSP has not been tested yet for tropical soils of Brazil. WSP reflects the soluble P of each soil type, corresponding to their respective composition and pH value. Consequently, the WSP-DPS approach can be applied to all soil types, which is advantageous in comparison to risk estimation based on soil type-dependent methods such as most DPS methods evading P sorption isotherms or using substances, which interfere with the pH value and thus the natural P solubility of soils.

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, particle sizes 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. 2006b, 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^{-1} 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 surface runoff study, the observed relatively low dissolved P concentrations were supposed to result from sorption of dissolved inorganic fertilizer P to Al and Fe hydroxides (Fischer et al. 2016). This, however, has not been confirmed yet.

In this study, we investigated the risk of P losses from two different agricultural sites in the Rio São Francisco (RSF) catchment with contrasting dominating soil types: Entisols in the lower middle catchment of the São Francisco in Pernambuco and Oxisols representative for parts of the upper catchment in Minas Gerais.

The risk of P losses was assessed by i) testing the soil type-independent approach to estimate the DPS by WSP, previously established for different soil types of Germany and Switzerland (Pöthig et al. 2010), by laboratory soil analyses regarding its applicability on Brazilian soils ii) using the M1P-WSP correlation of a former study (Fischer et al. 2016) to estimate the risks of P losses from recommended M1P levels in agricultural soils based on DPS. Further, we assessed iii) the influence of superficial fertilizer application on risk parameters of P losses, namely WSP and DPS. To acquire complementary information regarding the influences of soil mineralogy on P sorption and P binding forms, FTIR spectroscopy analyses were executed. With our study, we complement a former study on agricultural sites in Minas Gerais and Pernambuco (Fischer et al. 2016) providing a comprehensive summary of a new method for assessing current and future risks of P losses in the RSF catchment and Brazil based on a soil type-independent approach.

2.2 Material and Methods

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 Köppen 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 1464 mm and an annual mean temperature (AT) of 20.7°C, INMET-BDMEP 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 = 428mm; AT = 24.3°C, INMET-BDMEP n.d.) and persistent water scarcity

problems (ANA 2013, Koch et al. 2015). The upper and the lower middle catchment are part of the Cerrado and Caatinga biomes, respectively (Fig. 2.2 A). Cropland currently accounts for 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 an almost doubling of cropland until 2035 (Koch et al. 2015, Fig. 2.2 B). The most important crops covering more than 75% of the total arable land are soybeans, maize, beans and sugar cane (IBGE-SIDRA n.d.).

Two sites were chosen in order to account for the contrasting soils and climate conditions of the catchment: One dominated by the soil types of Latossolos/Oxisols and representative of the upper catchment, the other one dominated by Neossolos/Entisols in the lower middle catchment (Fig. 2.2 C, EMBRAPA 2011, soil classification: Sistema brasileiro de classificação de Solos = SiBCS (EMBRAPA, 2006)/ USDA soil classification system (Soil Survey Staff 1999). These soil types cover a total of 63% of the RSF catchment (Fig. 2.2 C, see also Fischer et al. 2016). 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. For croplands, soils with permanent crops, such as banana, tangerine and coconut, as well as with temporary crops, such as maize, sugar cane, cabbage, bell pepper and melon were sampled. 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, five samples were taken from the 0-20 cm layer in both MG and PE. This depth range is usually sampled for deriving fertilizer recommendations based on M1P analyses (Ribeiro et al. 1999, Cavalcanti et al. 2008).
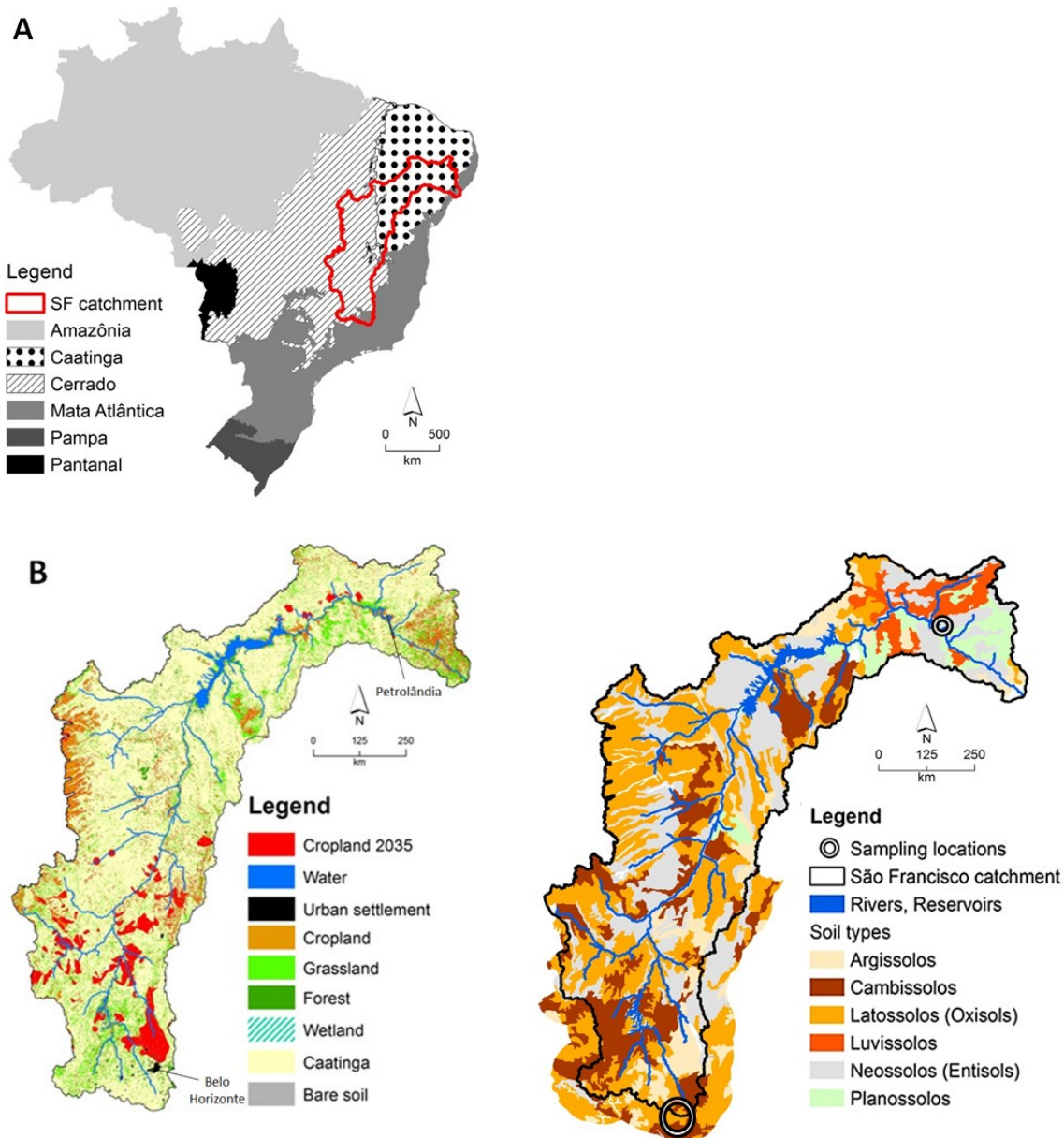
Figure 2.2: The São Francisco catchment: A) Location in Brazil and its biomes (IBGE, 2004), B) current land use in the São Francisco catchment with predicted maximum expansion of crop area until 2035 according to Koch et al. 2015 (map: Koch et al. 2015, modified), and C) sampling locations and soil types in the São Francisco catchment (Fischer et al. 2016, modified, source soil map: EMBRAPA 2011).

Soil analyses

Soil samples were air-dried and sieved (2 mm mesh size) prior to analysis. Soil pH values were determined with 0.01M $CaCl_2$ in a 1:2.5 soil-$CaCl_2$ suspension. Soil densities were determined by weighing 50 cm³ of soil. The investigation of WSP, DPS and total phosphorus content (TP), Al, Fe, Ca and Mg were executed according to Pöthig et al. (2010). Additionally, results of soil analyses from another study were used (Fischer et al. 2016). In some samples of Oxisols after filtrations of WSP extracts with 0.45 µm filters a second filtration with 0.2 µm filters was necessary in order to obtain a clear solution for photometrical analyses.

Because of low P concentrations in soils (commonly < 0.1%), the emerging P binding forms due to reaction with fertilizer phosphates were difficult to study directly on soil samples (Lindsay et al. 1989). Consequently, fertilizer grains collected from soil samples of Oxisols in

Minas Gerais were used to study emerging P binding forms by Fourier transform infrared spectroscopic (FTIR) analyses. Thirty soil samples (14 from MG, and 16 from PE) and 6 samples of fertilizer grains separated from soil samples of MG were analyzed by FTIR analyses. 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. Infrared 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. After each extraction the supernatant was removed and analyzed for P, and the remaining soil sample was extracted again. All P concentrations were measured photometrically (Murphy and Riley 1962) with a UV–VIS photometer (UV 2102, Shimadzu Corp.).

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 × 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).

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 = $100/(1+a \times WSP^{-b})$. 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 previously published relationships (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 soils samples without excess fertilizer in the present study.

2.3 Results and Discussion

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 mg/kg, respectively (Table 2.1; Fischer et al. 2016). Dependent on the specific composition of soil samples, their color varied from light beige over beige brown, orange, red to red brown.

The investigated Entisols were characterized by the presence of significant amounts of quartz and higher soil densities than the Oxisols. Fe, Al, Ca and Mg contents differed widely between samples (Table 2.1) and were comparable to European soils of Germany and Switzerland of a former study (Pöthig et al. 2010). The predominant color of these soils was brown, but some variations from beige to red brown were also found.

Table 2.1: 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.

Sites		MG	PE	MG	PE
Soil type		Oxisols	Entisols	n	n
Soil density, g/cm3	min; max	0.83; 1.17	1.17; 1.56	30	51
	MEDIAN	1.00	1.40		
pH	min; max	3.9; 6.5	5.0; 6.6	12	12
	MEDIAN	4.8	6.2		
Ignition loss, %	min; max	6.4; 20.3	1.3; 8.7	26	28
	MEDIAN	12.6	3.0		
Fe, g/kg	min; max	30.0; 84.0	2.4; 22.3	22	33
	MEDIAN	45.0	6.5		
Al, g/kg	min; max	34.4; 134.3	3.7; 28.8	22	33
	MEDIAN	71.9	9.1		
Ca, g/kg	min; max	2.1; 7.1	1.4; 59.2	8	32
	MEDIAN	4.3	3.5		
Mg, g/kg	min; max	0.5; 1.4	0.2; 9.1	8	32
	MEDIAN	1.1	0.7		
TP, mg/kg	min; max	159.7; 1790.6	102.0; 932.1	26	28
	MEDIAN	471.7	179.7		
PSC, mg/kg	min; max	480.7; 2308.6	139.3; 1183.7	26	28
	MEDIAN	749.7	343.9		
DPS, %	min; max	31.3; 78.5	30.9; 86.4	26	28
	MEDIAN	62.6	67.8		
WSP, mg/kg	min; max	0.8; 19.8	0.7; 36.5	26	28
	MEDIAN	4.3	9.0		

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

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, but hematite (Fig. 2.3, Table app.2.1). 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.
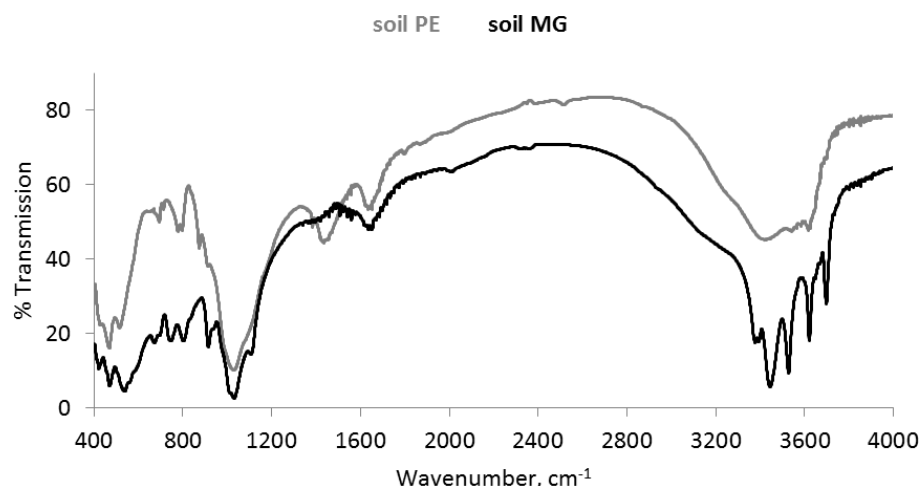
Figure 2.3: Typical examples of FTIR spectra from soils of Minas Gerais (MG) and Pernambuco (PE).

Quartz was detected in only some of the Oxisols. Besides the bands of quartz, the FTIR spectra of all studied Oxisol soil samples showed the same bands (see Table app.2.1), but with differences in their intensities. 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 cm^{-1} (Vaculikova et al. 2011) and gibbsite by bands at 3620, 3525, 3436 and a double band at 3377/3394 cm^{-1} (Kloprogge et al. 2002). Differences in these band intensities were used to identify, which of the two minerals is dominant in the soil: Gibbsite was considered to be dominant when the band at 3525 cm^{-1} was more intensive than the kaolinite bands. From 15 studied (FTIR) soil samples, 7 samples were dominated by kaolinite and 8 by gibbsite with associated Fe hydroxides and oxides. This knowledge is relevant for our understanding of 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).

Entisols

The characteristic double bands at around 800 cm^{-1}, which were found in all investigated Entisols, showed a significant amount of quartz. In contrast to the studied Oxisols, which contain kaolinite as the main clay mineral, montmorillonite was identified as the main clay mineral in some of our investigated Entisols. Soil samples of two sites with Ca and Mg contents > 4g/kg showed the typical bands of calcite and additional bands, which could be

related by their characteristic frequencies to the minerals palygorskite $(Mg,Al)_2Si_4O_{10}(OH)\cdot4H_2O$ and sepiolite $Mg_4Si_6O_{15}(OH)_2\cdot6H_2O$ (Frost et al. 2001, Madejova and Komadel 2001, wavenumbers and mineral identification see Table app.2.1).

These two clay minerals occur exclusively in xeric-, aridic- and semi-aridic soils as neoformed minerals and are associated with carbonates and smectite minerals (in our case montmorillonite), as well as quartz, and 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 X-ray diffraction (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 palygorskite and sepiolite 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. In the case of irrigation practices on palygorskite and sepiolite containing soils, Mg^{2+} is released into the soil solution. Magnesium as an exchangeable cation is known to decrease aggregate stability of the soil clay fractions and to improve phosphorus availability in arid soils (Neaman and Singer 2004), thereby increasing the risk of P leaching or P loss by surface runoff.

Fertilizer grains from Oxisols

In a previous runoff study on Oxisols with superficially applied P fertilizer in our study region in Minas Gerais, very low P concentrations in runoff water, but considerable particulate P export was found (Fischer et al. 2016). To gain insights in the underlying processes of P sorption/fixation on Oxisol particles, we separated fertilizer grains from soil samples to investigate their mineral composition by FTIR spectroscopy.
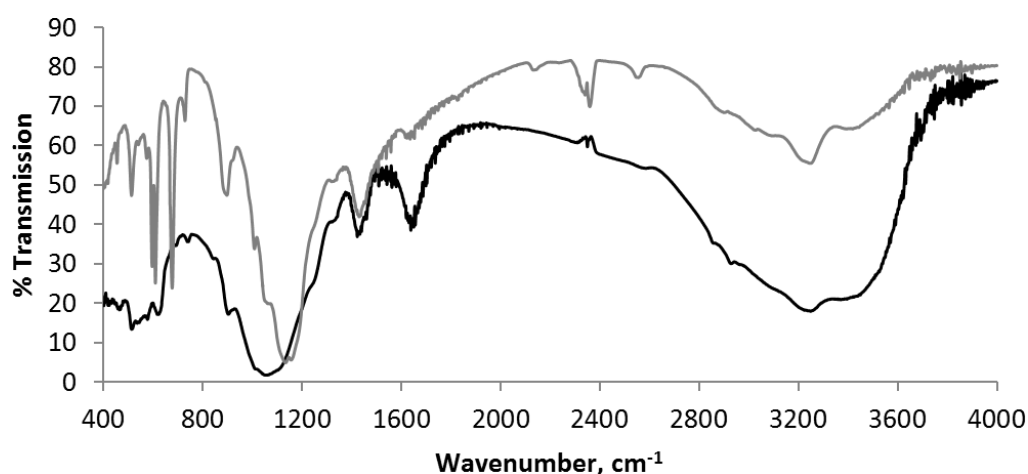
Figure 2.4: FTIR spectra of two fertilizer grains from Oxisols of Minas Gerais with $CaSO_4$ (grey) and without $CaSO_4$ (black).

Although raw phosphates (apatite) can be used as mineral P fertilizer on acid tropical soils (Lopes et al. 2012), most of the fertilizer samples showed enormous amounts of $CaSO_4$ arising from "superphosphate" due to sulfuric acid treatment of raw phosphates that

generates $Ca(H_2PO_4)_2$ as a water-soluble P fertilizer:

$$(2.1) \quad Ca_{10}(PO_4)_6(OH)_2 + 7H_2SO_4 \rightarrow 3\ Ca(H_2PO_4)_2 + 7\ CaSO_4 + 2H_2O \uparrow$$

(raw phosphates simplified as hydroxyapatite).
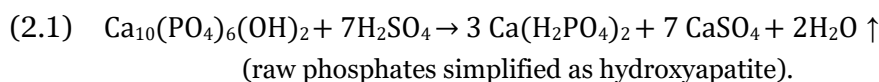
Accordingly, all FTIR spectra but one were dominated by SO_4^{2-} bands from very well crystallized $CaSO_4$ bands (anhydrite) at 597, 616, 676, 1130 and 1159 cm^{-1} (Moenke 1962), partially overlying the less intensive phosphate bands, which were poorly dissolved, caused by the low degree of crystallization (Table app.2.2, Fig. 2.4). However, despite of the different appearance of the two spectra caused by the sulfate bands, these spectra show the same frequencies for the phosphate bands. Considering Oxisols dominated by gibbsite/goethite and soil pH values in the range from 4.4 to 5.8, reactions of the $H_2PO_4^-$ and HPO_4^{2-} 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^+, Ca^{2+}, Mg^{2+}, Mn^{2+}, Al^{3+}, Fe^{2+}, Fe^{3+}) and anions (PO_4^{3-}, HPO_4^{2-}, SO_4^{2-}) by comparing them with published FTIR-mineral data. The FTIR spectra showed no indications of Ca-phosphates originating from superphosphate or their aged products. 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 [$CaAl_3(PO_4)_2(OH)_5 \cdot H_2O$]. Our spectra were compared to published data of five crandallite spectra of four different sources including one pure synthetic and four natural crandallite minerals (see Table app.2.2 for detailed discussion and observed wavenumbers of fertilizer grains with mineral identification).

The formation of crandallite may happen by a simple reaction between the OH^- ions on the gibbsite surface and the H^+ ions of the fertilizer phosphate:

$$(2.2) \qquad 3\ Al(OH)_3\ +\quad (H_2PO_4)_2Ca \quad \rightarrow \quad CaAl_3(PO_4)_2(OH)_5 \cdot H_2O + 3H_2O\uparrow.$$
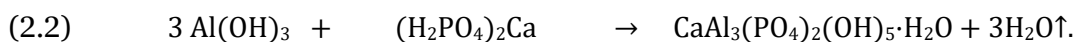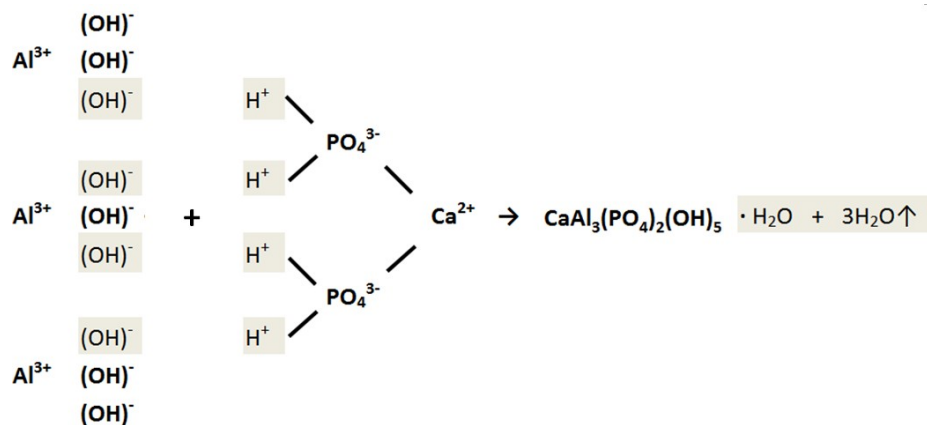
Figure 2.5, Equation 2.2: Proposed reaction of gibbsite with fertilizer phosphate forming crandallite in Oxisols.

However, the spectra showed also strong similarities to other hydroxyl phosphates particularly to sigloite ($Fe^{3+}Al_2(PO_4)_2(OH)_3 \cdot 7H_2O$), whose formation cannot be entirely excluded. The reaction mechanism may be analog to crandallite. Both minerals crystallize in the triclinic system and the protons of the OH^- units in their structures are mobile between the OH^- and PO_4^{3-} units resulting in the formation of HPO_4^{2-} units: The FTIR spectra showed both, PO_4^{3-} and HPO_4^{2-} bands, which were assigned according to (Frost et al. 2011, Frost et al.

2013, Table app.2.2). The formation of HPO_4^{2-} units in our samples is proven by the fact that the observed phosphate bands of the calcined (900°C) samples were partly caused from vibrations of $P_2O_7^{4-}$ ions due to the reaction:

$$(2.3) \qquad 2HPO_4^{2-} \rightarrow 900°C \rightarrow P_2O_7^{4-} + H_2O.$$
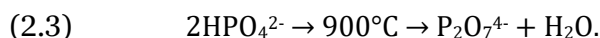
The FTIR spectra suggest the presence of crandallite with a poor degree of crystallinity as the main phosphate phase in the fertilizer grains. The chemical conditions of the soils (i.e. low pH values and high Al contents; see Table 2.1) would favor this reaction, whereas the formation of sigloite in soils has so far not been described. A final proof of the formation of crandallite would be possible by synchrotron-based high-energy X-ray diffraction (HEXRD) or a long-term study investigating the building of well crystallized soil specific P forms by FTIR and 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 with dissolved phosphates from superficially applied P fertilizer and 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).

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 2.1, Fig. 2.6). A comparison of representative sorption isotherms of the investigated Oxisol and Entisol samples with typical isotherms of a sandy soil and a clayey soil (both Inceptisols) of Brandenburg, northeastern Germany, indicates that some of the studied Entisols have not only similar compositions (Table 2.1), but also show a similar sorption capacity as a typical German sandy soil (Fig. 2.6). In contrast, sorption capacities were often higher for Oxisols than for typical clayey soils of northeastern Germany.
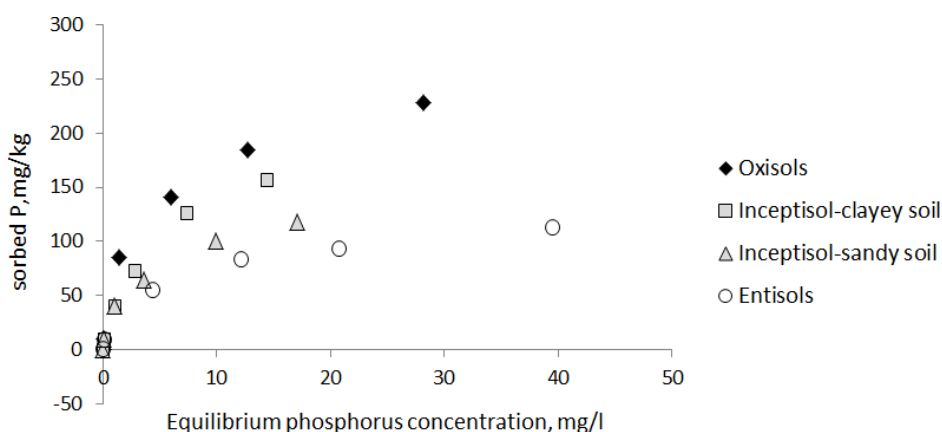
Figure 2.6: Sorption isotherms of two typical soil samples from the investigated Entisols and Oxisols in comparison with the ones of a typical sandy soil and a typical clayey soil (Inceptisols) from Germany.

The investigated Oxisols showed at similar degrees of P saturation PSC values about twice as high as the investigated Entisols (see also Table 2.1), reflecting their differences in composition and the resulting chemical and physical properties. 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. 2.7, Table 2.2).
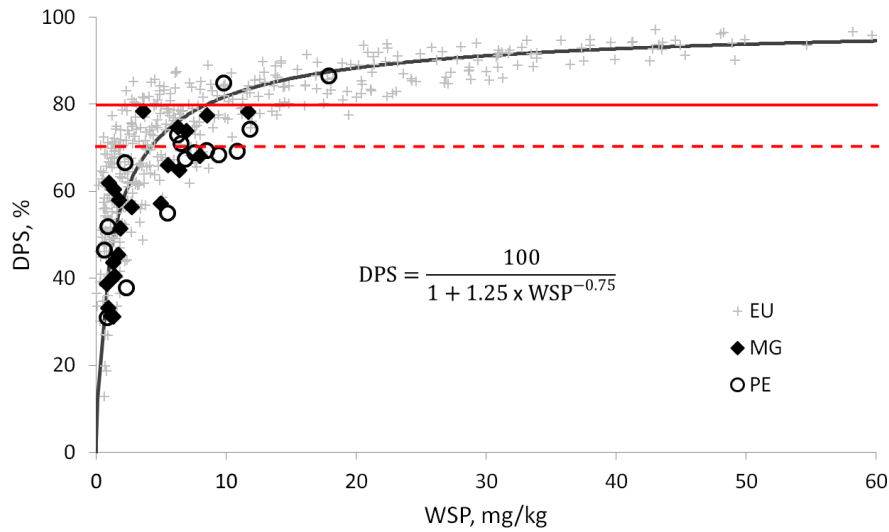
Figure 2.7: Relationship between WSP and DPS for the investigated Brazilian soils (only samples without excess fertilizer): Dashed and solid red lines mark elevated and high risks of dissolved P losses, respectively. The black line is the soil type-independent function derived for European soils.

This finding was confirmed by statistical analyses, as 99% confidence intervals of the parameter b of the regression equation DPS = $100/(1+1.25 \times WSP^{-b})$ overlapped for all investigated soil groups (Table 2.2), 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 2.2: Regression results for determinations of the parameter b, using the model DPS ~ $(100/(1 + 1.25 \times WSP^{-b}))$, 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	upper
MG	21	0.57	0.37	0.81
PE	16	0.53	0.37	0.71
EU	335	0.73	0.66	0.80

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. 2.7 C). 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 = $(1/(1+SP_{max}/TP)) \times 100$. 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. Whereas WSP can be predicted by DPS and vice versa, WSP cannot be predicted by TP or SP_{max} alone, when the soil type is not considered (Fig. 2.8 A, B).
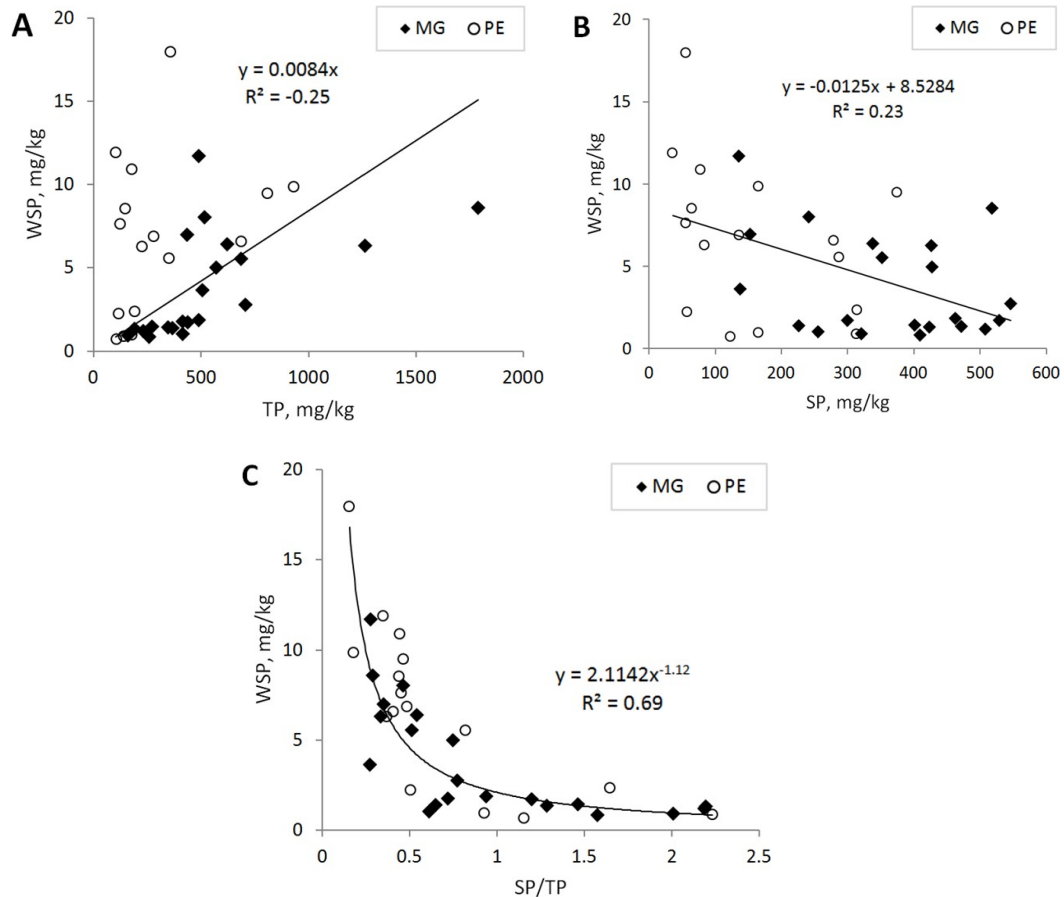
Figure 2.8: Relationship between water-soluble phosphorus (WSP) and (A) total phosphorus (TP), (B) remaining sorption capacity (SP_{max}), and (C) the quotient of SP and TP: The SP_{max}/TP ratio is related to WSP in a soil type-independent correlation (see Pöthig et al. 2010).

The higher the share of TP in relation to the maximum sorption capacity of a soil the higher is the share of loosely sorbed P in the soil and consequently also the WSP (Fig. 2.6). Different types and amounts of sorption and binding sites of P exist in different soils. However, the occupation of these sites apparently follows the same pattern, i.e. sites with strong affinity to bind or sorb P are occupied first, such as Fe and Al oxides and hydroxides reacting to Fe and Al phosphates in acid soils (Lindsay et al. 1989, Sanyal and De Datta 1991, Fig.2.4). Subsequently, sorption sites with lower strength for chemisorption are occupied and finally only loose adsorption processes such as physisorption of P are taking place (Blume et al. 2009). Independent of soil type, above a DPS value of about 60%, the stronger sorption and binding sites are apparently occupied and only weaker P sorption is possible resulting in a disproportional increase in WSP values with further increasing DPS values (Fig. 2.7, Pöthig et al. 2010).

Both median values of DPS in MG and PE (62.6% and 67.8% respectively, Table 2.1) 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 (Fig. 2.6, Table 2.1). Even though in some samples elevated risks of P losses (DPS > 70%) were determined, a high risk of P losses (DPS > 80%) was not measured.

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 2.1: 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 unfavorable environmental impacts in the future.

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 ± 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).

Future risks of P losses were assessed by the evaluation of recommended P levels for agricultural soils to ensure an optimum 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).
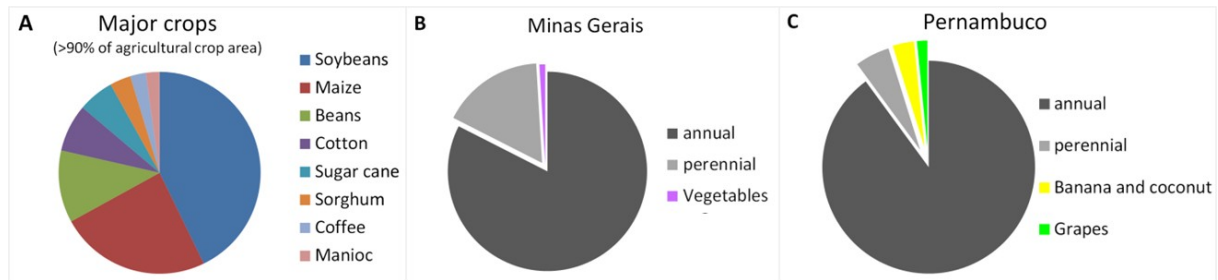
Figure 2.9: Percentage of occupied agricultural crop area per crop (-type) in A) the São Francisco catchment B) Minas Gerais C) Pernambuco: The dominating crop type is annual crops in all 3 regions covering more than 90% of the total crop area.

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. 2.10. 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% (Fig. 2.9, 2.10). However, a conflict with environmental goals was identified in the recommendation for vegetables (Fig. 2.10) 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 n.d.). 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. 2.10).
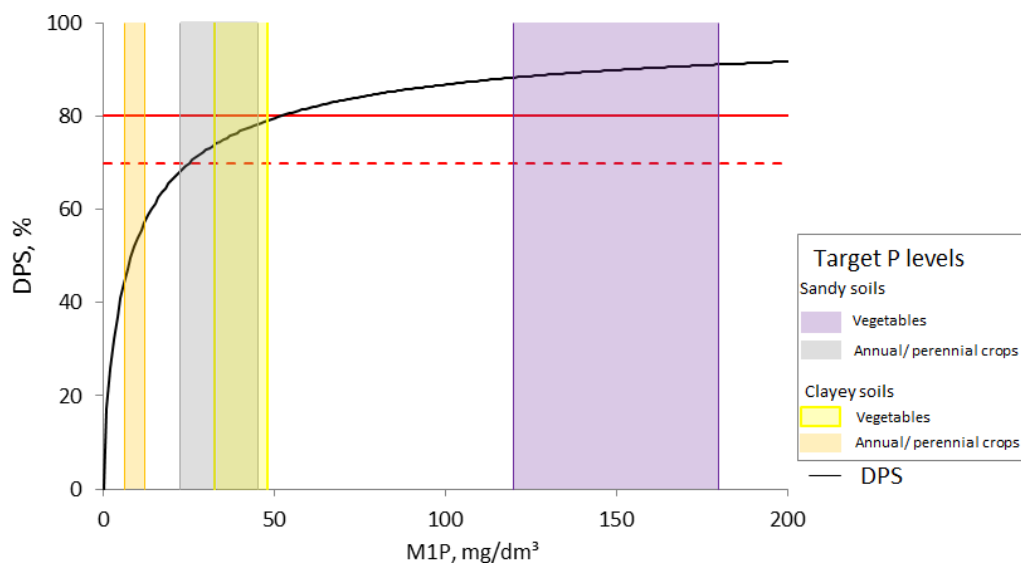
Figure 2.10: Recommended P levels for sandy soils of Minas Gerais (Ribeiro et al. 1999) and resulting risks of P losses estimated by DPS: dashed and solid red line represent elevated and high risks of dissolved P losses, respectively.

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 $\geq$ 30 mg/dm³ (Cavalcanti et al. 2010), which results in DPS values of $\geq$ 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 $\geq$ 40 mg/dm³ corresponding to DPS $\geq$ 77%), which cover about 4% of the crop area in Pernambuco (Fig. 2.9) and in some municipalities more than 35% of crop area (IBGE-SIDRA n.d.). 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. 2.9) 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%.

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 were 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.

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 identified to be conflicting with environmental goals (DPS = 72-87%, Fischer et al. 2017).

An environmental threshold for M1P in the São Francisco catchment

In the analyzed manuals for agricultural production, there was no recommendation for upper M1P levels in soils (Ribeiro et al. 1999, Cavalcanti et al. 2008, Cavalcanti et al. 2010). In order to balance agronomic and environmental interests, we suggest an upper limit of M1P of 51 mg/dm³ corresponding to average WSP and DPS values of 8.5 mg/kg and 80%, respectively. This value is similar to the M1P value of 59 mg/dm³ suggested for soils of southern Brazil with 20% clay content, but significantly below the suggestion of 118 mg/dm³ for soils with 80% clay content (Gatiboni et al. 2015).

In a previous study, no differences in the M1P-WSP correlations between Oxisols and Entisols were assessed, when relating the measured M1P values to the soil densities of the investigated soils (Fischer et al. 2016). However, the correlation between M1P and WSP can vary substantially, especially when $CaCO_3$ containing soils are considered (Kuo 1996, Pierzynski 2000, Arruda et al. 2015). Mehlich-1 is also not considered to be adequate to predict plant-available P in soils fertilized with both P and $CaCO_3$ (Arruda et al. 2015).

Several studies have investigated the risk of P loss from agricultural soils in Brazil by including the extraction methodology of M1P in risk assessments based on DPS and partially also WSP (e.g. Ghosh et al. 2011, Alleoni et al. 2014, Bortolon et al. 2016). However, different methodologies of M1P extraction as well as different DPS approaches in these studies hinder a straightforward comparison of the defined critical M1P and DPS values with the ones determined in the current study.

Superficial fertilizer application and its importance for risk assessment of 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. 2.11 A).
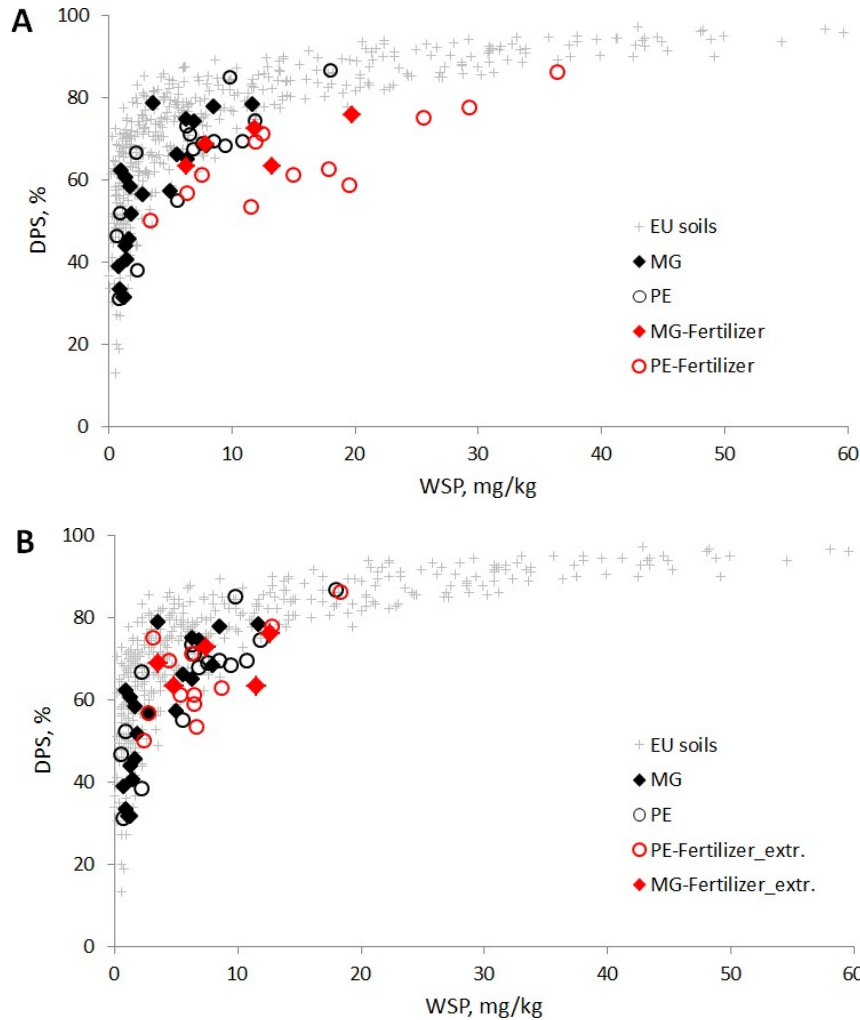

Figure 2.11: Relationships between WSP and DPS for the investigated Brazilian soils with superficial fertilizer application from Minas Gerais (MG) and Pernambuco (PE), (A) considering superficial fertilizer grains/fertigation and (B) after removing excess fertilizer by consecutive WSP extractions: WSP values of the second extraction are shown. Data from European soils (EU soils) are shown for comparison (Pöthig et al. 2010).

Whereas excess fertilizer in soil samples has an impact on WSP, the DPS determined with sorption isotherms remains nearly unaffected: The WSP analyses resulted in average P concentrations in the soil 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 2.1). 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 (Table 2.1). Though excess fertilizer has an impact on soil extractions with low P concentrations, such as occurring in WSP extractions, there is 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) is also low, particularly in Oxisols with higher TP values and sorption capacities than in Entisols. Consequently,

measured soil DPS values determined by TP and SP_{max} (DPS = TP x 100/TP+SP_{max}) remain virtually unaffected by excess fertilizer.

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. 2.12).
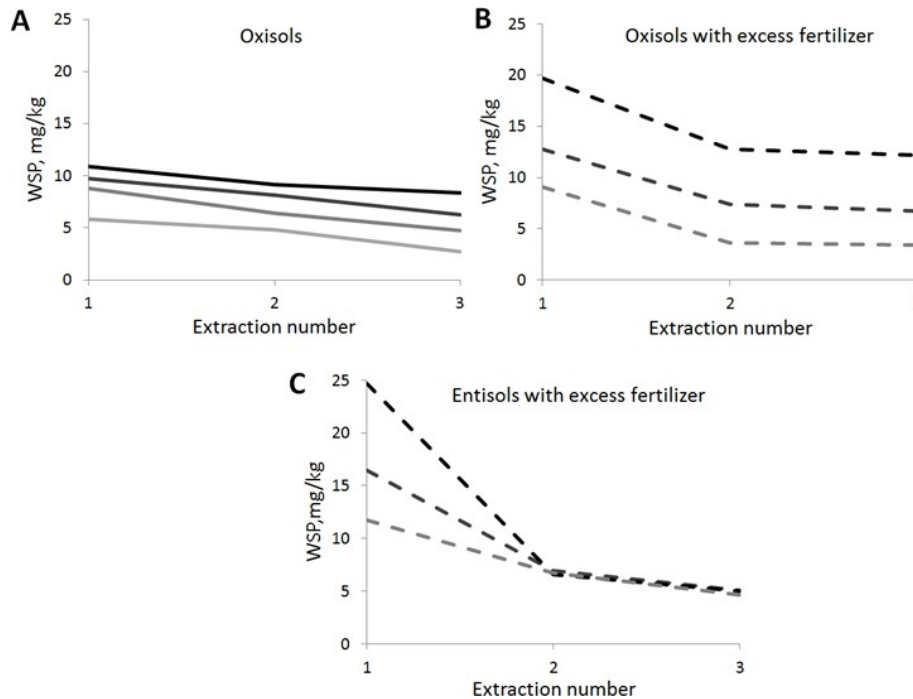
Figure 2.12: The decline of WSP in samples without (A) and with excess fertilizer (B, C) in subsequent WSP extractions.

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. 2.12 A). In contrast, the WSP extractions of soil samples from MG and PE with the presence of excess fertilizer (Figs 2.12 B and 2.12 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. 2.11 B, Fig. 2.7). 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. 2006b, Bertol et al. 2010). However, calculating DPS values from WSP is problematic for soils with superficial P fertilizer, because DPS can be overestimated. Similar effects can be expected for the Mehlich-1 extraction method used to estimate plant-available P. 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 superficial fertilizer.

In a previous surface runoff study (Fischer et al. 2016), P was mainly exported in particulate form, and we supposed the sorption of dissolved 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 entire fertilizer grains from Oxisol samples showed no bands of original fertilizer phosphate, and we hypothesized 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 PO_4^{3-} und HPO_4^{2-} ions on Fe and Al hydroxide surfaces in surface runoff events. Although the studied runoff event 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 exposing small P saturated soil particles to low P concentrations in surface waters, 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. From an environmental perspective, superficial fertilizer application should be avoided in general, but especially prior to the rainy season. The incorporation of P fertilizer into the soils may also be favorable from an agronomic and economic perspective (Withers et al. 2014).

2.4 Conclusions

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

Acknowledgements

Appendix FTIR spectra

To apply to Table app.2.1 and 2.2: Differences in the wavenumbers and intensities between the samples were characterized by a margin. Band shoulders were identified by the second derivative of the spectra.

Table app.2.1: Band positions, -assignments and mineral identification of the studied Brazilian soil samples from Minas Gerais and Pernambuco: Bands cited by references 1 and 11 (MG) were assigned by using reported assignments from Raman data (29).

A) Minas Gerais					B) Pernambuco				
Wavenumber		Band			Wavenumber		Band		
(cm⁻¹)	Int.	Assignment	Minerals	References	(cm⁻¹)	Int.	Assignment	Minerals	References
405-410	sh-w	vFe-OH/Al-O-vib	Gt/Gb	19,20/21					
					418-419	sh-w	δO-Si-O	S	11
418-425	w	Al-O-/δSi-O-vib	K/Gb	2,7/15,21	425-430	sh	δO-Si-O	K/P	2/11
	sh	Al-O-/Fe-O-vib	Gb/Gt	21/5,20					
468-470	vs	δSi-O-Si	K/Q	2,7/22/23	467-470	vs	δO-Si-O/δSi-O-Si	Q/M/K/P,S	23/2/2/11
517-520	sh	Al-O-vib	Ds	24	515-525	sh-m	δO-Si-O	M/P,S	2/11
535-540	s	δAl-O-Si/v(OH)	K/Gb	2,7/15,21					
560	sh	v(OH)	Gb	8,15,21					
630-635	sh	vFe-O	Gt	20,25	636-640	sh-vw	vSi-O-Si	K	26,2
667-670	w, br	v(OH)	Gb	15,21					
698-700	w	Si-O perp/vSi-O-Si	K/Q	2,7,26/4	694-695	w-m	δSi-O/Si-O perp	Q/K	4/7,2
					711-712	w-m	δCO₃	Ca	4,27
742-754	m	Si-O perp/Al-OH	K/Gb	2,26/15,21					
					778	w-s	vSi-O/OH-trans	Q/S	4/11
798-803	m	δ(OH)/δ(OH)	Gb/Gt/Q	15,21/20/4,24	798-800	w-s	vSi-O	Q	4,24
					836-838	sh	δAlMgOH	M	2,3
					873-874	sh-m	δCO₃	Ca	4,27
911-914	s	δ(OH)	K/Gb	2,7,26/21/8	908-915	w-m	δ(OH)/δAlAlOH	K/P/M	26/2,11/2
936-938	sh-w	δ(OH)	K	2,7,26	935-936	sh	δ(OH)	K	7,2
966-968	sh	δ(OH)	Ds/Gb	8,24/8,21					
					980-990	sh	vSi-O	P,S	2/11
1007-1010	vs	vSi-O	K	2,7	1005-1010	sh-w	vSi-O	K/S	26,2
1020-1029	vs	δ(OH)/vSi-O	Gb/K	15,21/2,7	1028-1035	vs	vSi-O	M/K/P	2/26/11
1075-1080	sh	vSi-O	Q	4,24	1075-1085	sh-m	vSi-O	Q/P	4/11
1105-1110	w	Si-O perp	K	2,22,26	1105-1115	sh	vSi-O	K/M/P,S	26/2/2,11
					1164-1166	sh-w	vSi-O-Si	Q	24
					1420-1460	w-m, br	vCO₃	Ca	4,27
1620-1630	m	δ(H-O-H)	K/Gb/Gt	22/15/5,19	1620-1640	m, br	δ(H-O-H)	K/M/P,S	26/2/2,11
					1795-1800	w	vCO₃	Ca	4
2000	sh-w	v(OH)	Ds	24					
					2513	w	vCO₃	Ca	4
3180-3200	sh, br	v(OH)	Gt	5,19	3235-3250	sh	v(H-O-H)	P,S	2/11
3375-3377	w	v(OH)	Gb	8					
3395-3397	w	v(OH)	Gb	8					
3440-3446	vs	v(H-O-H)	Gb/K	8/2,22	3400-3420	s, br	v(OH)	M/P,S	2,30/11
3524-3526	s-vs	v(OH)	Gb	8	3546-3550	w-m	v(OH)	P,S	2/11
3619-3620	s	v(OH)	Gb/K	8,/2	3612-3626	m	v(OH)	K/M/P,S	26/30/11
3648-3652	sh-w	v(OH)	K	2,7	3665-3668	sh	v(OH)	K	7,26
3667-3668	vw	v(OH)	K	2,7,22					
3694-3696	s	v(OH)	K	4,2,7	3690-3695	sh-w	v(OH)	K/S	7,26/2,11
					3719-3720	sh-w		S	11,30
Q: not occuring in all soil samples					**Ca, P, S**: not occuring in all soil samples				

Shortcuts: Int.- Intensity, **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, **H**- Hematite, **Ds**- Diaspore, **Ca**- Calcite, **K**- Kaolinite, **Q** – Quartz, **M**- Montmorillonite, **P**- Palygorskite, **S**- Sepiolite

Table app.2.2: Band positions, -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 (16) and cited crandallite spectra therein.

Wavenumber		Band		Wavenumbers (cm^{-1}) of published bands for crandallite					
(cm^{-1})	Int.	Assignments	Minerals	Margin	synthetic 16)	natural 16)	15)	17)	18)
418-425	vw	Al-O-vib	Gb						
455-457	sh	δs (PO$_4$/HPO$_4$)	Cr	455-465			465	455	456
510-511	m	δs (PO$_4$/HPO$_4$)	Cr	505-510			510	510	505
535-536	w	γ(OH)	Gb						
562-568	w	δs (PO$_4$)/γ(OH)	Cr/Gb	562-565			562sh	565sh	
594-596	vs	δas (SO$_4$/PO$_4$)	An/Cr	580-595			595	580sh	590s
609-611	vs	δas (SO$_4$/PO$_4$)	An						
630-631	sh-w	δas (PO$_4$)	Cr	614-630			620	630	614
676-678	s	δas (SO$_4$)	An						
725-728*	sh-w	δ(CO$_3$)	Ak	735*				735*	
805-810	sh-w	δ(OH)/γ(OH)	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	1040s	1037s
1057-1061	sh	vas (PO$_4$/HPO$_4$)	Cr/Gb	1055-1066		1066	1055		
1070-1075	sh	vas (PO$_4$/HPO$_4$)	Cr	1070-1078	1078			1070sh	1074s
1100-1102	sh	vas (PO$_4$/HPO$_4$)	Cr/Gb	1105-1113		1109		1105	1113
1130-1132	vs	vas (SO$_4$/HPO$_4$)	An/Cr	1120-1140	1133	1140	1120		
1156-1158	vs	vas (SO$_4$)	An						
1163-1175	sh	vas (PO$_4$/HPO$_4$)	Cr	1166-1172	1166		1175sh	1170sh	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	1220sh	1227
1320-1326	w	δ P-(OH)	Cr	1310-1330		1320	1330	1310	1325
1418/1452	m	v (CO$_3$)	Ak	1415-1492	1422/1492	1415/1452		1425	1477
1616/1648	m	δ (H$_2$O)	Cr	1630-1660	1547/1656	1585/1649		1630	1660
1825*	vw	v (CO$_3$)	Ak		1760			2320	2360
2841-2850	sh-w	v (OH)-P	Cr	2853/2890	2853/2890				
2921-2922	sh	v (OH)-P	Cr	2921		2921sh			
3115/3150	sh	v H$_2$O	Cr	3115-3140		3124	3140	3120	3115
3218-3240	s	v H$_2$O	Cr	3265	3265				3290
3290*		v (H$_2$O)	Cr	3300-3320		3314	3320	3300	3315
3400-3440	s	v (H$_2$O)	Cr/Gb	3437-3450		3437sh		3450	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 occuring in all samples				735*, 870* and 871*may be due to carbonate					

Shortcuts: Int.- intensity, **s** - strong, **vs** - very strong, **m** - medium, **w** - weak, **sh** - shoulder, **br** – broad, **vs** - symmetric stretching-, **δs** - symmetric bending-, **vas** - assymmetric stretching-, **δas** - assymmetric bending modes

Minerals: Cr- Crandallite: CaAl$_3$(PO$_4$)$_2$(OH)$_5$·H$_2$O, **An**- Anhydrite: CaSO$_4$, **Ak**- Ankerite: CaFe(CO$_3$)$_2$, **Gb**- Gibbsite: Al(OH)$_3$

General remarks on Table app.2.1 and Table app.2.2

The observed differences in the wavenumbers of the studied soil samples and fertilizer grains, shown as margins in Table app.2.1 and 2.2 are most likely caused by substitutions in the mineral structures: e.g. substitution of Fe^{3+} in goethite and hematite by Al^{3+} forming aluminous goethite and aluminous hematite (5). In clay minerals Al^{3+} can be partly substituted by Fe^{3+} as has been shown for kaolinite (6). 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 between 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.2.2).

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3 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

Fischer, P.[1,2]*, Pöthig, R.[3], Gücker, B.[4], Venohr, M.[5]

[1,3,5] Leibniz-Institute of Freshwater Ecology and Inland Fisheries (IGB), Department of Ecohydrology, Justus von Liebig Straße 7, 12489 Berlin, Germany^

[2] Humboldt-University Berlin, Geography department, Unter den Linden 6, 10099 Berlin, Germany

[4] Federal University of São João del-Rei, Department of Geosciences, Campus Tancredo Neves, R. Visconde do Rio Preto s/n, São João del-Rei, MG, Brazil

Abstract

The degree of phosphorus saturation (DPS) of agricultural soils is studied worldwide for risk assessment of phosphorus 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.

Keywords: Diffuse P loss, nutrient management, P risk assessment, risk map, São Francisco, surface runoff P

3.1 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 WSP or Mehlich-3 P (M3P), which are simpler to determine than DPS, are also correlated to runoff P (Sharpley et al. 1996, Vadas et al. 2005). However, of these extraction methods, WSP was shown to be 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. 2006b, 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 soil type-independent correlation 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[4]). In the present study, we further developed this investigation by correlating measured WSP and M1P values of agricultural soils from 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.

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[4] The title and the year of the paper changed to: Fischer, P., R. Pöthig, B. Gücker and M. Venohr. 2017. P saturation and superficial fertilizer application as key parameters to assess the risk of diffuse P losses from agricultural soils in Brazil; submitted to Science of the Total Environment on 30th of October 2017, accepted for publication in revised form on 2nd of February 2018, doi: https://doi.org/10.1016/j.scitotenv.2018.02.070 (see chapter 2 of this thesis).

3.2 Material and methods

Soil sampling and analyses
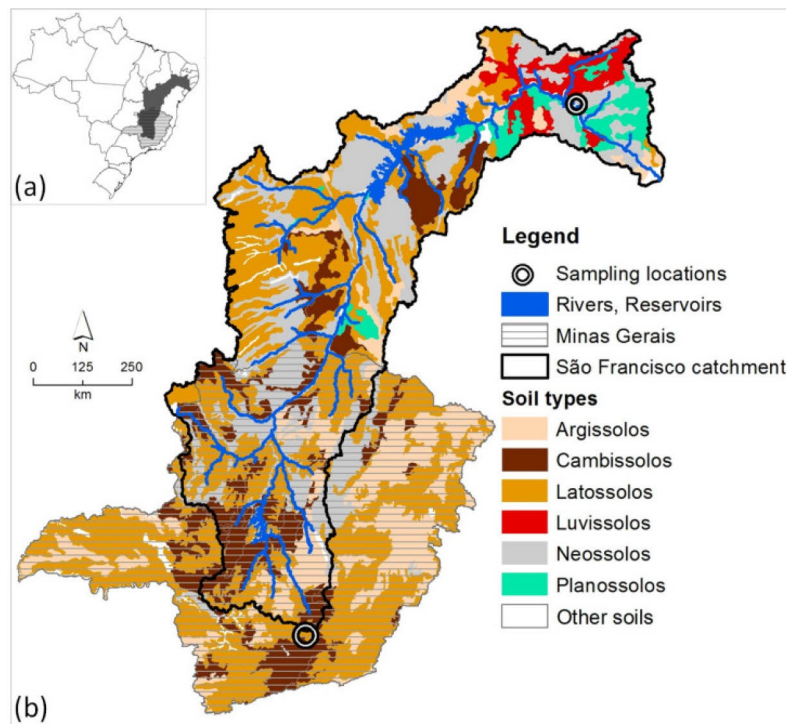
Figure 3.1: Location of the investigated areas in (a) Brazil and (b) Minas Gerais and the São Francisco catchment with soil types according to SiBCS (Brazilian soil classification system) (map sources: soils: EMBRAPA 2011; São Francisco river net (adapted) and catchment: IBAMA–SISCOM).

Soil samples were taken in 2013/2014 as a part of the INNOVATE project (website: 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 (Fig. 3.1). 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 < 2 mm. The soil density was determined by the weight of 50 cm^3 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/dm^3 by multiplication with the corresponding soil densities. All phosphorus concentrations were measured photometrically (Murphy and 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 soil surface on the investigated fields. Samples were taken during or after heavy rainfall events (>13 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 ($K_2S_2O_8$), according to EN ISO 6878:2004, was executed on filtered (GF/F, 0.45 μm) and unfiltered samples prior to photometric P analyses (Murphy and 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 concentrations (TSM, mg/l) 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/dm^3) 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 (DPS = $100/(1+1.25 \times WSP^{-0.75})$, 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.

3.3 Results and Discussion

Regression equation to predict the DPS of Brazilian soils

Table 3.1 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 Fig. 3.2). 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).

Table 3.1: Soil types, fertilizer application and investigated soil parameters of agricultural soils from MG and PE (minimum = min, maximum = max, arithmetic mean = AM, n = 59).

Sites		**MG**	**PE**
Soil type		Oxisols	Entisols
Fertilizer, kg/ha		310	60
Soil density, g/cm3	min; max	0.83; 1.17	1.17; 1.56
	AM	1.00	1.38
WSP, mg/kg	min; max	0.3; 36.4	0.7; 52.7
	AM	9.4	14.1
M1P, mg/kg	min; max	1.6; 199.0	0.8; 247.6
	AM	56.2	61.2
DPS, %	min; max	31.3; 79.7	30.9; 86.4
	AM	60.2	64.6
Fe, g/kg	AM	52.8	8.6
Al, g/kg	AM	78.7	11.8

The correlation between measured WSP and M1P values (Fig. 3.2) was highly significant ($p < 0.01$) and described by a single linear equation: WSP (mg/kg) = $0.1662 \times$ M1P (mg/dm^3). Subsequently DPS was calculated using the equation: 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 (Fig. 3.2). However, our investigated samples did not contain significant amounts of $CaCO_3$. The pH buffering of the acid in Mehlich-1 solution by soils containing $CaCO_3$ 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.
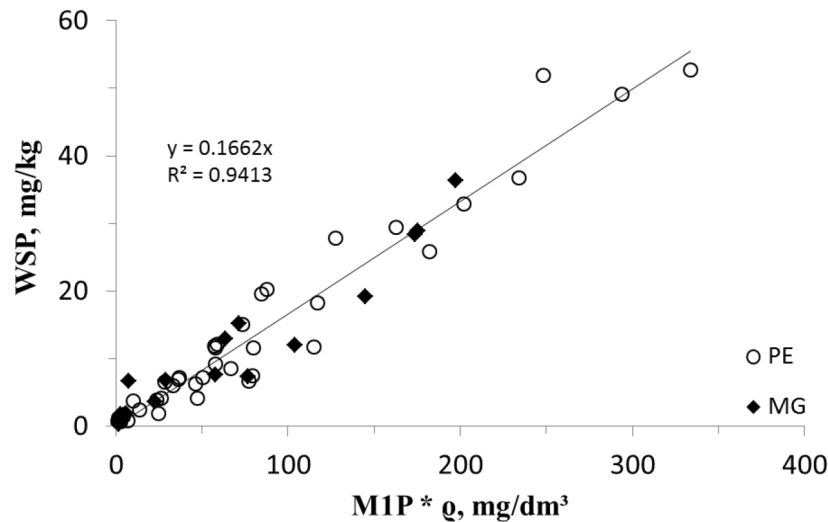
Figure 3.2: Correlation (p < 0.01) between M1P and WSP for soil samples from Minas Gerais (MG, n = 21, black diamonds) and Pernambuco (PE, n = 38, white circles); ρ = soil density.

Nevertheless, the soil orders investigated here (Oxisols and Entisols) are major soil orders in the São Francisco catchment, MG (Fig. 3.1) and Brazil, occupying 63%, 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 $CaCO_3$ 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 $CaCO_3$ 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 (Fig. 3.3 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: 63 ± 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 3.1, Fig. 3.3). 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[5]).

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[5] Meanwhile the paper was published: Fischer et al. (2017); see chapter 4 of this thesis.
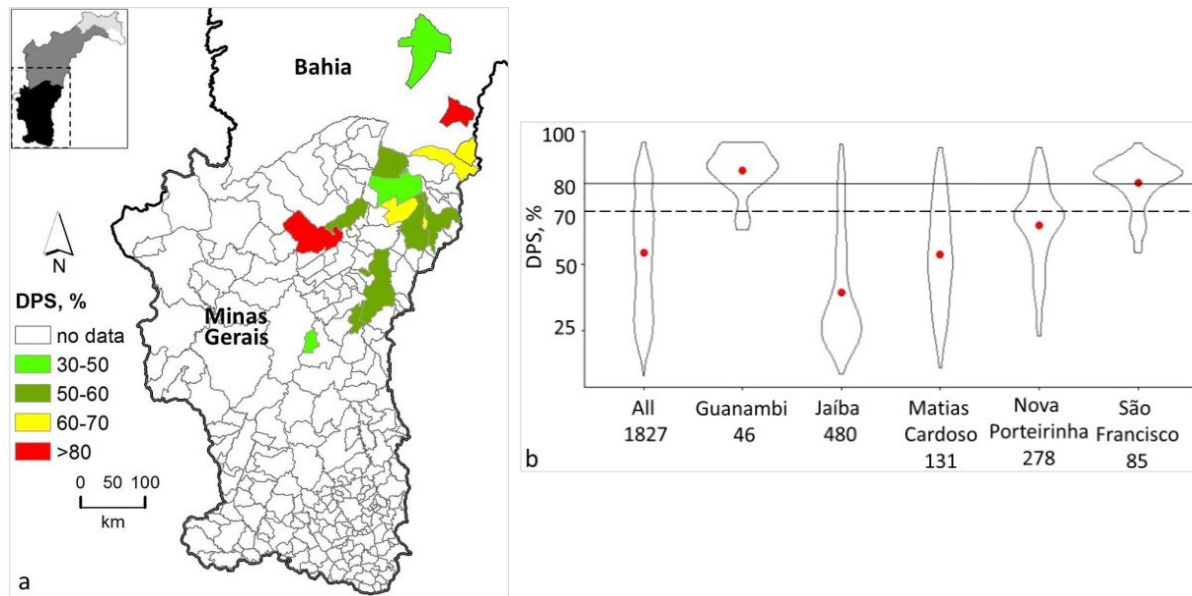
Figure 3.3: DPS values estimated from M1P monitoring data: a) Map of municipalities in Minas Gerais and Bahia (map source: municipality borders, IBGE geociências) b) Violin plots showing the complete distributions of DPS values for all obtained data and five selected municipalities of Minas Gerais and Bahia (red points show arithmetic means, n is given below names in x-axis labels): DPS threshold values of dissolved P losses are marked with a dashed and solid line).

Arithmetic means and the distribution of DPS values for different municipalities as well as for the entire region were compared via violin plots (Fig. 3.3 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% (Fig. 3.3 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 3.2). 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 3.2).

Table 3.2: 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.

Agricultural field	Date 2014	n [-]	RI [mm/h]	TSM [g/l]	P in surface runoff water		Soil WSP
					TSP [mg/l]	TDP [mg/l]	[mg/kg]
Tangerine	21.01.	3	19.2	0.8 10.4 23.1	min: 0.13 max: 0.19 AM: 0.16	min: 0.08 max: 0.19 AM: 0.14	min.: 0.0 max.: 47.9 (F)
Cabbage	23.01.	1	21.6	10.4	1.94	0.40	min.: 1.8 max.: 30.5 (F)
Cabbage	15.02.	2	36.7	3.7 9.6	1.93 1.68	0.14 0.10	min.: 1.8 max.: 30.5 (F)
Cabbage	16.02.	2	no data	4.1 6.1	1.64 1.65	0.06 0.07	min.: 1.8 max.: 30.5 (F)
Mixed cultures	30.03.	3	13.5	2.1 6.9 24.6	min: 1.28 max: 1.81 AM: 1.61	min: 0.08 max: 0.15 AM: 0.12	min.: 2.8 max.: 33.6 (F)
Mixed cultures	30.03.	1	36.0	9.2	2.03	0.13	min.: 2.8 max.: 33.6 (F)
Mixed cultures	31.03.	6	24.0	min: 6.6 max: 25.9	min: 0.96 max: 2.18 AM: 1.74	min: 0.09 max: 0.36 AM: 0.15	min.: 2.8 max.: 33.6 (F)

The soils of the runoff study showed a wide range in WSP values in all investigated fields, with some extremely high values (Table 3.2). 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 two factors. First, extremely high WSP values were only found in planting rows with not incorporated fertilizer. These areas are not representative of the entire field, and only contribute a difficult to estimate share of the dissolved P in runoff water. Second, a reduction of dissolved P concentrations in runoff may have occurred 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. 1981b). 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 3.1), 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.

3.4 Conclusions

A highly significant correlation between M1P and WSP suggests that the DPS of agricultural soils in Brazil with low or no $CaCO_3$ 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.

4 The degree of phosphorus saturation of agricultural soils in Germany: Current and future risk of diffuse P loss and implications for soil P management in Europe

Fischer, P.[1,2]*, Pöthig, R.[3], Venohr, M.[4]

1,3,4) Leibniz-Institute of Freshwater Ecology and Inland Fisheries (IGB), Department of Ecohydrology,
  Justus von Liebig Straße 7, 12489 Berlin, Germany

2) Humboldt-University Berlin, Geography department, Unter den Linden 6, 10099 Berlin, Germany

Highlights:

- Accomplishment of the first DPS risk map for German arable soils
- High risks of P losses were derived for 76% of monitoring data (n > 337,000).
- Hitherto recommended P levels in soils are in conflict with environmental goals.
- Recommended reduction of P levels is crucial to lower future risks of P losses.
- For future P-monitoring WSP is recommended as agri-environmental soil P test in Europe.

Graphical abstract
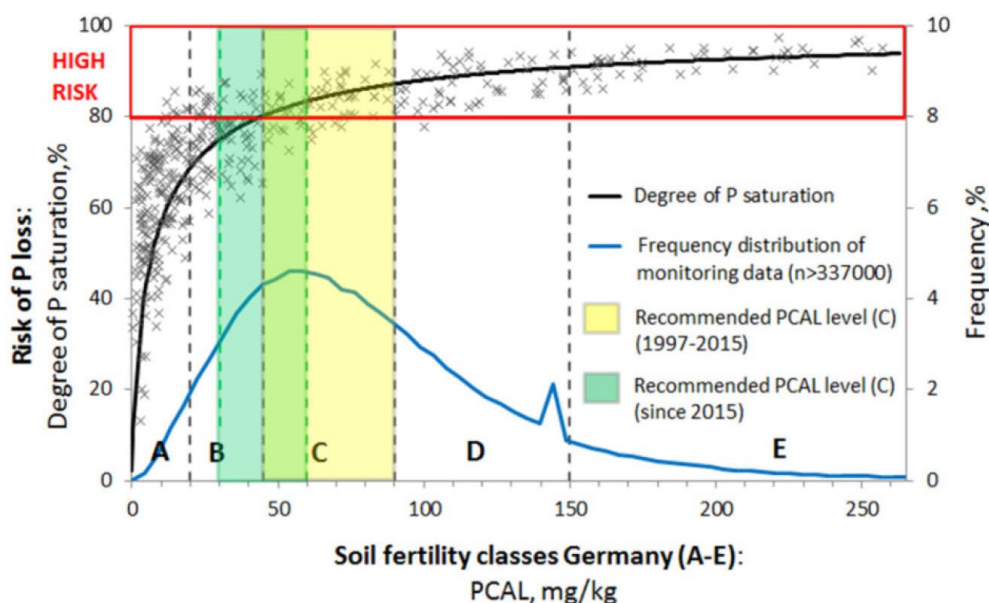
Figure 4.1: Graphical abstract.

Abstract

Decades of intensive agricultural production with excessive application of P fertilizer have resulted in the accumulation of P in soils, threatening water bodies in most industrialized countries with eutrophication. In our study, we elucidated the risk of P loss of German agricultural soils by transforming provided monitoring data of plant-available P determined by the calcium-acetate-lactate (PCAL) and double-lactate method (PDL) into the degree of phosphorus saturation (DPS). As water-soluble phosphorus (WSP) is correlated to DPS, we derived a pedotransfer function (PTF) between PCAL and WSP for different soil types. Considering all soils together resulted in WSP $= 0.1918 \times$ PCAL ($R^2 = 0.80$, n $= 54$). Subsequently, risk parameters DPS and EPC0 were calculated from PCAL and PDL monitoring data (n $>$ 337,000) by using the determined PTF and soil type-independent correlations with WSP, as published in an earlier study. Calculated DPS values from monitoring data indicated high risks of dissolved P loss for $>$ 76% of German arable soils. Recent suggestions by the Association of German Agricultural Analytical and Research Institutes (VDLUFA) to reduce recommended PCAL levels are crucial for the reduction of P loss risks in the future. The accuracy of predicted DPS and EPC0 values by CAL and other methods used in Europe to estimate plant-available P is limited by the soil type-dependency of these methods. Consequently, we recommend considering WSP as an agri-environmental soil P test across Europe. Our results indicate that a WSP level in soils can be defined that constitutes a reasonable compromise between the securing of agronomic production and the fulfillment of environmental goals.

Keywords: Water-soluble phosphorus, equilibrium phosphorus concentration, plant-available phosphorus, calcium-acetate-lactate, agri-environmental soil P test, soil fertility classes

4.1 Introduction

Raw material rock phosphate is a limited resource. More than 80% of this resource is currently used as fertilizer (Liu et al. 2008, Chowdhury et al. 2014, Reijnders 2014). Because of increasing awareness of the limitations of P as a resource, regaining P from wastes and bio-resources has become a major concern in Europe in the last decade (e.g. Withers et al. 2015).

In the past, P fertilizer was applied excessively to European agricultural soils, particularly in the 1960s through 1980s (Reijneveld et al. 2010, Sattari et al. 2012, Tóth et al. 2014, Schoumans et al. 2015). In Central Europe, the amount of P fertilizer applied to agricultural fields was numerous times greater than the P exported with harvested crops, resulting in high P accumulation in soils (Sattari et al. 2012) and diffuse P losses to surface waters (e.g. Kronvang et al. 2007, Venohr et al. 2011). In Germany, for example, a cumulative P surplus of approximately 1,100 kg ha^{-1} was reported for the year 2010 (Nieder et al. 2010). Currently, in Europe, excessive P fertilization (resulting in increasing P accumulation) on agricultural land tends to be taking place primarily owing to manure application in areas with high livestock densities or intensive crop production (Tóth et al. 2014, Schoumans et al. 2015).

Accumulated P, also referred to as residual soil P, has been a major concern because of its role in the impairment of water quality through diffuse P losses (e.g. Sibbesen and Sharpley 1997, Bouwman et al. 2009, Kleinman et al. 2011, Sattari et al. 2012). The contribution of diffuse P losses to the eutrophication of surface waters is well-known (e.g. Carpenter et al. 1998, Diaz and Rosenberg 2008, Carpenter and Bennett 2011). An example is the spreading bottom anoxia in the Baltic Sea, which is considerably influenced by diffuse P losses from agricultural areas (HELCOM 2011, Carstensen et al. 2014). In Germany and many other countries in Europe, P inputs from point sources have been strongly reduced by the construction of wastewater treatment plants. Nowadays, the share of diffuse P emissions from agriculture contributes ca. 50% of total P emissions in these countries (Behrendt et al. 2003, EEA 2005, HELCOM 2011, Umweltbundesamt 2014). Consequently, diffuse P losses from agricultural areas have become a major concern for water quality in Europe and must be assessed in the Water Framework Directive (WFD, Directive 2000/60/EC).

For identifying so-called critical source areas (CSAs) of diffuse P losses, the hydrological connectivity of agricultural areas to water bodies, as well as parameters describing potential P loss of agricultural areas (e.g., type of fertilizer application, degree of phosphorus saturation), must be known (Heathwaite et al. 2000, Buczko and Kuchenbuch 2007, Sharpley et al. 2012). The degree of phosphorus saturation (DPS) is an established parameter used to assess the risk of P losses from soil to water. It has been shown to be well-correlated with dissolved P concentrations in surface runoff and leakage (Sharpley 1995, Maguire and Sims 2002, Vadas et al. 2005). Several studies have assessed the risk of P losses from soil to water by correlating soil test methods to estimate plant-available P with DPS (e.g. Kleinman et al. 1999, Kleinman and Sharpley 2002, Houben et al. 2011). Such predictive functions of soil properties from existing soil data are known as pedotransfer functions (PTF) (Bouma 1989). Ideally, a soil test method can serve as an agri-environmental soil P test that takes into account both agronomic needs and environmental risks due to P losses (e.g. Magdoff et al. 1999, Khiari et al. 2000, Sims et al. 2002) .

The DPS is primarily determined by methods that consider only a fraction of the sorption sites of a soil (e.g., Fe and Al on acidic sandy soils and Ca and Mg on calcareous soils), which restricts the application of these approaches to selected soil types (e.g. Sharpley et al. 2012). Including all sorption sites of different soil types is only possible with sorption isotherms, which are, however, time-consuming and expensive to measure. An extensive study investigating over 400 soils in Germany and Switzerland by sorption isotherms identified a standard extraction method of water-soluble Phosphorus (WSP) as a soil-independent predictor of DPS (Pöthig et al. 2010). In this WSP-DPS approach, DPS was found to be equal to DPS = $100/(1+1.25 \times WSP^{-0.75})$, $R^2 = 0.71$.

Fertilizer recommendations in European countries are based on a three-step process (e.g. Jordan-Meille et al. 2012): 1. Soil test methods, which are used to estimate plant-available P from soil samples via laboratory analyses (e.g., calcium-acetate-lactate (CAL), Olsen, Mehlich-3); 2. Calibration of necessary plant-available P levels in field trials based on yields for ensuring optimal agronomic production; and 3. Calculation of necessary fertilizer amounts for optimal agricultural yields, generating fertilizer recommendations. Currently > 10 different soil test methods are in use across Europe. Strong contradictions between the different countries concerning P levels which are assumed necessary for optimal agronomic productions for similar soil-crop systems have been reported in the last two decades (Tunney et al. 1997, Neyroud and Lischer 2003, Jordan-Meille et al. 2012, Tóth et al. 2014). Environmental constraints that may occur by achieving optimum P levels for agronomic production have gained relatively little attention (Jordan-Meille et al. 2012). A simple and cost-effective method to define P levels in soils that allows for a concomitant soil type-independent risk assessment of P losses has to our knowledge not been introduced yet.

In federal states of Germany plant-available P is mostly estimated using an extraction method with either calcium-acetate-lactate (PCAL, VDLUFA 1991, 2002) or double lactate (PDL, Table 1). Based on these methods, a classification system for soils (A: lowest to E: highest PCAL, PDL levels) that determines fertilization needs was introduced in the late 1970s (e.g. Übelhör and Hartwig 2012). Class C is the target class, considered to be necessary for optimal agricultural production. Only recently, the Association of German Agricultural Analytical and Research Institutes (VDLUFA) corrected the recommended PCAL values for class C to lower values (Taube et al. 2015) replacing the former recommendation (Kerschberger et al. 1997).

In this study, we derived a PTF between the extraction methodologies of PCAL and WSP. Subsequently, DPS and equilibrium phosphorus concentration (EPC0) were estimated by soil type-independent correlations to WSP (Pöthig et al. 2010, see material and methods). This procedure was applied to PCAL monitoring data (n > 337,000) and recommended PCAL levels in German arable soils (Kerschberger et al. 1997, Taube et al. 2015) to evaluate current and future risks of diffuse P losses.

Based on our results, we present an approach to determine P levels in agricultural soils that considers the securing of agronomic production and the protection of surface waters from diffuse P losses.

4.2 Materials and Methods

Soil sampling

Soil samples were taken from two regions: a region of unconsolidated rock in the Northern Plains of Germany (Brandenburg, northeast of Fürstenwalde; n = 39) and a region of solid rock in the South German Scarplands (Bavaria, west of Neumarkt/Oberpfalz; n = 15). Within the two regions, a total of 11 sites that differed in soil type (sandy, loamy, calcareous and decomposed peat soil), as well as in land use (arable land, grassland, and former fens), were sampled. The samples were collected primarily from top soil (ca. 0-45 cm) using either Eijkelkamp Soil & Water drilling equipment or a shovel.

Soil analyses

Soil samples were air-dried and sieved (<2 mm) prior to analyses. Soils containing $CaCO_3$ were identified qualitatively by testing with HCl (10%). CAL extraction was executed according to the manual of German Agricultural Analytic and Research Institutes (VDLUFA 2002), but instead of ascorbic acid/$SnCl_2$, $SnCl_2$/$NH_2OH\cdot HCl$ was used as the reducing agent. The reducing agent was changed because of the observation of a yellowish/greenish color of the reduced phosphate-molybdate-complex with the original reducing agent for some soil CAL extracts, revealing imperfect reduction. Using a stronger reduction solution (0.125 g $SnCl_2$ + 0.5 g $NH_2OH\cdot HCl$ + 1 ml $HCl_{CONC.}$)/50 ml resulted in a turquoise P-molybdate-complex, stable from 15 to 45 minutes after coloring (Fig. 4.2 a) with an absorption maximum of 715 nm (Fig. 4.2 b).
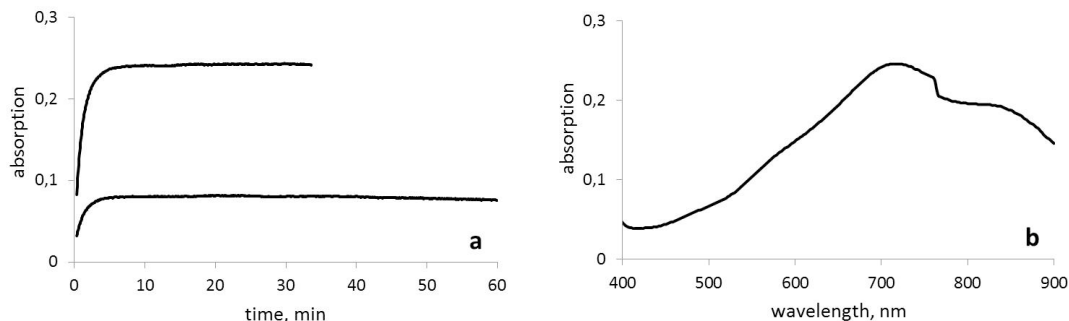
Figure 4.2 (a): Time dependence of the phosphate-molybdate complex in calcium-acetate-lactate extract using $NH_2OH\cdot HCl$ as reducing reagent (curves of two different P concentrations, measured at 715 nm), (b): Dependence of absorption from the wavelength.

The P calibration curves were prepared with the same amount of CAL as that in the soil extractions. After soil extraction, the pH values of the CAL extraction solutions were measured. In contrast with VDLUFA (2002), PCAL values were not corrected according to pH elevation of the extractant. WSP was analyzed according to Pöthig et al. (2010). The WSP extract of peat soils was digested with $K_2S_2O_8$ for including the determination of the organically bound P and thus total soluble P (TSP) (EN ISO 6878:2004). For comparison of different WSP methods, extraction methodologies were carried out according to Pöthig et al. (2010), Sissingh (1971) and Pote et al. (1996), with the inclusion of Brazilian Oxisols and Entisols of a former study (Fischer et al. 2016). All P concentrations were measured according to Murphy and Riley (1962) and as described above using a UV-VIS-photometer (UV 2102, Shimadzu Corp.).

Pedotransfer function for calculation of WSP by PCAL

The correlations found by soil analyses in this study were described by linear regression equations in order to transform PCAL data into WSP data. The PTF was compared to published correlations for parameters including WSP, equilibrium phosphorus concentration and PCAL using the dataset of Pöthig et al. (2010), which contains measured values of WSP, EPC0 and DPS for 429 soils, including sandy, loamy, calcareous and decomposed peat soils.

Analyses of monitoring data

PCAL and PDL data from the topsoil (ca. 0-30 cm) of agricultural soils of arable land were provided by German authorities (see Table 4.1). PCAL and PDL monitoring data were transformed into WSP as follows: PDL data were first transformed into PCAL data using a conversion factor of 0.833 (PCAL = 0.833 × PDL, Hoffmann, 1991). PCAL data were transformed into WSP data by the PTF determined in this study. Subsequently, DPS data were calculated according to Pöthig et al. (2010), where $DPS = 100 / (1 + 1.25 \times WSP^{-0.75})$, and compared to threshold values for elevated and high risks of P losses from soil to water of 70 and 80%, respectively. EPC0 values were calculated using an unpublished correlation from the same above-mentioned study: $EPC0 = 0.0018 \times WSP^2 + 5 \times 10^{-6}\,WSP$.

For the calculation of DPS and EPC0 values from the monitoring data, only values of up to 265 mg/kg PCAL were considered (98% of all monitoring data), as greater values result in exceptionally high WSP values of > 50 mg/kg for agricultural soils. In a previous study, such high WSP values were only found in soils used as sewage farms (Pöthig et al. 2010). We assumed that these data reflect direct fertilizer effects or erroneous results, rather than the P saturation of arable soils and, therefore, excluded them from our evaluation. For monitoring data below the detection limit (<0.001% of all monitoring data), PCAL and PDL values were assumed to be half of the detection limit.

For visualization on maps, point and cadaster data were extrapolated to the municipality level via arithmetic means. Data from Federal Agency for Cartography and Geodesy (BKG) were used for spatial allocation of monitoring data to administrative areas and arable land (© GeoBasis-DE/BKG (2013, 2014).The ggplot2 package in the R software (R Core Team 2015, Vienna, Austria) was used to create violin plots of the DPS of selected federal states and to investigate the loss of information on hotspot areas of high DPS values due to spatial data aggregation in BW.

Threshold values of soil P (in mg CAL extractable P/100 g soil) used for fertilizer recommendations were evaluated with regard to the risk of P losses by calculating corresponding WSP, DPS and EPC0 values, as described above.

Table 4.1: Soil phosphorus data provided by authorities of federal states of Germany.

Federal state	M	CAL-ph-correction	Time span	Spatial resolution	n
Baden-Württemberg (BW)	CAL	No	2007-2013	Cadaster	318,902
Bayern (BY)	CAL	Yes	2005-2010	District	96 (985,859)
Brandenburg (BB)	CAL	No	2005-2013	Point	40
Hessen (HE)	CAL	Yes	2008-2014	Point	4,262
Mecklenburg-Vorpommern (MV)	DL	-	1994-2009	Point	174
Niedersachsen (NDS)	CAL	No	2001-2013	Point	103
Nordrhein-Westfalen (NRW)	CAL	No	1993-1997	Point	7,377
Rheinland-Pfalz (RP)	CAL	Yes	2004-2013	Point, municipality	225
Saarland (SL)	CAL	Yes	2005	Municipality	6
Sachsen (SN)	CAL	No	2004, 2010	Municipality	166 (1,310)
Sachsen-Anhalt (ST)	DL	-	2005-2007	Municipality	6,156
Schleswig-Holstein (SH)	DL	-	2009-2013	Point	99
Thüringen (TH)	CAL	Yes	2010-2012	District	20 (52,013)

M = methodology; CAL = calcium-acetate-lactate; DL = double-lactate; CAL-pH-correction: correction of measured PCAL values according to change in pH value of extraction solution (VDLUFA 2002); n = number of delivered values: if delivered data were aggregated, number of values forming aggregated values is shown in brackets; sources of data: see references.

4.3 Results and Discussion

Pedotransfer functions for determination of WSP of German soils

The soil analyses resulted in two highly significant correlations (p < 0.01) between PCAL and WSP (Fig. 4.3): one for soils without $CaCO_3$ (WSP = 0.2801 × PCAL) and one for soils with $CaCO_3$ (WSP = 0.1621 × PCAL). The latter comprises calcareous soils and all other soil types containing $CaCO_3$, including samples with lime shells (Fig. 4.3 A). The six investigated decomposed peat soils containing fossil shells behaved similarly to the calcareous soils, but four soil samples with high peat portions only fit the correlation with the use of TSP instead of soluble reactive P (SRP) for WSP. This indicates that decomposed peat soils can also be included in this correlation, but for peat soils, a more intensive study would be necessary to delineate WSP values from PCAL data also considering dissolved organic P.
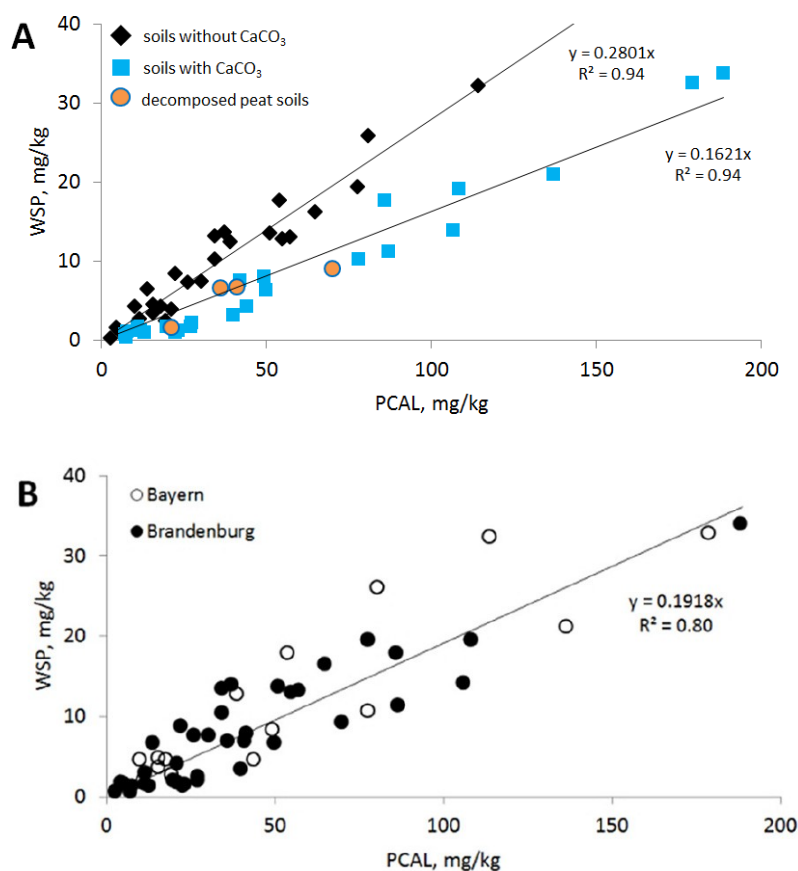
Figure 4.3: Relationship between water-soluble P (WSP) and P determined by the calcium-acetate-lactate method (PCAL): A) Sandy and loamy soils without $CaCO_3$ (n = 26) and sandy, loamy, and decomposed peat soils with $CaCO_3$, as well as calcareous soils (n = 28); B) All soils from A (n = 54).

CAL extraction led to higher PCAL values compared with WSP values in soils with $CaCO_3$ than in soils without $CaCO_3$. Calcium phosphates are not stable at such acidic pH values and produce soluble P concentrations ca. 2 to 5 dimensions greater than Fe- and Al-bound phosphates, which are more stable under these conditions (Lindsay 1979, Lindsay et al. 1989). In addition to the greater solubility of calcium phosphates at low pH values, the mechanisms of complexation and anion exchange of lactate and acetate increase the extraction of Ca-associated P in fossil shells and calcareous soils (e.g. Kamprath and Watson 1980). An increase in pH values of the CAL extraction solution from 4.1 to at most 4.75 was

observed for some of the $CaCO_3$-containing soils (soils with up to 72% $CaCO_3$). However, the preferential dissolution of calcium phosphates by CAL under these conditions is stronger than the effect of the lowered extraction efficiency of Ca bound phosphates due to higher pH values in the CAL extraction solution. The two different WSP-PCAL correlations are the result of the different soil compositions and thus different soil pH and specific P binding forms. The most likely P binding forms are Ca/Mg-bound phosphates in soils with $CaCO_3$ and pH values > 6 and Fe/Al-bound phosphates in the other soils (e.g. Beauchemin et al. 2003).

For use as a PTF, a linear regression was derived for all investigated soils (Fig. 4.3 B: WSP = 0.1918 × PCAL, R^2 = 0.80). When applying the PTF to monitoring data one should be aware that risk parameters are underestimated for soils without $CaCO_3$ and overestimated for soils with $CaCO_3$. The correction of PCAL values according to pH elevation in the CAL extraction solution, following the approach by VDLUFA (2002) contradicts our results and strengthens the overestimation of risk parameters for soils with $CaCO_3$. Consequently, uncorrected PCAL monitoring data were used where possible (see Table 4.1).

Comparison to published correlations

Schick et al. (2013) published a WSP-PCAL correlation for different soil types of Germany and Poland using slightly different soil test methods (Schüller 1969, van der Paauw and Sissingh 1971, Fig. 4.4). The obtained regression equation is characterized by a Y-intercept and a lower slope than is our PTF. These differences are most likely caused by the effect of coal used in the extraction methodology of Schüller (1969), which sorbs P in the extraction process, leading to smaller PCAL than WSP values at low P levels in the investigated soils.
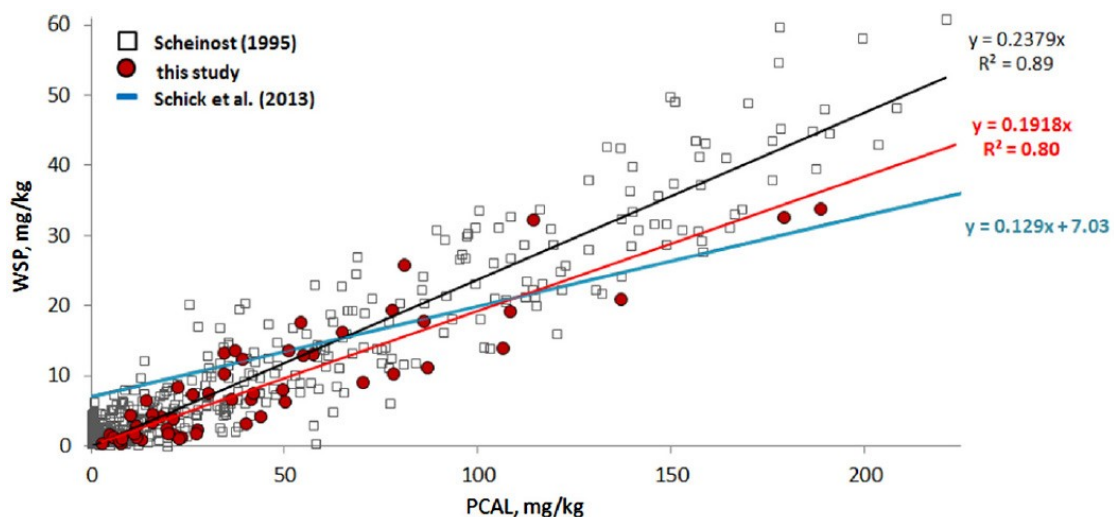
Figure 4.4: Relationships between water-soluble P (WSP) and P extracted by the calcium-acetate-lactate method (PCAL): red line = PTF of measured data (Fig. 2 B, this study), blue line = WSP-PCAL relationship published by Schick et al. (2013), squares: WSP-PCAL relationship derived by applying a published equation relating PCAL and EPC0 (Scheinost 1995) to a dataset of Pöthig et al. (2010).

Scheinost (1995) found highly significant correlations between PCAL and the parameter Pl_0, which is comparable to EPC0. The correlation between Pl_0 and PCAL was described by the following equation: log Pl_0 = -2.3 + 6.9 $\sqrt{PCAL}$ (R^2 = 0.80, n = 52). 429 measured EPC0 values of an existing dataset were inserted into this function and corresponding PCAL values were calculated. Subsequently, the PCAL values were correlated to the corresponding WSP

values of the dataset (Fig. 4.4, rectangles). Although the P sorption methods through which the correlations of Scheinost (1995) and this study were developed are different, both produced similar results for the correlation between PCAL and WSP, with mean slopes of 0.1918 (PTF: Figs. 4.3 and 4.4) and 0.2379 (Fig. 4.4) in the linear regressions. The slopes of the WSP-PCAL correlations (Fig. 4.4) are affected by the number of investigated soils with and without $CaCO_3$ because of the preferential dissolution of Ca-bound P in the $CaCO_3$-containing soils leading to a lower slope of the regression line. In the dataset of our PTF, the ratio of investigated soils without $CaCO_3$/soils with $CaCO_3$ is 0.9, in contrast to the database of 429 soils, with a ratio of > 1. This may explain the differences in the WSP-PCAL relationships. Applying the function of Scheinost (1995) to our dataset confirms our PTF and the calculated results of risk parameters WSP, EPC0 and DPS.

Relationship between WSP and EPC0
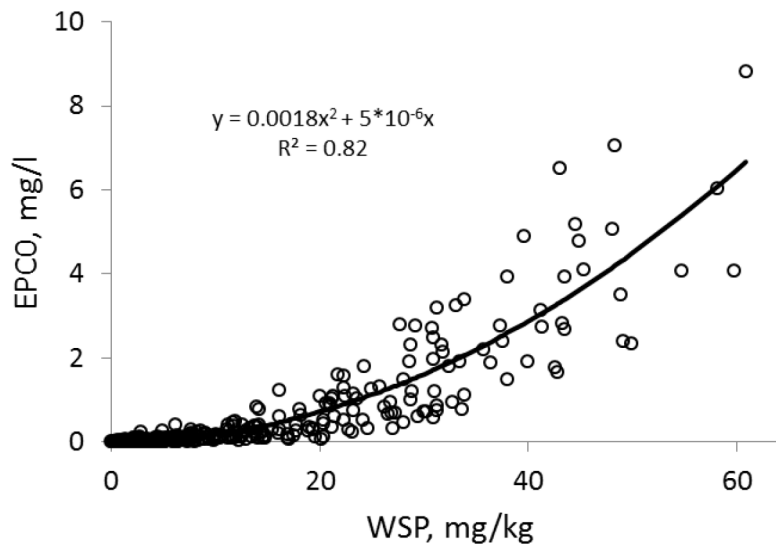
Figure 4.5: Relationship between equilibrium P concentration (EPC0) and water-soluble P (WSP) determined on soil samples of different soil types and land uses (n = 429, based on data presented in Pöthig et al. 2010, unpublished).

EPC0 data were estimated from PCAL data via the above-described PTF and subsequently using the function shown in Fig. 4.5 and as follows: $EPC0 = 0.0018 \times WSP^2 + 5 \times 10^{-6} WSP$ ($R^2 = 0.82$, n = 429, Fig. 4.4).

Risk of P loss from soil to water in arable German soils

The spatial distribution of DPS and EPC0 in arable soils in Germany estimated by PCAL and PDL monitoring data are shown in Fig. 4.6.
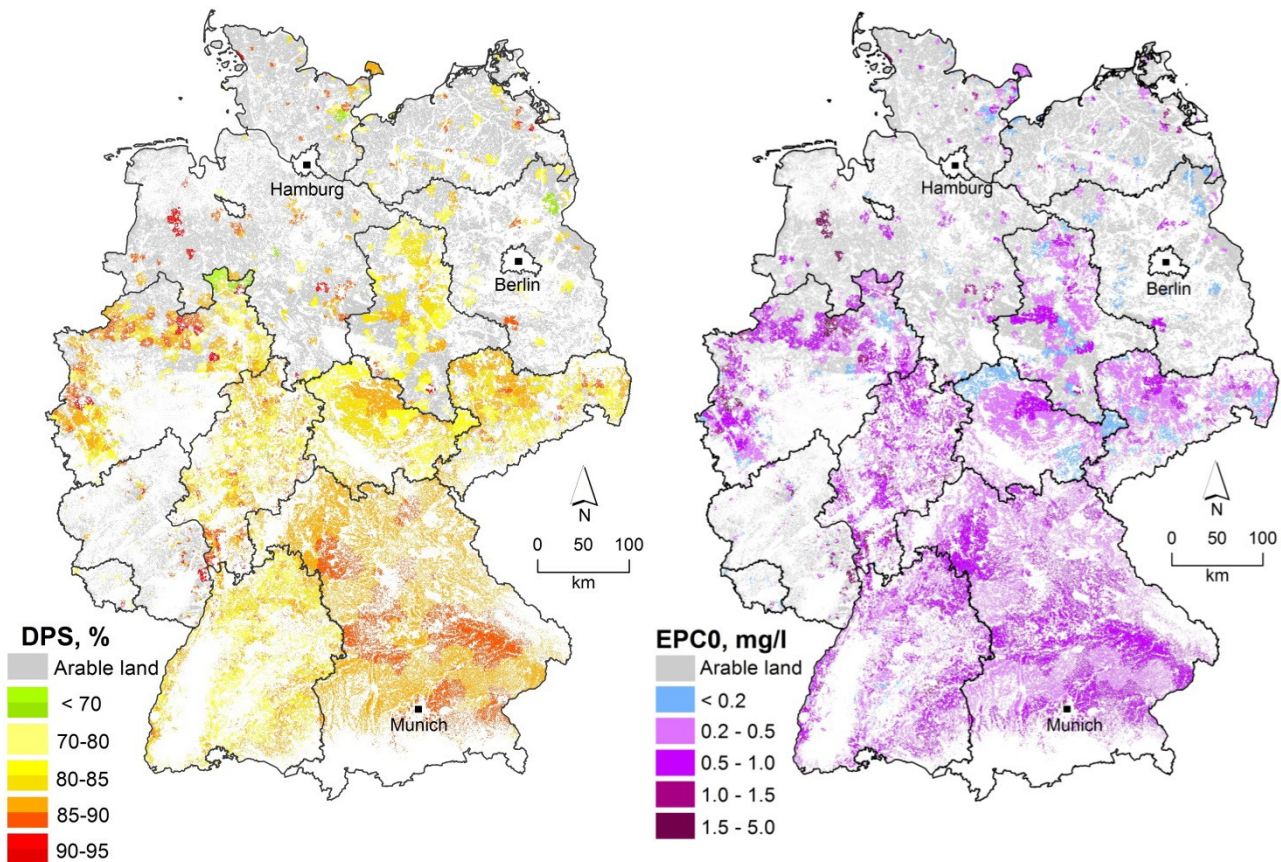
Figure 4.6: Spatial distribution of degree of P saturation (DPS) and equilibrium P concentration (EPC0) in arable soils in Germany: Point data were extrapolated to municipality level; data from Thüringen and Bayern were provided on a district level; no data were available for arable land marked in grey (map sources: arable land: © GeoBasis-DE/BKG (2013); administrative borders:© GeoBasis-DE/BKG (2014), adapted).

Monitoring datasets provided by German federal states differed in size and spatial resolution (Table 4.1). The high spatial aggregation of monitoring data (BY, TH) and fragmentary data (e.g., northern Germany) hinders the proper identification of hotspot regions of soils highly saturated by P. For 18% of the municipalities shown in our map, only three or fewer values were reported. Consequently, our map cannot provide a representative picture for all of the regions but rather presents a first evaluation of DPS and EPC0 in arable German soils by our method.

A comparison of our results with threshold values of DPS from Pöthig et al. (2010) revealed that 96% of monitored data indicate elevated risk (DPS > 70%) and 76% indicate high risk (DPS > 80%) of dissolved P losses from arable land in Germany (Figs. 4.6 and 4.7). This is in contrast to a study of tropical soils in Brazil, where only 38% and 16% of analyzed monitoring data indicated elevated and high risks of dissolved P losses, respectively (Fischer et al. 2016). These differences are explainable by the shorter time period of intensive agricultural production in Brazil and concomitant lower P accumulations (e.g. Sattari et al. 2012, Roy et al. 2016).

Arithmetic means and distribution of estimated DPS values were compared via violin plots (Fig. 4.7). In all federal states, the arithmetic mean of all DPS values was > 80%. In municipalities, the arithmetic mean of estimated DPS values ranged between 52 and 94%.
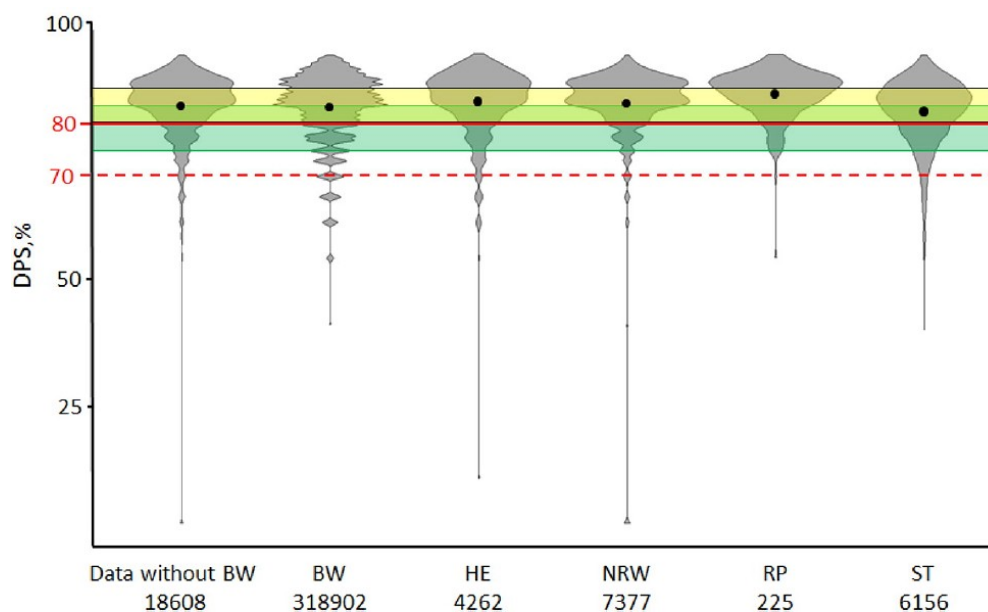
Figure 4.7: Degree of P saturation (DPS) values estimated from P monitoring data determined by the methods of calcium-acetate-lactate (PCAL) and double-lactate (PDL) for selected federal states (visualized by violin plots showing the complete distributions of DPS values): Black points = arithmetic means; n is given in x-axis labels below state acronyms (see Table 4.1). DPS threshold values of P losses are marked with dashed and solid red lines. Resulting DPS of recommended PCAL levels in German soils (soil P class C) is marked in yellow (Kerschberger et al. 1997) and green (Taube et al. 2015).

The analyses of the two biggest federal state-specific datasets provided by German authorities, aggregated once at the cadaster level (BW; n = 318,902; at least 10 values and, on average, 300 values per municipality) and once at the district level (BY; n = 985,859; at least five values and, on average, 10,269 values per district), reveal two major aspects of risk assessment of P losses from agricultural areas in Germany:

1) A spatial resolution of monitoring data of at least the municipality level is necessary for the identification of areas with exceptionally high risk of P losses. A comparison of the monitoring dataset of BW, aggregated at different administrative levels, clarifies that spatial variability cannot be represented by monitoring data aggregated at the district level (Fig. 4.8). Of the monitoring data in BW, 0.1% exhibits an exceptionally high risk of P losses (DPS > 90%) when data are aggregated at the municipality level, compared with 9.8% when data are not aggregated. Consequently, the information loss is still high even when delivered data is aggregated on a municipality level.
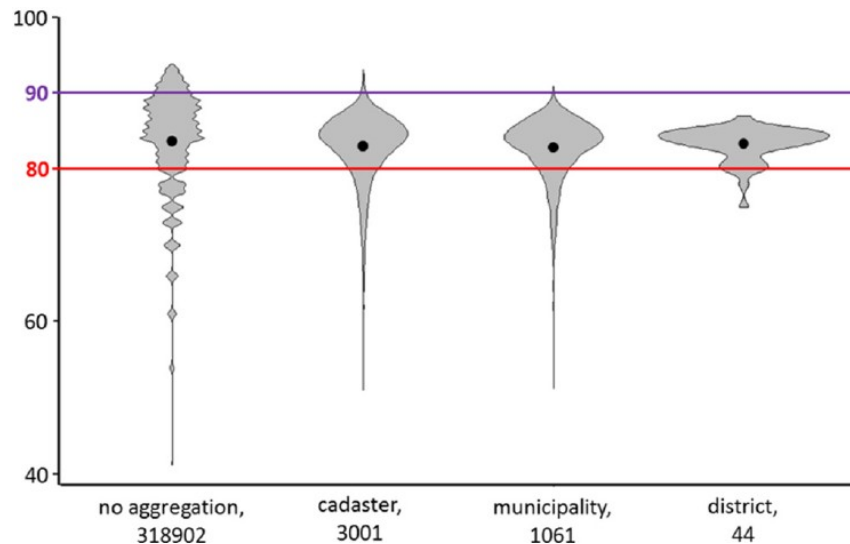
Figure 4.8: Loss of information on hotspot areas of high degree of P saturation (DPS) due to spatial data aggregation in BW (visualized by violin plots showing the complete distributions of DPS values): black points = arithmetic means; n is given in x-axis labels below aggregation levels.

Through the combination of information on areas with high risk of P losses from soil to water with that on hydrological pathways and hydraulic connectivity to surface water bodies, critical source areas (CSAs) can be defined (e.g. Lemunyon and Gilbert 1993, Venohr et al. 2011, Sharpley et al. 2012). These areas have been reported to cover only 20% of catchments but contribute 80% of P emissions (Sharpley et al. 2009). A high spatial resolution of input data is a prerequisite for the effective identification of CSAs.

2) PCAL values that are not corrected according to the pH of the CAL extraction solution of $CaCO_3$-containing soils are necessary for the effective risk assessment of P losses. Corrected PCAL data result in overestimation of the DPS (see explanation above). In BW, where measured and corrected values were provided, the difference in resulting DPS was moderate between the two when the arithmetic means of all monitoring values were considered ($\Delta DPS = 0.5\%$). In contrast, when this comparison was performed for data aggregated on a municipality level and for single PCAL values, the differences in the resulting DPS values reached up to $\Delta DPS = 6\%$ and $\Delta DPS = 44\%$, respectively, confirming the importance of the use of uncorrected data. The higher DPS and EPC0 values calculated for BY compared with those for BW might have been due to the use of corrected monitoring data for BY.

The EPC0 values derived from monitoring data (21% of values > 0.8 mg/l) indicate a high risk of dissolved P losses through surface runoff and P leaching from the topsoil layer to deeper soil horizons. For the protection of surface waters, Auerswald et al. (2002) recommended thresholds of dissolved P of 0.08 to 0.15 mg/l in tile drainages and soil solutions in the relevant soil layers. The analyzed monitoring data in this study refer to the topsoil layer (ca. 0-30 cm). An evaluation of PCAL monitoring data of drainage-relevant soil layers (ca. 60-100 cm) would be important in the estimation of the risk of P leaching into drainages using the PTF of our study.

The high DPS and EPC0 values are a result of fertilizer application and concomitant P accumulation over the last few decades. Excessive P application, especially in the 1970s and 1980s, led to a P accumulation of approximately 800 kg P ha^{-1} in the soils of the new federal states and 1,200 kg P ha^{-1} in the old federal states of Germany (Nieder et al. 2010). As in other industrialized countries, e.g., in the United States or the Netherlands, this accumulated soil P in Germany and its concomitant high DPS values are a major concern for efforts to reduce P losses from agricultural areas (Kleinman et al. 2011, Schoumans and Chardon 2015). This is confirmed through the comparison of our dataset in the derived WSP values from German monitoring data with reported WSP values from the Netherlands (Reijneveld et al. 2010), which indicate a greater risk of P losses from soil to water for Dutch soils.

Interpretation of German fertility classes with regard to potential P losses

Recommended PCAL levels are defined by class C and have been corrected to lower values several times since the introduction of the A-E class system in the late 1970s (Übelhör and Hartwig 2012). Since 1997, the class C recommendation of VDLUFA has ranged from 4.5 to 9.0 mg P in 100 g of soil (Kerschberger et al. 1997). A recent position paper by VDLUFA suggested lowering the target C class of German agricultural soils once more to the range of 3.0 to 6.0 mg PCAL in 100 g of soil (Taube et al. 2015).

Until 2015, the recommended PCAL values for class C corresponded to DPS values between 80% and 87%, entailing high risks of P losses from soil to water. Up to this point, discussions were ongoing regarding the fact that class C PCAL values exceeded the values required to avoid P limitation for plant growth; unambiguously, they were too high to protect water bodies from diffuse P pollution. Of the analyzed monitoring data, 42% correspond to the former recommended class C, 34% are even greater, and only 24% are below the recommended range (Fig. 4.9).
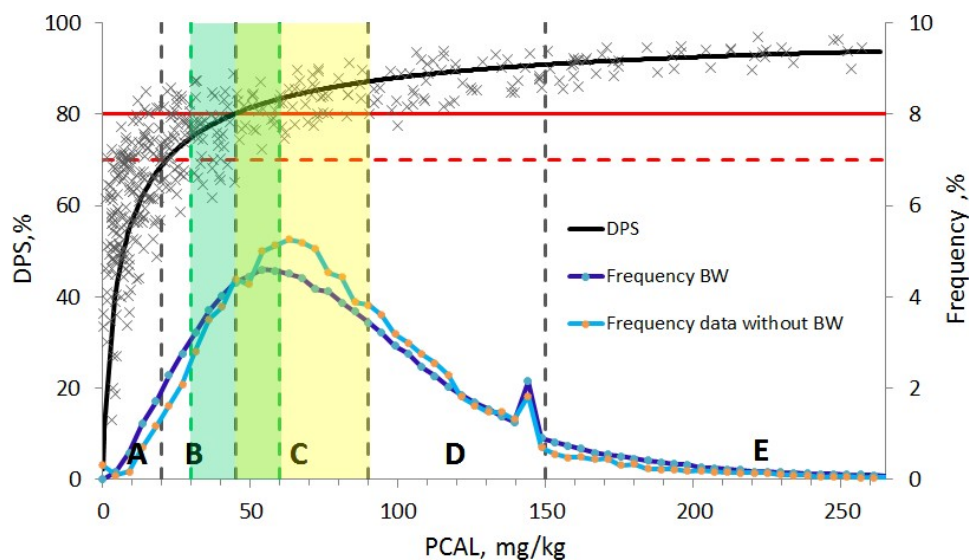
Figure 4.9: German soil fertility classes for fertilizer recommendations, corresponding degree of P saturation (DPS) values and frequency distribution of monitoring data (n > 337,000, values grouped in PCAL classes of 4.5 mg/kg): former recommended target class C is marked in yellow (Kerschberger et al. 1997); recent adaption of class C is marked in green (Taube et al. 2015). DPS threshold values of elevated and high risks of P losses are marked with dashed and solid red lines. Grey x: PCAL-DPS relationship, obtained using the database of Pöthig et al. (2010) and the PTF of this study.

The recent reduction of recommended PCAL level (class C) to the range of 3.0 to 6.0 mg P in 100 g of soil (Taube et al. 2015), corresponds to DPS values of 75 and 83%, respectively (Figs. 4.7 and 4.9). The consequent and complete fulfilment of the latest recommendations for PCAL thresholds would reduce the accumulated P in arable German soils and substantially lower the risk of dissolved P losses from these soils. However, especially in soils without significant amounts of $CaCO_3$, DPS would still range between 80 and 87% (WSP = 0.2801 × PCAL, Fig. 4.10), resulting in high risks of P loss from soil to water. Accordingly, in soils with $CaCO_3$ (WSP = 0.1621 × PCAL, Fig. 4.10), the resulting DPS, ranging between 72 and 82%, would considerably reduce the risk of dissolved P losses. An exact definition of minimum P levels in soils, which is necessary for securing agronomic requirements, is essential for surface water protection, as the P loss risk rises exponentially with increasing PCAL levels in soils (Figs. 4.9 and 4.10).
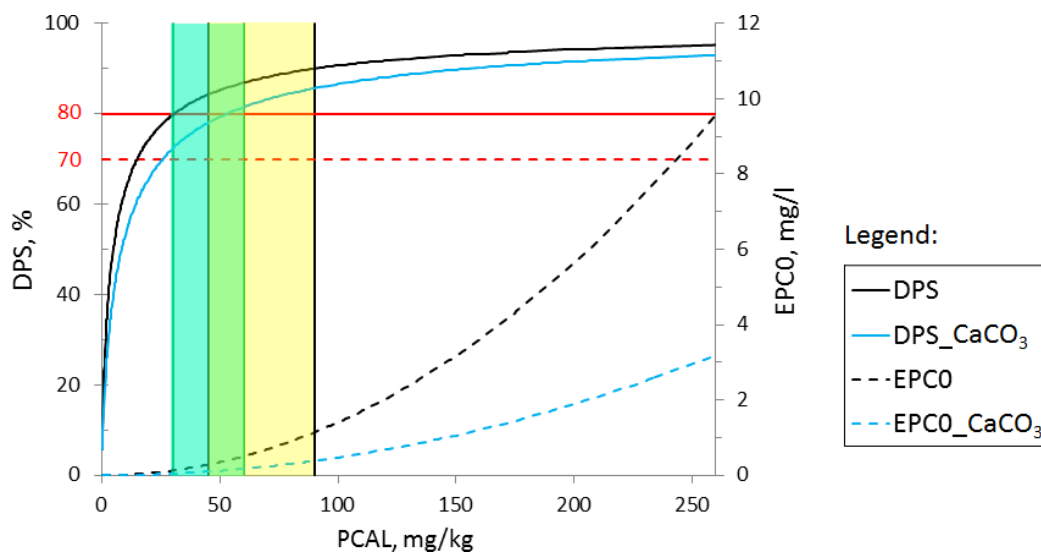
Figure 4.10: Degree of P saturation (DPS) and equilibrium phosphorus concentrations (EPC0) values delineated from P values determined by the calcium-acetate-lactate method (PCAL) for soils with and without $CaCO_3$: Same PCAL values correspond to different average DPS/EPC0 values and, consequently, entail different risks of P losses from soil to waters between the two soil groups. Former recommended class C marked in yellow (Kerschberger et al. 1997); recent adaption of class C marked in green (Taube et al. 2015).

WSP as agri-environmental soil P test in Germany and Europe

Several studies over the last two decades have shown that fertilizer recommendations resulting from soil test methods vary widely between countries and for different soil types in Europe. This has led to the unsatisfying situation in which different P levels in similar soil and crop systems are assumed necessary for agricultural production (Tunney et al. 1997, Neyroud and Lischer 2003, Jordan-Meille et al. 2012, Schick et al. 2013, Tóth et al. 2014).

Soil test methods used in Europe, such as the Olsen, Mehlich-3, or ammonium lactate methods, to estimate plant-available P are similar to CAL soil-type dependent methods owing to the pH values and chemical compounds comprising the extraction solutions (e.g. Zbiral and Nemec 2002, Blume et al. 2009, Otabbong et al. 2009). Consequently, as shown for PCAL (Fig. 4.10), different EPC0 and DPS values at the same plant-available P value can be expected for these methods in different soil types. Therefore, the prediction accuracy of plant-available P across different soil types by these methods is limited (e.g. Blume et al. 2009,

Delgado et al. 2010, Reijneveld 2013). Soil parameters determined by sorption isotherms like EPC0 are known to be crucial for the availability of soil P to plants (Moody et al. 1988, Barber 1995). However, EPC0, determined laboriously by sorption isotherms, is not a suitable parameter for routine analyses.

In contrast to EPC0, WSP is suitable for routine analyses. WSP reflects the genuine P solubility of a soil by adapting to the specific soil pH and P solubility conditions of different soil types. Therefore, the correlations of WSP to the soil parameters DPS and EPC0, determined by sorption isotherms, are independent of soil type (Pöthig et al. 2010, Fig. 4.4).

WSP methods that differ in their extraction times and/or the soil-to-water ratio are well- known to be highly significantly correlated (e.g. Koopmans et al. 2001, this study - Fig. 4.10 A). Fig. 4.11 shows correlations of two WSP methods by Sissingh (1971) and Pote et al. (1996) with the WSP method by Pöthig et al. (2010) investigated in this study. Highly significant correlations (p < 0.01) were found between the different WSP methods for different soil types of German and Brazilian soils. Consequently, results of the different methods are translatable, independent from the investigated soil types.
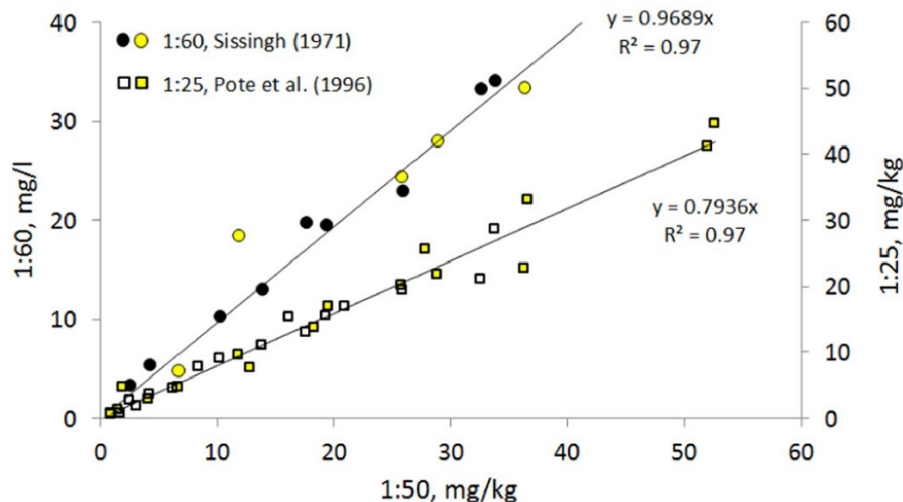
Figure 4.11: Correlation between water-soluble P extraction methods with different soil-to-water ratios and extraction times according to Sissingh (1971) and Pote et al. (1996) in relation to Pöthig et al. (2010) on the x-axis: Brazilian soil samples are marked in yellow.

WSP was shown to be a good estimator of plant-available P over a wide range of investigated soil types (van der Paauw 1971) and is used as a plant-available P predictor for arable soils in the Netherlands according to the method of Sissingh (1971). Furthermore, WSP is a frequently used method for assessing the risk of P losses from agricultural areas, e.g., by correlating it with dissolved P concentrations in surface runoff or the degree of P saturation (e.g. Torbert et al. 2002, Vadas et al. 2005, Xue et al. 2014). The correlation between WSP and dissolved P concentrations in surface runoff was similarly good or better than that of other traditional soil test methods, such as Olsen or Mehlich-3 (Pote et al. 1996, Vadas et al. 2005, Penn et al. 2006).

WSP determined by the method of Sissingh (1971) which is used as an estimator of plant-available P in the Netherlands, can be directly compared with the method of WSP used as a risk parameter for estimating DPS (Figs. 4.11 and 4.12). A comparison of the P level

"sufficient" in the Netherland with the recommended P level of class C in Germany (Fig. 4.12) reveals that a similar target WSP is assumed necessary for agricultural production (van Dijk 1999, Taube et al. 2015). In both cases, these P levels are in conflict with environmental needs (WSP < 8.5 mg/kg, corresponding to DPS < 80%). This is particularly the case for the Dutch class "ample sufficient" and for German soils without $CaCO_3$ (Fig. 4.12: upper dashed black and green lines).
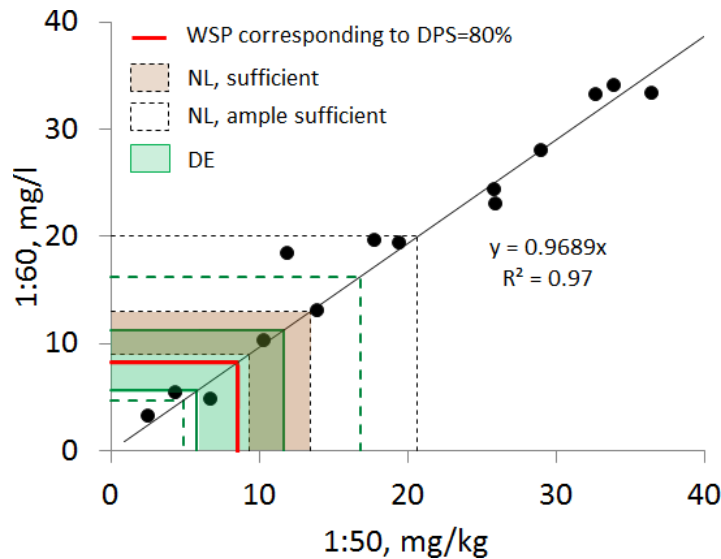
Figure 4.12: Water-soluble P (WSP) as agri-environmental soil P test: Comparison of threshold WSP value indicating high risk of P losses (WSP = 8.5 mg/kg, corresponding to DPS = 80%) with P levels considered sufficient for agronomic production in the Netherlands (van Dijk 1999) and recommended P levels in Germany (DE, Taube et al. 2015): PCAL values were transformed into WSP values by the PTF (solid green lines) and the equations determined for soils with $CaCO_3$ /without $CaCO_3$ (lower and upper dashed green lines) of this study.

During the last few decades, a PCAL level of about 4.0 mg P/100 g of soil was considered sufficient for agricultural production based on the analyses of PCAL-yield correlations in German field trials (Köster and Schachtschabel 1983, Hege et al. 2008, Römer 2009, Kuchenbuch and Buczko 2011). Transforming this PCAL value using our PTF results in risk parameters of P losses (PCAL = 4.0 mg P/100 g corresponds to WSP = 7.7 mg/kg, DPS = 79%) below the critical threshold of high risk of dissolved P losses (WSP = 8.5 mg/kg, DPS = 80%). However, using the equations for soils with/without $CaCO_3$ the resulting WSP range is 6.5 to 11.2 mg/kg which is partly conflicting with environmental goals.

Recommendations and perspectives for risk assessment and modelling of diffuse P losses

Critical source areas of diffuse P losses are determined by several factors, including hydraulic connectivity to water bodies and soil parameters that define the risk of P loss from soil to water. Consequently, the high risk of P losses from soil to water determined for German agricultural soils in this study does not automatically indicate critical P concentrations in water bodies and concomitant eutrophication processes. Nutrient emission models (e.g. Schoumans et al. 2009, Neitsch et al. 2011, Venohr et al. 2011) are useful tools for determining the risk of eutrophication by connecting soil P data with hydrological data to identify hotspots of diffuse P emissions. We recommend the integration of PCAL monitoring

data and their associated risk parameters (WSP, DPS and EPC0, as determined in this study) into nutrient emission models to improve these models' prediction accuracy. This would allow for better identification of critical source areas of diffuse P losses, through which best management practices (e.g. Schoumans et al. 2014) could be implemented most cost-efficiently to reduce diffuse P losses and secure high surface water quality, e.g., in the frame of the Water Framework Directive.

4.4 Conclusions

Arable soils in Germany are in many areas highly saturated with P, corresponding to a high risk of P loss. Compliance with the recent suggestion to lower recommended PCAL values is crucial to reducing the high risk of dissolved P losses from soil to water. A combination of soil P data with hydrological parameters is needed in the assessment of the share of agricultural P in P loads in surface water of Germany. The soil type-dependency of traditional soil test P methods such as CAL or Olsen can be considered a major obstacle for identifying critical source areas of P losses based on DPS, as shown in our study. The use of WSP as an agri-environmental soil P test may help researchers and stakeholders overcome this difficulty in the future and concomitantly define optimal P levels in soils for agricultural production while also considering the risk of P losses. An intensive discussion among experts in the fields of soil and water chemistry, ecology, plant physiology and agriculture would be necessary to define synchronized WSP values across Europe that will secure agricultural needs, prevent eutrophication of surface waters, and support the efficient use of the limited resource P.

Sources

Soil phosphorus data provided by authorities of federal states of Germany with year of delivery:

Brandenburg: Projekt "Boden-Dauerbeobachtung im Land Brandenburg", Landesamt für Umwelt, Gesundheit und Verbraucherschutz Brandenburg, Referat Altlasten, Bodenschutz (Dr. Joachim Tessmann) (2015).

Baden-Württemberg: Landwirtschaftliches Technologiezentrum Augustenberg (2014).

Bayern: Bayerische Landesanstalt für Landwirtschaft (2014).

Hessen: Landesbetrieb Landwirtschaft Hessen (2015).

Mecklenburg-Vorpommern: Landesamt für Umwelt, Naturschutz und Geologie Mecklenburg-Vorpommern (2015).

Niedersachsen: Daten aus Bodendauerbeobachtungsflächen © Landesamt für Bergbau, Energie und Geologie, Hannover (2015).

Nordrhein-Westfalen: Landesamt für Natur, Umwelt und Verbraucherschutz © Land NRW, Recklinghausen (2015).

Rheinland-Pfalz/ Saarland: Dienstleistungszentrum Ländlicher Raum Rheinhessen-Nahe-Hunsrück/Fritsch (2015).

Schleswig-Holstein: Landesamt für Landwirtschaft, Umwelt und ländliche Räume des Landes Schleswig-Holstein (2015).

Sachsen: Sächsisches Landesamt für Umwelt, Landwirtschaft und Geologie (2015).

Sachsen-Anhalt: Ergebnisse der Standardbodenuntersuchung 2005-2007, Landesanstalt für Landwirtschaft, Forsten und Gartenbau Sachsen-Anhalt (2015).

Thüringen: Thüringer Landesanstalt für Landwirtschaft (2013).

5 Discussion

In the previous chapters the core results of the thesis were presented. In the following part these chapters are discussed together and additional results of the thesis are included, complementing and linking the different chapters.

5.1 The risk of P losses in the São Francisco catchment derived from soil and surface runoff analyses

5.1.1 Relationship between water-soluble phosphorus and degree of P saturation

The soil type-independent correlation between water-soluble phosphorus (WSP) and degree of phosphorus saturation (DPS) was shown to be valid for the investigated Oxisols and Entisols of the Rio São Francisco (RSF) catchment in Brazil. This further confirms the applicability of the WSP-DPS approach to all soil types, and underlines the suitability of this approach for a fast and cheap risk assessment of diffuse P losses from agricultural areas worldwide.

5.1.2 Soil chemistry and soil mineralogy

Phosphorus sorption capacities (PSC) in the investigated Entisols were about half the PSC of the Oxisols. Thus, the Entisols reach critical DPS values (>80%) at lower P accumulations (i.e. total phosphorus (TP) contents). TP contents as determined for the investigated Oxisols would lead to DPS values > 80% in most of the investigated Entisols. Considering the reported increases in agricultural areas as well as fertilizer use and TP accumulations in the RSF catchment and Brazil (Koch et al. 2015, Dias et al. 2016) special focus should be given to areas with soils having low PSCs. In these areas high P accumulations have to be avoided in order to prevent high DPS values leading to high risks of dissolved P losses.

The exceptionally high PSC of the Oxisols could be explained by: 1) the analyzed high contents of Fe and Al, which are known to be decisive for sorption of P in acidic soils (Van der Zee et al. 1987, Blume et al. 2009), 2) the occurrence of Fe and Al as Fe-and Al-hydroxides identified by FTIR analyses of soils with high affinities to sorb P (Börling 2003, Melo et al. 2015), and 3) the reaction with P identified by FTIR analyses of fertilizer grains which indicated the building of crandallite, a hydrated hydroxy phosphate [$CaAl_3(PO_4)_2(OH)_5 \cdot H_2O$] with PO_4^{3-}/ HPO_4^{2-} groups in its structure. The fact that crandallite was built in fertilizer grains of superphosphate, originally being composed of $Ca_2(H_2PO_4)$ and $CaSO_4$ suggests a high reactivity between the Al-hydroxides of the soils and the $H_2PO_4^-$ ions under the given pH conditions. Crandallite is yet more stable than ordinary Al-phosphates without OH^- groups in their structure, and thus has a lower P solubility (Savenko et al. 2005). Crandallite was reported to turn into more stable forms at excessive amounts of Ca by further replacement of Al in weakly basic to weakly acid medium (Savenko 2005, Savenko et al. 2005). Assuming that crandallite is a major phosphate occurring in Oxisols, the commonly used applications of huge amounts of $CaCO_3$ (Yamada 2005, Lopes et al. 2012) might be counterproductive to improve the P availability to plants. Here further research is necessary.

In some of the Entisols two minerals have been identified that are relevant for the risk of P losses: palygorskite and sepiolite. These Mg-containing clay minerals have been reported to reduce P sorption and enhance P solubility in arid soils under irrigation practices

(Shariatmadari and Mermut 1999, Neaman and Singer 2004) and thus enhance the risk of P losses. Consequently, in particular for semi-arid climates, increased risks of P losses from Entisols compared to Oxisols might additionally be amplified by mineralogical soil properties. Apparently, palygorskite and sepiolite have not been identified yet in the investigated region of the Itaparica reservoir (Coelho and Santos 2007). Palygorskite has been reported to have negative consequences for agriculture, such as a reduction of water permeability through soil pore clogging and building of palycretes (Neaman and Singer 2004). Palycretes are duripans, i.e. cemented soil horizons (Soil Survey staff 1999) in which palygorskite is the dominant cementing material that seriously impedes plant growth when occurring close to the soil surface (Neaman and Singer 2004). Further analyses are necessary to confirm the occurrence of both minerals by X-ray diffraction (XRD) analysis.

5.1.3 Superficial fertilizer application and dissolved P losses in surface runoff

Whereas most investigated soil samples (Oxisols and Entisols) revealed relatively low DPS values, superficial fertilizing led to high risks of P losses as indicated by measured WSP values. In planting rows, where fertilizer was applied superficially, high WSP values (WSP > 30 mg/kg) were measured, whereas values remained low (WSP < 5 mg/kg) between the rows. The spatial heterogeneity of high and low risks of P losses in the agricultural field raised the question of the effects of such a distribution on dissolved P and particulate P concentrations in the surface runoff.

Whereas different studies have investigated average P losses over whole surface runoff events under standardized plot-scale conditions in Brazil (e.g. Bertol et al. 2007, Mori et al. 2009, da Silva et al. 2012), no study has 1) reported P concentrations in surface runoff under natural rainfall at the slope toes of the fields of Oxisols, i.e. in surface runoff water, which actually leaves the agricultural areas in the direction of water bodies, or 2) related the total suspended matter concentrations in runoff to particulate and dissolved P concentrations measured in the time course of single runoff events. Both aspects have been considered in the surface runoff studies of this thesis.

In Chapter 3, the minimum, maximum and mean values of total suspended P (TSP) and total dissolved P (TDP) concentrations gathered during the surface runoff events were discussed. In the following, the results obtained from the observed runoff events at the cabbage and mixed culture sites are compared and evaluated. The observed concentrations at the tangerine culture site were excluded from the regression analyses shown in Fig. 5.2, as the presence of small erosion gullies caused conditions that were not comparable to those found on the cabbage and mixed culture sites.

High dissolved P concentrations of > 1 mg/l, as observed in first surface runoff events immediately after inorganic surface fertilizer application (Bertol et al. 2007), were not observed. However, the study by Bertol et al. (2007) reported a strong decrease in dissolved P concentrations from > 1 mg/l to a range of 0.25 to 0.35 mg/l in subsequent surface runoff events. This range is similar to that observed in the surface runoff study, i.e. between 0.07 mg/l and 0.40 mg/l (Chapter 3).

Studies on soils of temperate regions of the USA and Finland reported the adequateness of WSP extractions with water/soil ratios (w/s ratio) of 40:1 and 100:1 to 250:1 to estimate dissolved P concentrations in surface runoff (Sharpley et al. 1981a, Yli-Halla et al. 1995).

Similarly, the observed range in dissolved P concentrations in surface runoff in this thesis (0.07 mg/l to 0.40 mg/l) could be estimated by the WSP method (1g soil extracted with 50ml water equaling w/s ratio = 50:1). However, this was only possible when WSP extractions of both soil samples with superficial fertilizer (median of WSP = 19.9 mg/kg corresponding to 0.40 mg/l, Table 5.1) and without superficial fertilizer (median of WSP = 1.8 mg/kg corresponding to 0.04 mg/l, Table 5.1) were considered.

The investigation of WSP, including soil samples both with and without superficial fertilizer of the surface relevant soil layer of 0-4 cm, offers a new approach for estimating the range of dissolved P concentrations in surface runoff of superficially fertilized agricultural fields of Oxisols with a simple laboratory method. A testing of this approach on other soil types is recommended.

Table 5.1: Median of measured WSP of all soil samples of MG of the topsoil layer (0-4 cm) with and without superficial fertilizer application (Chapter 2 and 3): values in mg/kg and in mg/l are shown (conversion factor between mg/kg and mg/l = 50); min/max = minimum and maximum values, n = number of samples;*below detection limit.

Soil samples, 0-4 cm	n	WSP, mg/kg			WSP, mg/l		
		MIN	MAX	MEDIAN	MIN	MAX	MEDIAN
Superficial fertilizer	13	6.3	47.9	19.9	0.13	0.96	0.40
Without superficial fertilizer	26	<0.25*	13.1	1.8	<0.005*	0.26	0.04

Bertol et al. (2007) reported a strong decrease in dissolved P concentrations between the first and the second surface runoff event on a superficially fertilized soybean field. Similarly, a strong decrease in dissolved P concentration was observed between the first measurement at the beginning of the surface runoff event and the second measurement after 10 min at the mixed culture site on the 31st of March 2014 (Fig. 5.1 A).
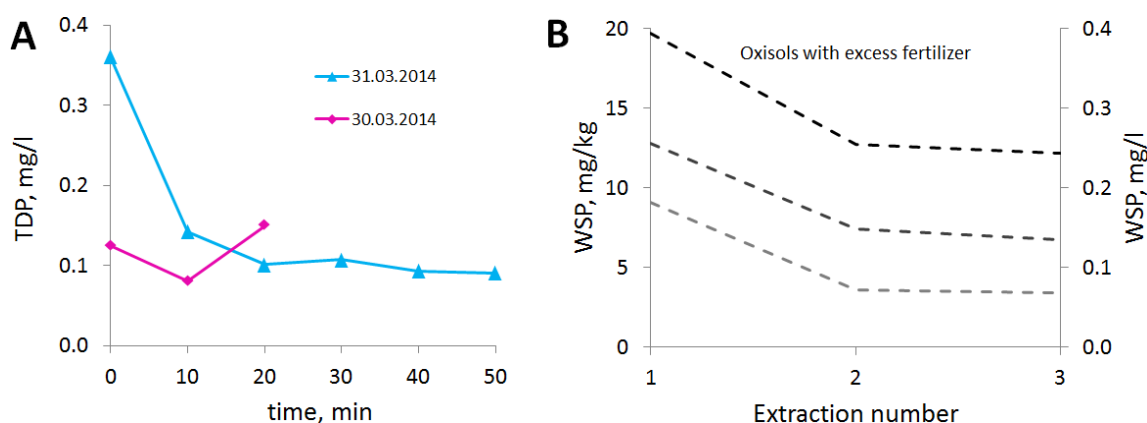
Figure 5.1: A) Decline of dissolved P concentrations (TDP) in surface runoff observed on the 30th/ 31st of March 2014 in comparison to B) consecutive WSP extractions of soil samples: TDP = total dissolved phosphorus, WSP = water-soluble phosphorus.

At the beginning of the surface runoff event, the dissolved P concentration in surface runoff (TDP = 0.36 mg/l) corresponded to the median of WSP of soil samples with superficial fertilizer grains found in planting rows (0.4 mg/l, Table 5.1), whereas in subsequent extractions the WSP values rather corresponded to the range of measured WSP values of soil samples without superficial fertilizer grains (0.01 mg/l to 0.26 mg/l, Table 5.1) and WSP values of consecutive extractions 2 and 3 of soil samples with excess fertilizer (Fig. 5.1 A, B).

Apparently, excess fertilizer from superficial fertilizer application had a major effect on dissolved P concentrations at the beginning of the surface runoff event of 31st of March 2014 (first flush effect). With increasing time of the surface runoff event, the dissolved P concentrations were apparently rather determined by the DPS of the soils reflected by the lower WSP values of extraction number 2 and 3 and WSP of soil samples without superficial fertilizer (Fig. 5.1 A, B, see also explanations Chapter 2: Fig. 2.10 A, B). This finding indicates that consecutive extractions of WSP intentionally including soil samples with superficial fertilizer are a new simple approach capable of assessing the temporal variation of dissolved P concentrations in surface runoff of superficially fertilized fields. However, a first flush effect and a subsequent constant decline of dissolved P concentrations were not observed in the surface runoff event on the same agricultural field one day earlier, on the 30th of March 2014. Consequently, this approach has to be tested in a study with a higher number of replicates than those delivered in this study.

Sharpley et al. (1981b) and Barbosa et al. (2009) reported significant negative correlations between total suspended matter (TSM) and dissolved P concentrations in surface runoff with low TSM concentrations (range: ca. 0.1-2.5 g/l). Our surface runoff study with much higher TSM concentrations neither revealed significant correlations between TSM and dissolved P concentrations (TDP) nor between TSM and particulate P concentrations (TSP) (Fig. 5.2 B, D). However, concentrations of both TSP and TDP per mass of TSM (TSP$_{mass}$ and TDP$_{mass}$, equation 5.1) were highly significantly and negatively correlated with TSM concentrations (Fig. 5.2 A, C, $p \leq 0.01$).

$$(5.1) \qquad TSP_{mass} = (TSP/TSM) \times 1000; \; TDP_{mass} = (TDP/TSM) \times 1000;$$

Units: TSP$_{mass}$ and TDP$_{mass}$ in mg/kg, TSP and TDP in mg/l, TSM in g/l
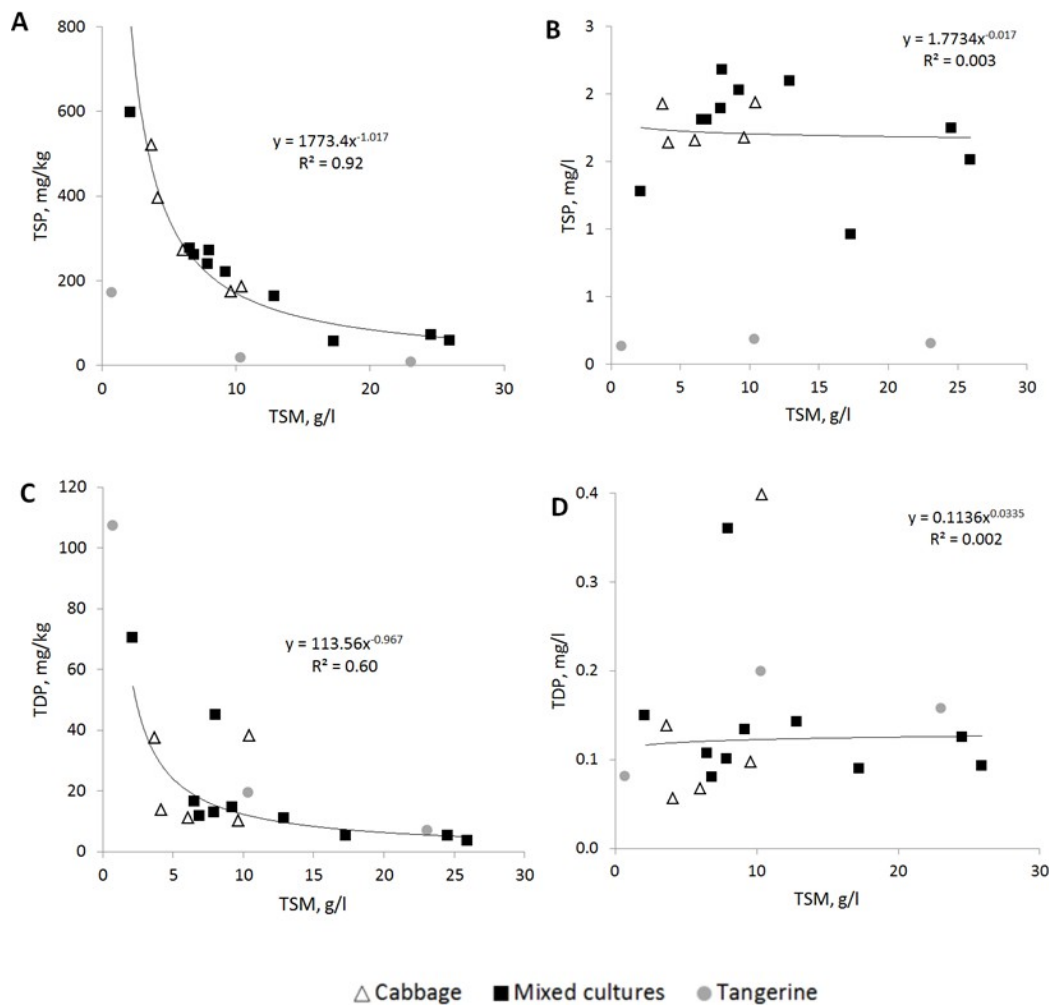
Figure 5.2: Relationship between particulate P (TSP), dissolved P (TDP) concentrations per mass (A, C) and per volume (B, D) and suspended matter concentrations (TSM) in surface runoff.

As found through FTIR analyses of the investigated Oxisols, the fine particles contained a large amount of Fe and Al-hydroxides. During filtration these particles partly passed through 0.45 μm and occasionally even- through 0.2 μm filters, which is proof of their large surfaces, enhancing the ability to sorb and even bind P (own observations). At lowest TSM concentrations, the share of fine particles (and thus also Fe-and Al-hydroxides) enriched in P is the highest (Sharpley 1980, Quinton et al. 2001, Barbosa et al. 2009). Thus, highest TSP_{mass} and TDP_{mass} values at lowest TSM values are explainable. The sorption of dissolved P from superficial fertilizer (and from other sources such as plant residues) to Fe and Al-hydroxides in surface runoff might in addition lead to a pronounced transport of P in the particulate phase. Here the FTIR analyses of inorganic fertilizer grains from Oxisol provided more insight. A formation of crandallite with a poor degree of crystallinity was indicated. This suggested that the water-soluble $Ca(H_2PO_4)_2$ of "superphosphate" has reacted according to the soil specific conditions, i.e. low pH values and the occurrence of reactive Fe- and Al-hydroxides, resulting in the formation of the soil specific hydrated Ca-Al-hydroxy phosphate crandallite $[CaAl_3(PO_4)_2(OH)_5 \cdot H_2O]$. First steps of such a reaction are also likely to happen in surface runoff events, and might be the underlying chemical process that leads to relatively low dissolved P concentrations in surface runoff and is a second explanation for the highest TSP_{mass} values at lowest TSM concentrations. Further soil analyses would be necessary to also

assess the influence of the soil to water ratio in surface runoff on the relationships shown in Fig. 5.2.

The relationships between TSM and TSP_{mass} as well as TDP_{mass} lead to the following conclusions regarding variations in surface runoff events of superficially fertilized Oxisols: 1) P exports per mass-unit of exported TSM are highly variable in single events (a variation of factor 10 and 20 for particulate and dissolved P exports, respectively); 2) P exports per mass of TSM (mg/kg) are significantly correlated to TSM concentrations in surface runoff.

Whereas previous surface runoff studies on Brazilian Oxisols mainly focused on artificial rainfalls of very high intensities > 60 mm/h on plot scales, this study reported P exports under natural rainfall of moderate of about 20-40 mm/h in surface runoff at the slope toes of agricultural fields. It was assessed that per mass of suspended sediment, high amounts of P are exported at surface runoff events with low TSM values (reflecting surface runoff at moderate rainfall intensities). This impacts the potential P desorption from particles after entering surface waters and thus the potential contribution to eutrophication processes (Correll 1998).

Summarizing, the detailed chemical analyses of the Oxisols and Entisols delivered important insights into the risk of dissolved P losses from contrasting soil types of the São Francisco catchment. In the Entisols a higher risk of dissolved P losses could be identified due to: 1) lower P sorption capacities, and 2) smaller reactive surfaces of the soil particles dominated by quartz, calcite and kaolinite/montmorillonite in comparison to the Oxisols with significant amounts of Fe and Al-hydroxides. Additionally, the indicated occurrence of sepiolite and palygorskite in some of the Entisol soil samples enhances the risk of P losses. Consequently, dissolved P concentrations in surface runoff of Entisols with superficial fertilizer application may be substantially higher than under comparable conditions on Oxisols.

5.2 Risks of P losses in the São Francisco catchment and Germany derived from monitoring data

5.2.1 Pedotransfer functions to estimate the risk of P losses in Brazil and Germany

Highly significant correlations were found between: 1) WSP and phosphorus determined by the method of Mehlich-1 (M1P) as well as 2) WSP and phosphorus determined by the method of calcium-acetate-lactate (PCAL). The linear regression equations of the PTFs resulted in determination coefficients of $R^2 \geq 0.80$. A $R^2 \geq 0.80$ justified the applicability of PTFs in various previous studies (Schick et al. 2013, Schnug and De Kok 2016). However, the prediction accuracy of the determined PTFs for both M1 and CAL is limited for soils with significant amounts of $CaCO_3$. In the following the underlying mechanisms are described and consequences for risk assessment of P losses by monitoring data are discussed.

As stated in Chapter 3, more analyses are needed to better understand the M1P-WSP relationship, especially on soils with $CaCO_3$. Mehlich-1 does apparently not correctly reflect soil P levels in soils fertilized and limed at the same time, as shown by Arruda et al. (2015). This is explainable by a buffering of acid extractor M1, and might have a significant effect on the assessment of P loss risks from Brazilian soils, which are commonly limed (Ribeiro et al. 1999, Yamada 2005). In these soils, the risk assessment based on M1P would drastically underestimate DPS values and thus the risk of diffuse P losses. In contrast, other studies

reported an overestimation of plant-available P on calcareous soils due to preferential dissolution of Ca associated P by acid extractor Mehlich-1 (Kuo 1996, Pierzynski 2000) leading to the opposite effect, i.e. an overestimation of M1P in these soils.

Thus, further research is needed to determine a correction factor for the acid extractor on calcareous and limed soils, which would allow including monitoring data of M1P in risk assessments of P losses. Beyond $CaCO_3$, other soil parameters possibly leading to deviations from the determined PTF between M1P and WSP are high contents of organic matter, and different phosphates that occur naturally in Brazilian soils.

The anion exchange resin method (van Raij et al. 1986, Bissani et al. 2002) is also in use in Brazil to estimate plant-available P, and seems to be more adequate to estimate soil P levels in limed and calcareous soils (Arruda et al. 2015). The creation of a PTF between anion exchange resin P and WSP, especially on $CaCO_3$ rich soils is required in order to allow for an inclusion of more Brazilian soil P monitoring data in the WSP-DPS risk assessment.

In the investigated German soils, at the same WSP values, $CaCO_3$ containing soils showed higher PCAL values than soils without $CaCO_3$. This is a consequence of preferential dissolution of calcium phosphates at acid pH values (pH of CAL extraction solution = 4.1). Under these conditions, calcium phosphates are not stable and have a solubility that is two to five dimensions higher than those of Fe-and Al-bound phosphates (Fig. 5.3, Lindsay 1979, Lindsay et al. 1989). Additionally, the anion exchange and complexation mechanisms of acetate and lactate increase the dissolution of Ca-bound P (Kamprath and Watson 1980). As discussed in Chapter 4, the soil type-dependency of the WSP-CAL correlation is crucial for the prediction accuracy of risk parameter WSP and associated parameters DPS/EPC0 from PCAL monitoring data.
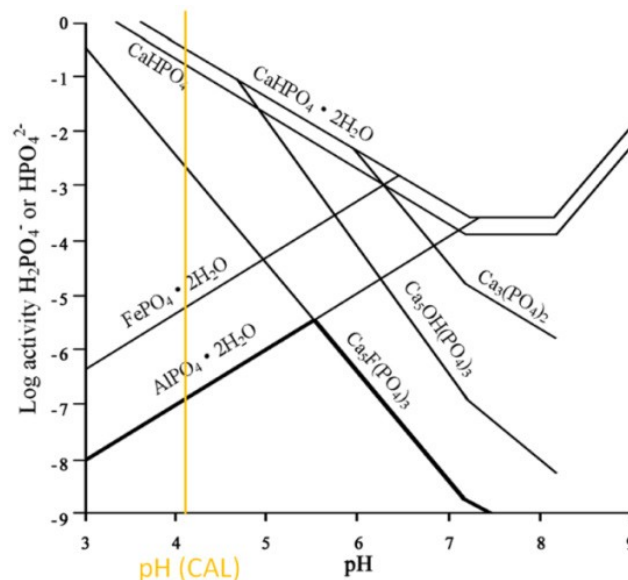
Figure 5.3: Solubility of phosphate minerals in dependency of the pH value: Solubility of Ca-phosphates at the pH value of the CAL extraction solution (pH = 4.1) is 3 to 5 dimensions higher than for Al and Fe-bound phosphates. Source: Liu et al. (2008) based on Schlesinger (1991)/ Lindsay and Vlek (1977) – modified (reprinted with permission from John Wiley and Sons, Elsevier).

In Germany, for soils at pH ≥ 7.1, measuring pH values of the CAL filtrate after extraction is recommended (VDLUFA 2002). If the original pH value of 4.1 of the CAL solution increases to values between 4.3 and 5.6, the measured PCAL values have to be corrected according to equation 5.2 (Zorn and Krause 1999) :

$$(5.2) \qquad \text{PCAL}_{corrected} = \text{PCAL}_{measured} \times [1 + 0.83 \times (\text{pH}_{filtrate} - 4.1)]$$

In CAL filtrates pH values were measured after extraction for 24 of the 28 soils containing significant amounts of $CaCO_3$. In 15 of these 24 samples, the pH value was ≥ 4.3 (median = 4.4, min = 4.3, max = 5.0). Fig. 5.4 A, B shows the corrected PCAL values according to equation 4, added to the PCAL-WSP relationship of Chapter 4 (marked in red).
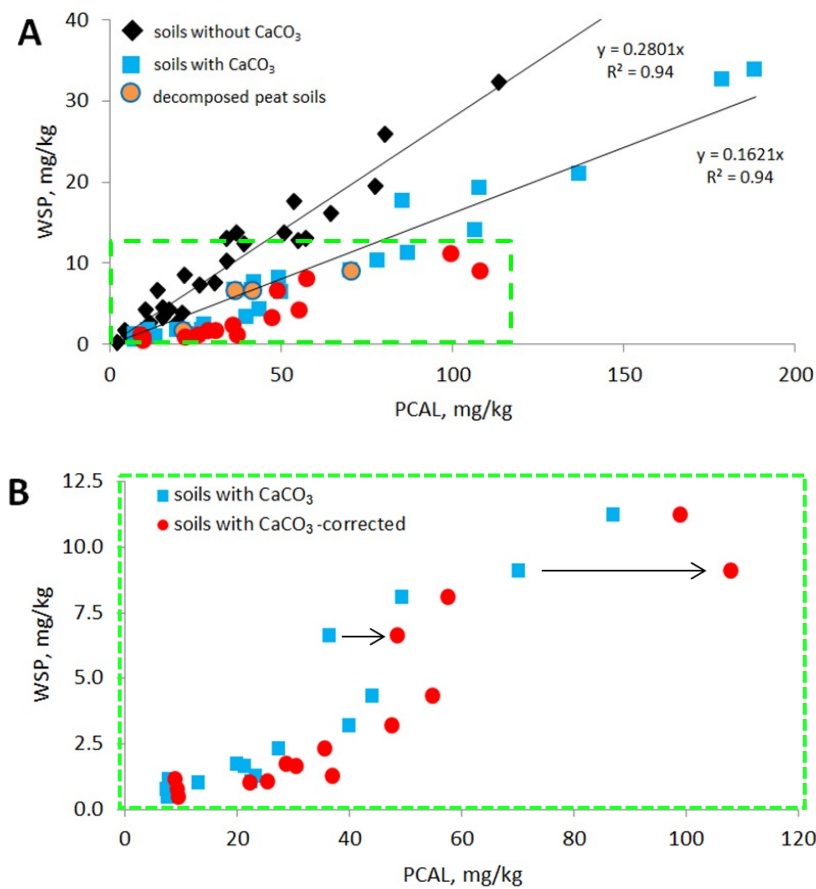
Figure 5.4: Soil type dependency of the CAL method: A) effect of correction of PCAL values according to elevation of pH in the extraction solution, corrected PCAL values added in red, and B) measured/ corrected PCAL values from A.

The corrected PCAL values were up to 71% greater than the measured ones. The correction of PCAL values by equation 4 strengthens the discrepancies between the two different soil groups, i.e. an overestimation of PCAL values on $CaCO_3$ containing soils. Thus, we used uncorrected monitoring data where possible for calculating risk parameters of P losses WSP, DPS and EPC0.

5.2.2 Derived risks of P losses from monitoring data and recommended P levels in soils

The risk of P losses derived from monitoring data was low for Brazilian soils (DPS = 54 ± 22% arithmetic mean and standard deviation, n = 1,827) and high for German soils (DPS = 84 ± 7% arithmetic mean and standard deviation, n = 337,510) when compared to the threshold of high risk of P losses (DPS = 80%). This difference is explainable by the shorter duration of intensive Brazilian agricultural production and concomitant lower P accumulations in the soils in comparison to Germany (Sattari et al. 2012, Roy et al. 2016). Apparently, the high P fertilizer applications reported for Minas Gerais (ANA 2013) have not yet resulted in high risks of P losses. This was also confirmed by measured DPS values in the investigation area (DPS: MEDIAN = 62.6%; min = 31.3%; max = 78.5%, Table 2.1). The mean of derived DPS values from all M1P monitoring data best corresponded to M1P levels recommended for annual and perennial groups on clayey soils in Minas Gerais (Ribeiro et al. 1999, Figure 5.5). This recommended P level was identified to be below the threshold of elevated and high risks of P losses of 70 and 80%, respectively. In contrast, recommended P levels for vegetables on sandy soils were above the critical threshold, reaching values of up to 90% and thus are conflicting with environmental goals.

At single locations Brazilian monitoring data indicated high risk of P losses (Fig. 5.5, Chapter 3 - Fig. 3.3). Apparently, intensive agricultural production as reported for the municipality of Guanambi has already led to hot spots of high P saturations, comparable to those found for German agricultural soils (Fig. 5.5, Chapter 3 - Fig. 3.3). In this context the strong sensitivity of soil extraction methodologies like M1P or WSP to superficial fertilizer has again to be mentioned (see also discussion Chapter 2). This suggests that the high DPS values found for some soil samples might also result from superficial fertilizer in soil samples that were taken unintentionally by the farmers, leading to exceptionally high M1P values and thus derived DPS values. As described in Chapter 4, exceptionally high PCAL values derived from German monitoring data (>265 mg/kg; 2% of monitoring data) were excluded. This was reasonable, as such values result in WSP values > 50 mg/kg which were not measured on agricultural soils of former studies investigating more than 400 soil samples (Pöthig et al. 2010). For Brazil, the reduced availability of samples for individual soil types and thus measured WSP and DPS values did not allow the exclusion of exceptionally high M1P values and outliers from the data set. An increased monitoring of DPS is highly recommended in particular in regions of Brazil that are in intensive agricultural use. Considering the low number of monitoring data, which were only available for Minas Gerais and Bahia, the presented analyses can only be considered a first estimate of DPS values in the RSF catchment. The variability of estimated DPS values within and between municipalities shows that a high spatial resolution of monitoring data is needed for a reliable risk assessment of P losses.
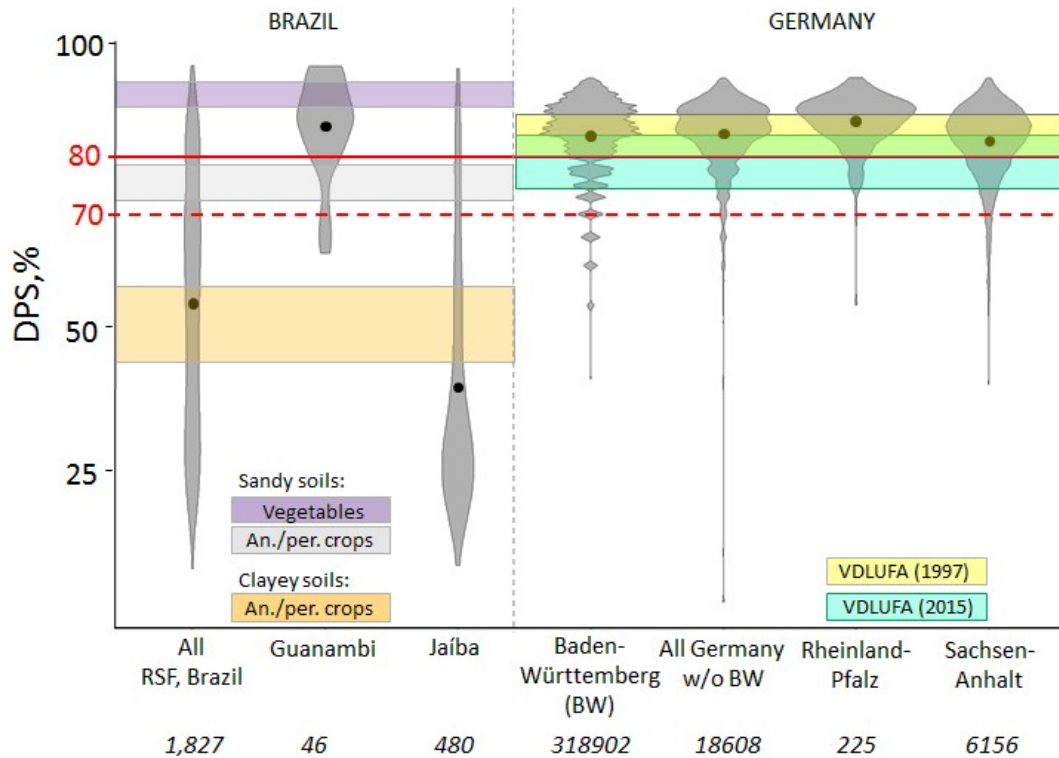
Figure 5.5: DPS estimated from monitoring data and resulting risks of recommended P levels in soils of Brazil and Germany: Sources of monitoring data: see Chapter 3 and 4; fertilizer recommendations: Brazil-Minas Gerais: Ribeiro et al. (1999), Germany: VDLUFA (1997): Kerschberger et al. (1997); VDLUFA (2015): Taube et al. (2015); number of monitoring values is given in the x-axis below municipality and federal state names; An./per. crops = annual/perennial crops; RSF = River São Francisco catchment; BW = Baden-Württemberg; w/o = without.

In Germany, the high derived DPS values can be explained by the corresponding high P accumulations reported for German soils (Nieder et al. 2010). Thus, the P accumulation has led to high risks of dissolved P losses. Mean DPS values in agricultural soils estimated for German federal states agreed with P levels recommended before 2015 (Kerschberger et al. 1997) which are in conflict with the environmental protection threshold of DPS < 80% (Figure 5.5). A reduction of recommended P levels (Taube et al. 2015) was introduced to lower the risk of P losses from soils, but they still exceed the P levels needed to ensure minimal environmental impact (DPS < 70%).

This thesis did not investigate whether high DPS values in Germany originate from either: 1) farmers following fertilizing recommendations of P, 2) locally concentrated manure applications in regions of high livestock densities where produced manure by far exceeds the required amount of fertilizer for plant growth, but is commonly still applied on adjacent agricultural areas, or 3) organic fertilizer application of manure based on nitrogen (N) needs of the soils. In the manure of cattle, pigs and poultry the N:P ratio varies between 2:1 to 6:1 and is thus lower than the N:P ratio targeted in soil, i.e. 7:1 to 11:1 (Smith et al. 1998). Consequently, more P than necessary is commonly spread on the fields. Most probably all above-mentioned factors contribute to the high DPS values in German arable soils, but to a different extent in different parts of the country.

5.3 WSP as agri-environmental soil P test in Germany and Europe

Over the last two decades, studies which compared the target P levels in different European countries, reported big differences, even for the same soil P test methods in similar soil-crop systems (Tunney et al. 1997, Neyroud and Lischer 2003, Jordan-Meille et al. 2012, Tóth et al. 2014). The concomitant risk of P losses resulting from recommended P levels has been assessed by using various parameters, e.g. DPS, P concentrations in leachates, WSP or soil P buffering power (Celardin 2003, Glaesner et al. 2013, Renneson et al. 2015). In these studies some conflicts between recommended P levels and environmental protection goals have been identified.

Not only the target P levels in soils, but also the adequacy of extraction methods to estimate plant-available P has been widely discussed. As stated in Chapter 3, based on field studies in Germany and Austria, a PCAL level in soils of about 4.0 mg P/100g soil was often identified to be sufficient for agricultural production (Köster and Schachtschabel 1983, Hege et al. 2008, Römer 2009, Kuchenbuch and Buczko 2011). Applying the PTF, this equals average WSP and DPS values of = 7.7 mg/kg and DPS = 80%, respectively. However, a PCAL value of 4.0 mg P/100g, depending on the $CaCO_3$ content (see Chapter 3), results in WSP values between 6.5 and 11.2 mg/kg, partially conflicting with environmental goals when applying the correlations between PCAL and WSP for soils with and without $CaCO_3$. Apparently, no available study in Europe recommended target soil P levels equal or lower than WSP = 4.1 mg/kg or DPS = 70%, which would be needed to minimize P loss risks to surface waters. This result confirms former studies from the Netherlands, which conclude that inevitable P losses in soils have to be accepted when an optimal agronomic production is targeted (Noordwijk et al. 1990, Van der Molen et al. 1998).

Munk (1985) and Munk et al. (2005) determined a PCAL range of 7.4 to 11.7mg P/100g and 8.0 to 10.0mg/P 100g, respectively, vastly exceeding the 4.0mg P/100g mentioned before. Both studies focused on neutral to basic soils, including sites with soil pH values > 7 and high amounts of $CaCO_3$. Additionally, Munk (1985) used basic slag from iron ore melting (so- called "Thomasmehl"), which is a calcium silico phosphate, i.e. a Ca-bound phosphate that contains large amounts of $CaCO_3$. Besides P, Thomasmehl contains other nutrients (Mn, Fe or Mg) and elevates the soil pH. Both effects are known to be beneficial for plant growth (Blume et al. 2009). Thus, the observed yield increases even at higher PCAL values were assumed to be a result of these effects, and not of the higher P level (Kuchenbuch and Buczko 2011). The results of this thesis suggest another explanation, based on the different calculated EPC0 values from PCAL values for soils with and without $CaCO_3$.

EPC0 is a decisive soil parameter for P uptake by plants (Moody et al. 1988). Figure 5.6 shows derived EPC0 values from PCAL data by calculating WSP values from the relationships for soils without $CaCO_3$ (WSP = 0.2801 × PCAL) and with $CaCO_3$ (WSP = 0.1621 × PCAL) and subsequently calculating EPC0 values by the relationship between WSP and EPC0 (EPC0 = 0.0018 WSP^2 + 5 × 10^{-6} WSP). The derived EPC0 values for the studies identifying a PCAL value of about 4.0 mg P/100g soil are almost identical to the EPC0 values derived for the studies on rather alkaline and calcareous soils of 7.4 to 11.7 mg P/100g. Thus, the apparent differences in P levels needed to secure optimal agronomic production are the result of the

soil type-dependency of the CAL method. This supports the findings that "mild extractants" such as WSP are better indicators than "harsher extractants" like CAL, Olsen and others for estimating plant-available P when a wide range of different soil types is investigated (van der Paauw 1971, van Rotterdam-Los 2010, Yli-Halla et al. 2016).
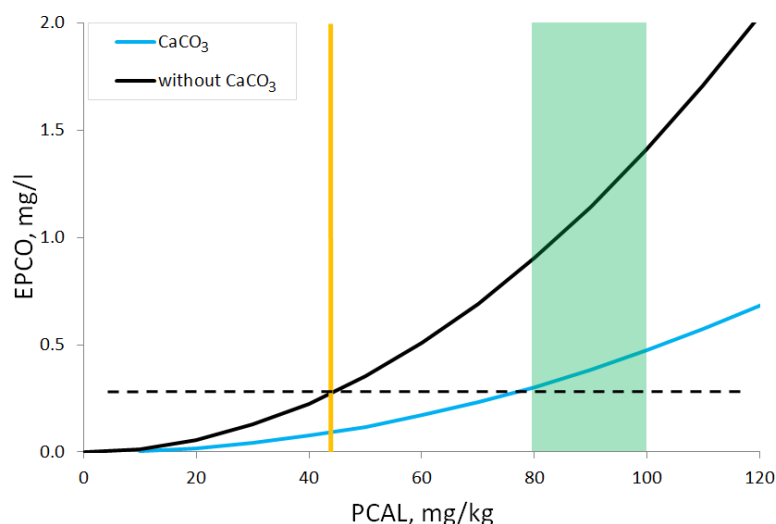
Figure 5.6: Average EPC0 values estimated from PCAL values for soils with and without CaCO3 in comparison to defined PCAL values needed to secure an optimal agricultural production by Munk et al. (2005) in green and Kuchenbuch and Buczko (2011) as orange line.

DPS, which is labor intensive when determined directly by sorption isotherms and total phosphorus analyses, can also be derived from WSP through a soil type-independent correlation. Thus, WSP provides the option to jointly estimate plant-available P (Sissingh 1971) and the risk of P losses (Pöthig et al. 2010), as both methods are related in a soil type-independent correlation (Chapter 4: WSP (Sissingh 1971) = $0.9689 \times$ WSP (Pöthig et al. 2010), $R^2 = 0.97$). Consequently, WSP is suggested as an agri-environmental soil P test for future agronomical and environmental sustainable soil P management in Europe.

However, limitations have often been described of WSP as a standard methodology to estimate plant-available P. For example, low P concentrations in the extraction solution of P poor soils are difficult to measure, and the use of expensive filters is necessary because of the dispersion of soil particles due to low ionic strength (Ehlert et al. 2003, Reijneveld et al. 2014). However, from a scientific rather than an economic point of view, analytical problems can probably be solved. Moreover, the soil type-independency of the method is a decisive factor, making WSP preferable over other soil extractants such as CAL or Olsen for a harmonization of soil P levels in Europe and a systematic, trans-border evaluation of the risk of P losses. The establishment of a soil P database of WSP, like the one established for Olsen P in the LUCAS topsoil database (Tóth et al. 2013, Tóth et al. 2014), could be a crucial step toward a more sustainable soil P management in Europe.

Besides WSP, $CaCl_2$ is another "mild extractant" that provides good predictions of immediately available P for plants across different soil types (van Rotterdam-Los 2010). $CaCl_2$ has been increasingly investigated and implemented in the Netherlands in recent years, partly substituting the WSP method of Sissingh (1971). In a study focusing on a better estimation of plant-available P by methods which are currently in use in Europe, $CaCl_2$ was

proposed as an additional soil P test (Reijneveld et al. 2014). For a wide applicability of the WSP-DPS risk assessment approach the correlation between soil P values determined by $CaCl_2$ and WSP was tested. $CaCl_2$ values were taken from the first value of the sorption isotherms ($CaCl_2$ without P, Chapter 2), corresponding to the $CaCl_2$ method of Houba et al. (2000) and correlated to the corresponding WSP values determined on agricultural soils of Brazil (see Chapter 2, 3) and Germany (unpublished data by R. Pöthig), also including samples from former German sewage farms.
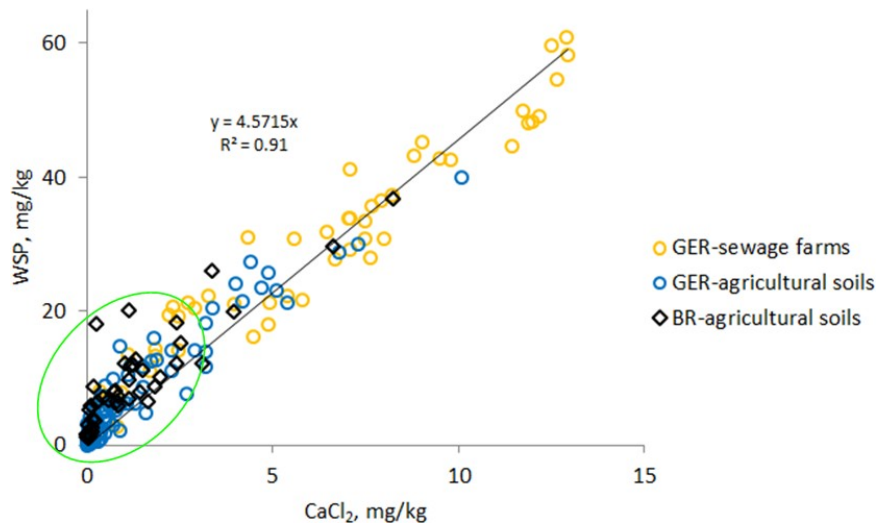
Figure 5.7: Relationship between WSP and $CaCl_2$: for Brazilian soils (BR) of Pernambuco and Minas Gerais (see Chapter 2 and 3) and soils of Germany (GER, Pöthig R.: unpublished data).

A highly significant relationship ($p < 0.01$) allows for transforming WSP to $CaCl_2$ values and vice versa by following PTF: WSP = $4.571 \times CaCl_2$ ($R^2 = 0.91$, Fig. 5.7). However, a pattern of higher WSP values in comparison to $CaCl_2$ can be identified at low $CaCl_2$ values (marked in green, Fig. 5.7). This can be explained by a lower extraction efficiency of Ca associated phosphate due to Ca contained in the extraction solution, influencing the solubility equilibrium of Ca associated P (e.g. Blume et al. 2009: equation 5.3).

$$(5.3) \qquad Ca_5(PO_4)_3(OH)(s) + 4H^+ \rightarrow 5Ca^{2+} + 3HPO_4^{2-} + H_2O$$
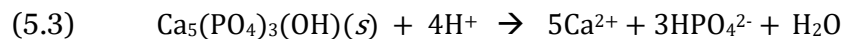
The Ca^{2+} of the $CaCl_2$ extractant shifts the solubility equilibrium to the reactant side and thus less hydroxyapatite is dissolved in $CaCl_2$ than in water. This also holds true for all other Ca associated P in soil samples, and implies a certain soil type-dependency of the $CaCl_2$ method which particularly seems to affect the $CaCl_2$-WSP relationship at $CaCl_2$ values of 0 to 2.5 mg/kg (green circle, Fig. 5.7). Nevertheless, P data determined by the $CaCl_2$ method can be transformed into WSP data, and consequently provides a strong basis for risk assessments of P losses based on these methods in combination with the WSP-DPS and WSP-EPC0 correlations found by Pöthig et al. (2010, WSP-EPC0 correlation published in Fischer et al. 2017).

5.4 Recommendations for future research

In the following, the central research outcomes of this thesis and recommendations for future research needs are summarized (Table 5.2). The occurrence of the clay minerals palygorskite and sepiolite as indicated by IR analyses should be confirmed by XRD analysis. In case the presence of these Mg-containing clay minerals can be confirmed, a systematic evaluation of the occurrence and its effect on soil fertility at the irrigation schemes of the Itaparica reservoir should be carried out. The building of palycretes in these agricultural soils might explain the decreasing productivity of the arable soils after a few years of agricultural usage (Neaman and Singer 2004, 2011). Furthermore, the influence of these minerals on the risk of P losses should be quantified by analyses of WSP and DPS of soil samples.

XRD analyses are only adequate to analyze crystalline forms. As the analyzed fertilizer grains showed a low degree of crystallinity, a confirmation by XRD was not possible. With increasing contact time, the crystallinity of newly shaped phosphates increases. Thus, synchrotron-based high-energy X-ray diffraction (HEXRD) or a long-term study is necessary to confirm the building of crystalline crandallite in fertilizer grains.

So far, analyses assessing the risk of P losses from Brazilian Oxisols either focused on soil analyses without superficial fertilizer or on analyses assessing the effect of superficial fertilizer application on dissolved P concentrations in surface runoff. The analyses of soil samples, including superficial fertilizer grains by consecutive WSP extractions, delivered the whole concentration ranges observed in surface runoff of two different agricultural fields and might be a simple approach to estimate the risk of dissolved P losses in surface runoff of superficially fertilized soils in Brazil. The found relationship should be tested on Entisols.

Further investigation is necessary to include calcareous soils and soils that receive $CaCO_3$ as fertilizers in the determined PTF between M1P and WSP. Although investigations concerning a correction factor of M1P on these soils, e.g. depending on pH changes in the extractant are worth a try, the differences in solubilities of different soil type specific phosphates probably impede an implementation of a simple correction of M1 P values. The investigation of a PTF between the anion exchange resin method and WSP is more promising, as the anion exchange resin method is carried out at a neutral pH and might thus better reflect soil type specific conditions of P solubilities.

Four investigated decomposed peat soils with very high peat portions only fitted the PTF between PCAL and WSP when using a digest for WSP to also include dissolved organic P in the analyses. A study of peat soils with varying peat portions is recommended in order to confirm this finding.

Although the overall DPS values estimated from monitoring data in Brazil were low, single locations indicated exceptionally high risks of P losses with DPS >> 90%. These findings might also be due to unintentionally included superficial fertilizer grains in soil samples, which led to an overestimation of M1P and thus derived DPS values. In the regions with exceptionally high derived DPS values, soil samples should be taken and DPS values determined by sorption isotherms and TP analyses to verify the high values.

Table 5.2: Recommendations for future research derived from the results of this thesis.

Analyses of thesis	Results of thesis	Research recommendation
IR – analyses	Indication of occurrence of clay minerals palygorskite and sepiolite	Confirmation of occurrence of palygorskite and sepiolite by XRD analyses
IR – analyses	Indication of occurrence of phosphate crandallite	Confirmation of building of crandallite by HEXRD or a long-term study investigating the building of well crystallized soil specific P forms by FTIR and XRD
Analyses of soil samples including samples with superficial fertilizer; surface runoff study	WSP extractions of soil samples with and without superficial fertilizer of surface soil layer 0-4 cm of Oxisols reflect: - ranges of measured dissolved P concentrations in surface runoff - temporal variation of dissolved P concentrations in surface runoff	Comparison of concentrations in WSP extractions of Entisols with and without superficial fertilizer to dissolved P concentrations in surface runoff on Entisols
PTF – Brazil	Highly significant correlation between M1P and WSP on soils with no considerable amount of $CaCO_3$	- Development of a correction factor for M1P values measured on $CaCO_3$ containing soils - Development of a PTF between anion exchange resin method and WSP
PTF – Germany	Influence of dissolved organic P of peat soils on PTF between PCAL and WSP	Study of PTF between PCAL and WSP focusing on peat soils
PTF - Brazil – Analyses of risk of P losses derived from monitoring data	Identification of hot spots of highly saturated areas of > 90%	Verification of exceptionally high DPS values indicated by monitoring data through analyses of M1P and DPS on soil samples in respective regions
PTF - Germany – Analyses of risk of P losses derived from monitoring data	Identification of hot spots of highly saturated areas of > 90%	Studies on leaching processes of soil P of ploughing layer to interflow and drainages in respective regions
Analyses of dissolved P emissions by integration of PCAL data in nutrient emission models	Derivation of dissolved P concentrations in surface runoff from PCAL monitoring data by applying PTFs of this thesis and published WSP-dissolved P correlations (e.g. Vadas et al. 2005)	Assessment of nutrient emissions of dissolved P losses from agricultural areas in Germany based on PCAL monitoring data

In contrast to Brazil, the overall risk of P losses for Germany was high. In areas with DPS values > 90% field investigations should be carried out in order to assess the transfer of P from the ploughing layer to deeper soil horizons. Leakage of P should be given special attention due to two reasons: 1) leakage losses by drainage and especially groundwater are much more difficult to reduce by mitigation measures than P losses by surface runoff, and 2) relationships between WSP and SRP in surface runoff have been reported to follow a linear relationship (Pote et al. 1996, Vadas et al. 2005), whereas the correlation between PCAL and EPC0 is an exponential function (Fig. 5.8, Scheinost 1995, Pöthig et al. 2010, Fischer et al. 2017). Special focus should be given to regions with low groundwater tables and drainages in soils with high PCAL values. In such regions P is transported from the ploughing layer to deeper soil horizons, which become gradually saturated with P. If the PCAL values of drainage relevant soil-layers correspond to DPS values > 80%, leaching losses of dissolved P can be expected to be high and potentially increase in the future. In such regions a reduction of P levels in the ploughing layers is urgently needed.
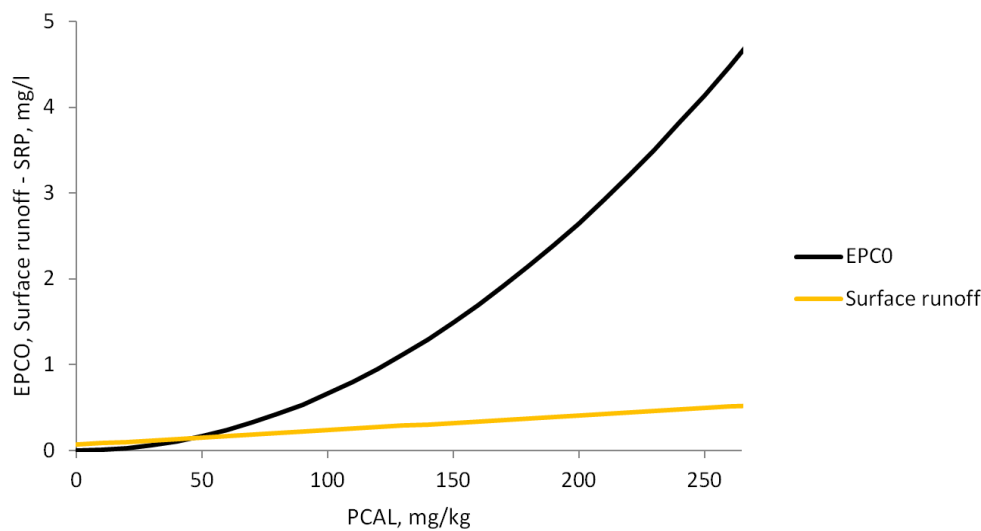
Figure 5.8: PCAL data transformed into: 1) dissolved P concentrations (SRP = soluble reactive phosphorus) in surface runoff (correlations of Chapter 4 - Vadas et al. 2005), 2) risk parameter for P leaching EPC0 (correlations of Chapter 4 - Pöthig et al. (2010).

Several studies showed the reliability of WSP methods to estimate dissolved P concentrations in surface runoff for temperate regions of the USA and Europe (Yli-Halla et al. 1995, Pote et al. 1996, Penn et al. 2006). Vadas et al. (2005) recommended the use of single extraction coefficients for estimating the dissolved P concentrations in surface runoff and WSP was identified to reliably estimate dissolved P concentrations in surface runoff covering a wide range of investigated soils, slopes and rainfall intensities. In the thesis the WSP method used in Vadas et al. (2005) was found to be correlated to the methodology of Pöthig et al. (2010) in a highly significantly soil type-independent correlation (Chapter 3 - Fig. 4.10, $WSP_{Pote\ et\ al.\ (1996)}$ = 0.7936 × $WSP_{Pöthig\ et\ al.\ (2010)}$, R^2 = 0.97). Consequently, monitoring data of PCAL can be translated by the PTF between PCAL and WSP and the WSP-WSP correlation into soluble reactive P (SRP) concentrations in surface runoff according to Vadas et al. (2005): SRP (mg/l) = (11.2 × $WSP_{Pote\ et\ al.\ (1996)}$ + 66.9)/1000. A study estimating and modelling SRP concentrations and TP concentrations in surface runoff based on a WSP soil test has also

been developed for European soils (Withers et al. 2007). This approach might also be usable for modelling SRP concentrations in surface runoff based on PCAL monitoring data, by the same principle as applied for Vadas et al. (2005). Here further laboratory analyses are needed.

5.5 Identification, prevention and assessment of P losses from critical source areas (CSA)

In general, high resolution monitoring data are a prerequisite for the effective identification of CSAs as regards DPS. Areas highly saturated with P were identified in single locations in both Brazil and Germany (Chapter 3 - Fig. 3.3, Chapter 4 - Fig. 4.7 and discussion - Fig. 5.5). In Brazil, the identification of critical source areas has to take into account superficial fertilizer application in addition to the analyses of DPS estimated by M1P monitoring data. Huge differences were found in recommended P fertilization for different agricultural crops in Brazil (Ribeiro et al. 1999, Cavalcanti et al. 2008) and also in recommendations for the application of superficial P. In the perspective of new irrigation projects that are planned in the RSF catchment (Chapter 1), the potential concentration of crops with recommended M1P levels resulting in high risks of P losses (e.g. as shown for grapes in Pernambuco and vegetables in Minas Gerais, see Chapter 2, Fig. 2.9) leading to enhanced risks of eutrophication processes in reservoirs, should be evaluated. The common practice of superficial fertilizer application resulting in high risks of dissolved P losses should be avoided. An incorporation of fertilizer in the soils and a placement of fertilizer close to the roots of the plants could be beneficial both from an agronomic and environmental perspective (Withers et al. 2014). As a complete abolishment of superficial fertilizer application is probably not feasible in the short term, crops receiving high rates of P fertilizer including superficial application should be planted in areas with low hydraulic connectivity to the reservoirs. Accordingly, crops with low P demands and without superficial fertilizer application should be planted in the more vulnerable regions. "Low P Crops" that additionally provide a good soil cover such as lemon grass could be planted at locations adjacent to the reservoirs and act as additional buffer strips. However, in no way can crops replace natural or constructed buffer strips, being fundamental to reduce P emissions to surface water bodies.

For Germany, as shown for the German federal state of Baden-Württemberg, monitoring data should be accessible on a high spatial resolution. Information on monitoring data indicating exceptionally high phosphorus saturations (DPS > 90%, 10% of all provided monitoring data from n > 318,000) is lost when monitoring data are aggregated, e.g. on a municipality level. For a spatial explicit modelling of diffuse P emissions, the identification of suitable management options, and quantification of the reduction potential as well as the required reduction to achieve environmental protection goals, spatially aggregated soil P monitoring values are most probably a crucial limiting factor (see Chapter 4).

For assessing P losses from critical source areas, a combination of soil P data with hydrology parameters is required and needs to be implemented in e.g. nutrient emission models (Kronvang et al. 2009, Schoumans et al. 2009, Neitsch et al. 2011, Venohr et al. 2011). This is particularly important as a relatively small share of catchments (20%) have been identified to

contribute major shares of the total nutrient emissions (80%) in a catchment (Sharpley et al. 2009). A most effective reduction of P losses and subsequent emissions to surface waters should ideally base on an assessment of the hydrological connectivity of agricultural areas to water bodies and be followed by more detailed analysis of CSAs.

Additionally, the high variability in dissolved P concentrations in surface runoff between sites and single events resulting from many different factors such as rainfall intensity, timing and type of fertilizer application before the rainfall as well as hydrological factors, e.g. amount of surface runoff depending on plant cover, should be considered (Hart et al. 2004, Shigaki et al. 2006b, Shigaki et al. 2007). Furthermore, the P levels in soils show variations in space and time, as shown for WSP in a German low mountain range catchment (Kistner et al. 2013). Thus, a combination of field studies and modelling studies is preferable for a more precise assessment of the P losses from the CSAs (Rode et al. 2010). For an effective risk assessment and modelling of P losses from CSAs, models with high spatial and temporal resolution should be applied.

6 Summary

Rock phosphate is a limited resource. Its use as fertilizer plays a pivotal role in the supply of humankind with food. However, phosphorus (P) applied in excess to agricultural soils leads to P accumulations that threaten water bodies with eutrophication processes through diffuse P losses. Humanity faces two major challenges regarding the element P: i) the reduction of P losses from agricultural areas to surface water bodies, and ii) the efficient use of the limited resource P.

In this thesis the degree of P saturation (DPS), the most commonly applied risk parameter for assessing the risk of P losses, was investigated for agricultural soils of Brazil and Germany. It has so far been tested whether common DPS approaches – that are valid for certain soil types only – can be adapted on different soil types and if they can be used to derive P loss risks by monitoring data of plant-available P. A soil type-independent approach developed on central European soils that allows estimating DPS by a simple standard extraction method of water-soluble phosphorus (WSP) has not yet been tested for Brazilian soils, and has not been used for deriving P loss risks from monitoring data.

The analyses of soil samples of two extremely different soil types (Oxisols, Entisols) of the São Francisco catchment in Brazil proved the applicability of the soil type-independent approach to tropical soils of Brazil. On the basis of this finding, pedotransfer functions (PTF) that relate different soil properties were determined between the soil test method WSP and standard methods used to estimate plant-available P in soils of Brazil (Mehlich-1) and Germany (Calcium-acetate-lactate = CAL). This was done in order to: i) transform monitoring data of plant-available P via WSP into DPS, and ii) investigate the resulting risk of P losses at P levels in soils that are currently recommended by agricultural institutions. The derived DPS values from monitoring data for the investigated region of the São Francisco catchment were overall low and did not indicate high risks of P losses. However, a high spatial variability and the occurrence of hot spots with high DPS values and correspondingly high risks of P losses were found. The recommended P levels for major crops of the São Francisco catchment did not correspond to high DPS values and risks of P losses. However, for single crops extremely high DPS values and thus risks of P losses were identified.

In Brazil, fertilization is customarily carried out by superficial fertilizer application on the soil. This leads to increased risks of P loss compared to the equal amount of fertilizer incorporated into the soil, and thus has to be considered in the risk assessment. However, the measured dissolved P concentrations in surface runoff on superficially fertilized Oxisols were relatively low due to the high sorption capacity of Oxisols with their high contents of Fe and Al-hydroxides. Analysis of fertilizer grains from Oxisols with FTIR spectroscopy indicated a reaction of the Al-hydroxides with fertilizer phosphate to crandallite [$CaAl_3(PO_4)_2(OH)_5 \cdot H_2O$] with Fe substitution in the structure. First steps of such a reaction are also likely to happen in surface runoff, which would explain the low dissolved P concentrations and high share of particulate P in surface runoff. WSP was found to reliably estimate ranges of dissolved P concentrations measured in surface runoff when including soils with and without superficial fertilizer. The observed variations in P concentrations per exported soil material indicated that also at surface runoff events of lower intensities, a high capability of eroded material to transport significant amounts of P to surface water bodies is given.

For German soils, the monitoring data indicated high DPS values and thus high risks of P losses, corresponding to formerly recommended P levels. Suggestions in 2015 to reduce recommended P levels in German soils were identified to be crucial to lower the risk of P losses, however still conflicted with environmental goals, especially in soils with no significant amounts of $CaCO_3$. The CAL method showed a strong dependency on $CaCO_3$ and Ca associated P forms, and limited the accuracy of the PTF for predicting P losses and soil parameter equilibrium phosphorus concentration (EPC0), which is crucial for estimating plant-available soil P. The determined soil type-dependency of the CAL method could also explain results of field trials investigating correlations between P levels in soils determined by the CAL method and crop yields. The correction of measured P values by changes in the pH value of the CAL extraction solution strengthened the discrepancies between different soil types. This finding augments the probability of misinterpretation of soil P levels determined by the CAL method in the German fertilizer recommendation system.

Defining adequate soil P levels that address both optimized agricultural production and the protection of surface water is a challenge for many countries. In Europe more than ten different standard soil tests methods are in use, which partly deliver contradictory results on soil P fertility. The soil type-dependency of most of these methods also complicates a harmonized definition of thresholds for DPS values and of targets to reduce P loss risks. In this thesis the standard soil test methods of water and $CaCl_2$ used for estimating plant-available P were combined with the soil type-independent approach to estimate DPS by WSP. This approach can be considered a first step toward a harmonized definition of P levels in Europe that allows for a concomitant soil type-independent risk assessment of P losses. The use of WSP as agronomic and environmental soil P test across Europe could help to solve the challenges humanity faces in the coming decades: the efficient use of the limited resource P and the protection of surface waters from diffuse P losses.

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[7] The title and the year of the paper changed to: Fischer, P., R. Pöthig, B. Gücker and M. Venohr. P saturation and superficial fertilizer application as key parameters to assess the risk of diffuse P losses from agricultural soils in Brazil; submitted to Science of the Total Environment on 30th of October 2017, accepted for publication in revised form on 2nd of February 2018, doi: https://doi.org/10.1016/j.scitotenv.2018.02.070 (see chapter 2 of this thesis).

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Risk assessment of phosphorus losses from agricultural soils in the São Francisco catchment

Peter Fischer[1,2], Rosemarie Pöthig[1], Björn Gücker[3], Markus Venohr[1]

[1] Leibniz-Institute of Freshwater Ecology and Inland Fisheries (IGB), Department of Ecohydrology, Justus von Liebig Straße 7, 12489 Berlin, Germany
[2] Humboldt-University Berlin, Geography Department, Unter den Linden 6, 10099 Berlin, Germany
[3] Federal University of São João del-Rei, Department of Geosciences, Campus Tancredo Neves, R. Visconde do Rio Preto s/n, São João del-Rei, MG, Brazil
Contact: peter_fischer@online.de

Introduction

Background:

Phosphorus (P) loss from agricultural areas by surface runoff is an important pathway of nutrient emissions that contributes to the eutrophication of freshwater systems [1]. In Brazil, relatively little is known about the impact of phosphorus of agriculture on the aquatic systems [2].

Degree of phosphorus saturation:

The degree of phosphorus saturation (DPS) of soils is a worldwide investigated parameter to estimate the risk of P losses. DPS was found to be closely correlated to water soluble P (WSP) [3] resulting in a soil type independent approach for European soils: $DPS=100/(1+1.25 \cdot WSP^{-0.75})$.

Aims of study:

1) Testing of the WSP/DPS approach on its applicability to Brazilian soils (Fig.1)

2) Inclusion of existing soil Mehlich 1 P (=M1P) monitoring data used for estimation of plant available P in the WSP/DPS risk assessment approach (Fig.2)

3) Creation of a risk map of P losses for parts of the upper São Francisco catchment based on M1P monitoring data (Fig.3)

4) Assessing the impact of superficial inorganic fertilizer application on WSP and P concentrations in surface runoff (Fig.1, Table 2)

Methods

Soil analyses:

- Soil samples were taken from top soil layer (0-4cm) of areas dominated by Oxisols and Entisols in Minas Gerais (MG) and Pernambuco (PE), respectively
- Analyses of total phosphorus, Fe, Al, Ca, Mg, WSP and sorption isotherms according to [3]
- Mehlich 1 extraction according to laboratory manual of Empresa de Pesquisa Agropecuária de Minas Gerais (EPAMIG) (pers.communication, [4]
- Existing M1P data from agricultural soils was provided by EPAMIG for the year 2009 and included by M1P-WSP and WSP-DPS correlations to create a DPS map

Water analyses:

- Runoff samples were taken during runoff events on sampling sites with superficial fertilizer application on Oxisols near São João del Rei (MG)
- Runoff samples were taken by collectors according to [5] or by placing openings of sampling bottles against flow direction in runoff
- Digestion with $K_2S_2O_8$ according to EN ISO 6878:2004 on filtered (GF/F, 0.45µm) and unfiltered samples prior to P analyses of total dissolved phosphorus (TDP) and of total suspended phosphorus (TSP), respectively
- All P analyses (soils and water) were done according to [6]

Results

1) Correlation between degree of P saturation (DPS) and water soluble P (WSP) [3,7]
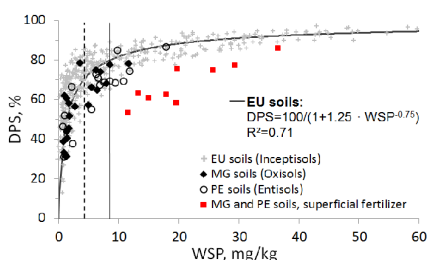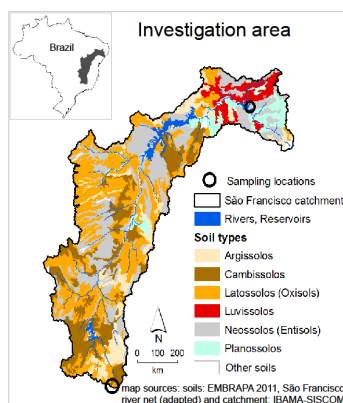

EU soils:
$DPS=100/(1+1.25 \cdot WSP^{-0.75})$
$R^2=0.71$

+ EU soils (Inceptisols)
♦ MG soils (Oxisols)
○ PE soils (Entisols)
■ MG and PE soils, superficial fertilizer

Fig.1: Threshold values of WSP for elevated and high risks are marked with a dashed and a solid line

2) Correlation between WSP and Mehlich 1P [8]

y = 0.1662x
$R^2 = 0.94$

◆ MG ○ PE

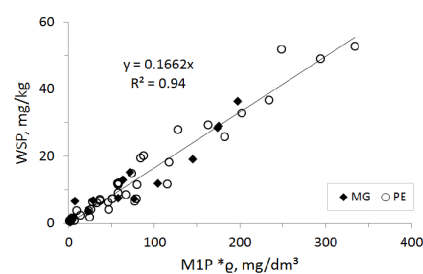**Fig.2:** Correlation (p<0.01) between WSP and M1P in soil samples from Pernambuco (PE, n=38, white circles) and Minas Gerais (MG, n=21, black diamonds), ϱ = soil density

Investigation area
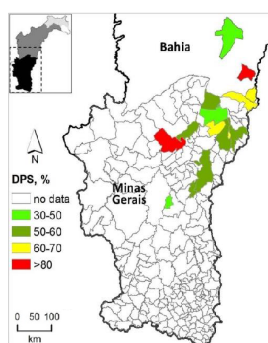

Brazil

○ Sampling locations
☐ São Francisco catchment
Rivers, Reservoirs

Soil types
Argissolos
Cambissolos
Latossolos (Oxisols)
Luvissolos
Neossolos (Entisols)
Planossolos
Other soils

N
0 100 200 km

map sources: soils: EMBRAPA 2011, São Francisco river net (adapted) and catchment: IBAMA-SISCOM

3) DPS risk map [8]

Bahia

Minas Gerais

DPS, %
no data
30-50
50-60
60-70
>80

N
0 50 100 km

Fig.3: Threshold values of DPS for elevated and high risks of dissolved P losses are 70% and 80%

Soil characterization

Table 1: Main sorption and binding partners of investigated brazilian soils (this study) and soils of Central Europe (EU soils, Pöthig, unpublished data)

	Oxisols (MG)	Entisols (PE)	EU soils
Fe, g/kg	52.8	8.6	9.7
Al, g/kg	78.7	11.8	12.0
Mg+Ca, g/kg	5.4	10.7	18.4

Superficial fertilizer

6 cm

Fig.4: Superficial fertilizer in an irrigation culture of Pernambuco

4) Concentrations of particulate and dissolved P in surface runoff [8]

Table 2: n=number of samples/ Surface runoff events; Precip. Intens.=Precipitaion intensity; for WSP, TSP (= total suspended P) and TDP (= total dissolved P) minimum and maximum values are shown; values with (F) represent soil samples which contained fertilizer grains

Agricultural field	Precip. Intens. [mm/h]	n [-]	TSP [mg/l]	TDP [mg/l]	Soil WSP [mg/kg]	[mg/l]
Tangerine	19	3/1	min.: 0.13 max.: 0.19	min.: 0.08 max.: 0.19	min.: 0.0 max.: 47.9 (F)	0.00 0.96
Cabbage	22 - 37	5/3	min.: 1.65 max.: 1.94	min.: 0.06 max.: 0.40	min.: 1.8 max.: 30.5 (F)	0.04 0.60
Mixed cultures	14-36	10/3	min.: 0.96 max.: 2.18	min.: 0.08 max.: 0.36	min.: 2.8 max.: 33.6 (F)	0.06 0.67

Conclusions

1) WSP-DPS approach valid for tropical soils in Brazil [7] (Fig.1).

2) Monitoring data (M1P) used for estimation of plant available P can be integrated in risk assessment of P losses for soils without considerable amounts of $CaCO_3$ [8] (Fig.2).

3) Derived DPS values were low (arithmetic mean (AM)=54%, n=1827, Fig. 3) when compared to Germany (AM=85%, n>337000) [8,9].

4) Superficial fertilizer application leads to high risks of dissolved P losses despite low DPS values [7,8] (Fig.1).

5) Extremely high contents of Fe- and Al hydroxides in Oxisols probably lead to sorption processes of dissolved P in surface runoff

→ P mainly transported in particulate phase (Table 2)

→ Concentrations of dissolved P might be substantially higher in soils with lower Fe and Al contents (e.g. studied Entisols).

References: see next page

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Acknowledgement

Declaration

I hereby declare that this thesis and the work presented in it is entirely my own except where otherwise indicated. I have only used the documented utilities and references.

Hiermit erkläre ich, dass ich die vorliegende Arbeit selbständig und nur unter Verwendung der angegebenen Literatur und Hilfsmittel angefertigt habe.

Berlin, den 22.11.2017 ....

(Peter Fischer)