

A universal method to assess the potential of phosphorus loss from soil to aquatic ecosystems

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Abstract

Background, aim, and scope Phosphorus loss from terrestrial to the aquatic ecosystems contributes to eutrophication of surface waters. To maintain the world's vital freshwater ecosystems, the reduction of eutrophication is crucial. This needs the prevention of overfertilization of agricultural soils with phosphorus. However, the methods of risk assessment for the P loss potential from soils lack uniformity and are difficult for routine analysis. Therefore, the efficient detection of areas with a high risk of P loss requires a simple and universal soil test method that is cost effective and applicable in both industrialized and developing countries. **Materials and methods** Soils from areas which varied highly in land use and soil type were investigated regarding the degree of P saturation (DPS) as well as the equilibrium P concentration (EPC₀) and water-soluble P (WSP) as indicators for the potential of P loss. The parameters DPS and EPC₀ were determined from P sorption isotherms. **Results** Our investigation of more than 400 soil samples revealed coherent relationships between DPS and EPC₀ as

well as WSP. The complex parameter DPS, characterizing the actual P status of soil, is accessible from a simple standard measurement of WSP based on the equation $DPS(\%) = \frac{1}{1+1.25 \times WSP^{-0.75}} \times 100$.

Discussion The parameter WSP in this equation is a function of remaining phosphorous sorption capacity/total accumulated phosphorous (SP/TP). This quotient is independent of soil type due to the mutual compensation of the factors SP and TP. Thus, the relationship between DPS and WSP is also independent of soil type.

Conclusions The degree of P saturation, which reflects the actual state of P fertilization of soil, can be calculated from the easily accessible parameter WSP. Due to the independence from soil type and land use, the relation is valid for all soils. Values of WSP, which exceed 5 mg P/kg soil, signalize a P saturation between 70% and 80% and thus a high risk of P loss from soil.

Recommendations and perspectives These results reveal a new approach of risk assessment for P loss from soils to surface and ground waters. The consequent application of this method may globally help to save the vital resources of our terrestrial and aquatic ecosystems.

In Memoriam Horst Behrendt

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1 Background, aim, and scope

Humans currently exploit more than a third of the production of terrestrial ecosystems and about half of the accessible freshwater. The degree of exploitation further increases with ongoing growth of the world population depending on agricultural products (Tilman et al. 2001, 2002). The intensification of food production of the last decades has

resulted in significant P enrichment in agricultural soil (Sharpley et al. 1993; Simard et al. 1995). The consequences are P loss from arable areas into freshwater and near-shore marine ecosystems leading to considerable eutrophication with algal blooms as well as shifts and losses of biodiversity in both terrestrial and aquatic ecosystems (Behrendt et al. 1996; Van der Molen et al. 1998; Filippelli 2008).

In addition to the problem of eutrophication, there is concern regarding the limitation of high-quality P resources, which requires actions considering both economic and ecological criteria in terms of precision farming (Tilman et al. 2002; Matson et al. 1997; Berry et al. 2003). Yet, there is an ongoing discussion within the scientific community about effective and practicable risk assessments for P loss from agricultural soils. However, there is a high variability among the applied soil test methods and a limited resolution of the empirical relationships between specific soil tests and the P loss potential where different soil tests were used (Nash et al. 2007). For the identification of soil with a high risk of P loss, the degree of phosphorus saturation (DPS) has been recognized widely (Behrendt and Boekhold 1993; Bolinder et al., 2000; Khiari et al 2000; Little et al. 2007; Nair et al 2004; Pöthig et al. 2000; Sims et al. 2000; Zhou and Li 2001). However, in the majority of cases, indirect methods for the determination of DPS are used (Table 1). That is why the measurement of DPS based on P sorption isotherms of soil samples (DPS_{SI}) is not a straightforward task but time consuming and expensive.

Experimentally, the risk of P pollution can be estimated from measured equilibrium P concentrations (EPC₀) in soils or from dissolved P concentrations in runoff. Both EPC₀ (Börling et al. 2004; Bridgham et al. 2001; Hughes et al. 2000) and dissolved P concentrations in runoff (Davis et al. 2005; Penn et al. 2006; Allen et al. 2006) have been shown to be well correlated to the concentration of extractable soil P and the degree of P saturation. The determination of extractable soil P is less laborious than the measurement of EPC₀ or dissolved P in runoff. Therefore, the definition of a threshold DPS value, above which P release becomes critical, usually is indicated by the ratio of DPS to extractable soil P. In practice, both parameters, DPS and extractable phosphorus are obtained by widely varying methods (see Table 1).

Although all of the methods listed in Table 1 are generally accepted for the assessment of the P pollution potential, the use of soil EPC₀ and DPS has not yet been implemented into standardized soil test methods probably because of the complexity of measurement that limits the applicability. In addition, the relationship between the most used DPS_{OX} and extractable phosphorus is specific for every individual soil type (Beauchemin and Simard 2000; Davis et al. 2005). In general, the methods of risk assessment for the P loss potential from soils lack uniformity and are difficult for

Table 1 The most frequently used methods for the determination of extractable or rather mobile phosphorus and the degree of phosphorus saturation

Extractable phosphorus	Degree of phosphorus saturation
Soil test P (STP) is obtained by various extraction methods: Olsen et al. (1954), Mehlich (1953; 1978; 1984)	DPS _{OX} (indirect method) relates ammonium oxalate extractable P to the sum of oxalate-extractable Fe and Al (Börling et al. 2004; Khiari et al. 2000; Little et al. 2007; Maguire and Sims 2002; Nair et al 2004; Pautler and Sims 2000)
EPC ₀ is calculated from P sorption isotherms (see Fig. 3)	DPS _{STP} (indirect method) is calculated from soil test P and a single point sorption index (Bridgham et al. 2001; Casson et al. 2006; Nair et al. 2004; Reddy et al 1998; Simard et al. 1995; Zhou and Li 2001)
WSP results from water extraction of soil (see Section 2)	DPS _{SI} (direct method) results from P sorption isotherms and accumulated P of soils (Börling et al. 2004; Bridgham et al. 2001; Pautler and Sims 2000; Pöthig et al. 2000; Van der Molen et al. 1998; Zhou and Li 2001)

routine analysis (Beck et al. 2004). This is a problem especially for developing countries. The efficient detection of areas with a high risk of P loss, however, requires a simple and universal soil test method that is cost effective and applicable in both industrialized and developing countries.

2 Materials and methods

2.1 Soil sampling

The investigated soil samples were collected from 11 sites in the Northeastern Lowland of Germany (regions of unconsolidated rock), one in the middle hills of Germany, and from four sites in Northern Switzerland (regions of solid rock; Fig. 1). The selected sites are located in small drainage basins with mostly shallow groundwater tables (northeastern lowland of Germany) and in river and lake catchments. The soil samples were collected as core samples from top soil (0–30 cm) and subsoil (30–90 cm, in some cases up to 250 cm) using Eijkelkamp drilling equipment.

The analyzed soil samples originated from areas with great differences in soil type and land use, which include grassland, areas with intensive and extensive farming, wastewater-treatment plants, and recultivated mining waste areas of previous opencast lignite mining. Altogether, 429 soil samples in the context of several research projects and a time span of

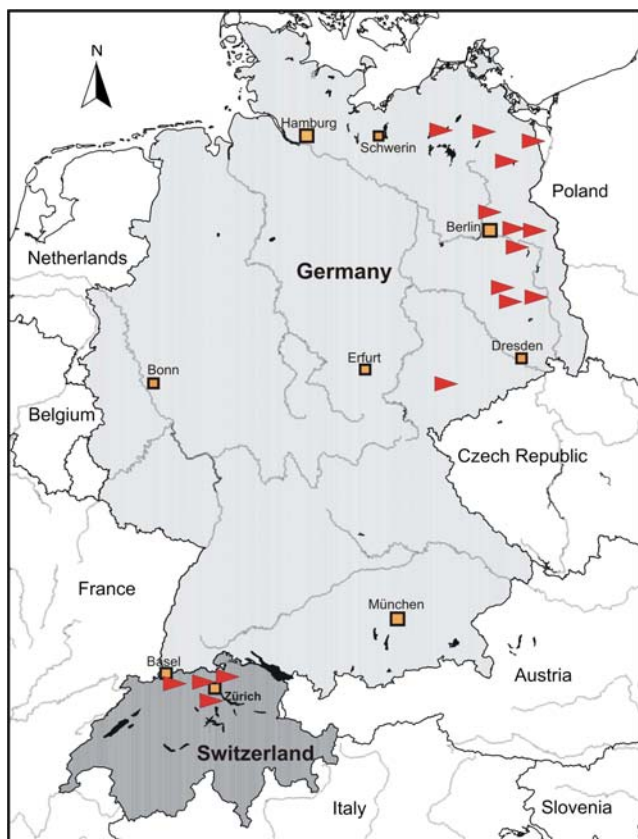


Fig. 1 Location of the 16 sites (red arrowheads) in Germany and Switzerland, where the analyzed 429 soil samples have been collected. As points of reference, some cities are indicated by orange squares

10 years were investigated regarding their P loss potential from terrestrial to aquatic ecosystem, in each case with uniform methods.

2.2 Soil characterization

2.2.1 Chemical analysis

The air-dried and sieved soil (<2 mm) was calcined at 550°C, finely ground and in the following analyzed for total phosphorus content (TP) and the total contents of Fe, Al, Ca, and Mg. TP was measured after aqua regia digestion photometrically (Photometer UV 2101, Shimadzu) using the molybdenum blue method (Murphy and Rilay 1962). From the same digestion, the cations were analyzed by atomic absorption spectrometry (AAS 3300, Perkin Elmer). Organic matter (OM) was estimated by ignition loss at 450°C. The pH value was measured in suspensions of 5 g air-dried soil in 20 ml of 0.01 M CaCl₂ solution.

2.2.2 Determination of water-soluble phosphorus

For the investigation of water-soluble phosphorus (WSP), air-dried and sieved soil samples (<2 mm) were used. WSP was

determined by suspending 1 g soil in 50 ml distilled water, shaking overhead for 2 h, filtration through a 0.45-µm filter, and determining P photometrically (Murphy and Rilay 1962). It has to be noted that the reproducibility of sample subdivision is limited due to natural heterogeneities in the particle size distribution of the soil samples. However, pulverization of the samples to overcome this problem is inapplicable since it would destroy the natural texture of the soil samples. This fact applies also to Section 2.2.3.

2.2.3 Degree of P saturation and equilibrium P concentration

The parameters DPS_{SI} and EPC₀ are based on P sorption isotherms and are described in Fig. 2. To obtain P sorption isotherms, 5 g of air-dried and sieved soil (<2 mm) was suspended in 50 ml of 0.01 M CaCl₂ solution containing various initial P concentrations (0–50 mg/L). After overhead shaking during 2.5 h, suspensions were filtered (0.45 µm), and sorbed P (SP) was calculated from the difference between the measured equilibrium P concentration of the filtrate and the initial P concentration. The P sorption isotherms are obtained from plotting SP against EPC (see Fig. 2a).

The equilibrium P concentration at zero net P sorption is defined by the intersection of the P sorption isotherm with the x-axis (see Fig. 2a, b). The magnification of the highlighted area in Fig. 2a illustrates how EPC₀ is calculated from the linear relationship between SP and EPC at the initial range of the sorption isotherm (see Fig. 2b). The sorption maximum (SP_{max}) was calculated from reciprocal slope obtained by plotting the quotient EPC/SP versus EPC (see Fig. 2c). The P sorption capacity (PSC) is the sum of SP_{max} and the accumulated total phosphorus, measured after aqua regia digestion of the samples. The degree of P saturation is defined as $DPS_{SI}(\%) = \frac{TP}{PSC} \times 100$.

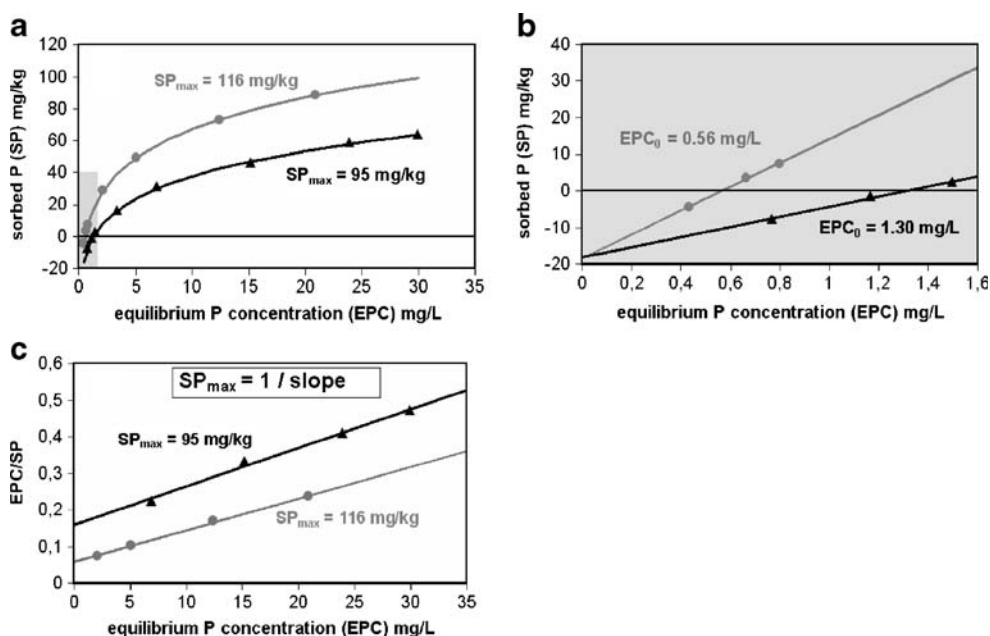
In the following, the term DPS will be used for simplicity instead of DPS_{SI} because no other methods for the determination of DPS are used in this study.

3 Results

3.1 Soil type and chemical data

The studied soil samples included sandy and loamy soils, organic soils, and calcareous soils. Because of the great differences in the soil properties, land use, and fertilization practice, the contents of accumulated total phosphorus, Fe, Al, Ca, and Mg, OM, as well as the pH varied over a wide range (Table 2).

Fig. 2 a–c How the equilibrium P concentrations and the P sorption maxima (SP_{max}) are derived from P sorption isotherms of two soil samples. **a** P sorption isotherms from two sandy soils. **b** Magnification of the highlighted sub-area of **a** to illustrate the calculation of EPC_0 from the linear relationship at the initial range of the sorption isotherm. **c** Plot of the quotient EPC/SP versus EPC for calculation of the sorption maximum



3.2 Relation between DPS and EPC_0

As mentioned above, the risk of P pollution can be estimated from equilibrium P concentrations in soils. Fig. 3 shows the relation of the degree of P saturation to the detected EPC_0 values of soils. The data are best fitted by an exponential equation. The plot shows that the values of EPC_0 slowly rise at $DPS > 70\%$ and increase strongly at $DPS > 80\%$, indicating a potential environmental risk (highlighted area, see Fig. 3).

3.3 Relation between DPS and WSP

In Fig. 4, the degree of P saturation is plotted against WSP under consideration of the different soil types. It is evident that WSP slowly increases up to a DPS of about 60% (similar to EPC_0 , see Fig. 3). Independent of soil type, at $DPS > 70\%$, WSP increases significantly and jumps up at $DPS > 80\%$, indicating a high amount of labile, water-extractable P and therefore a high potential of P loss from soil. The region of critical DPS values is marked by the highlighted area in Fig. 4. The corresponding WSP values at which DPS becomes greatly critical are around 5–10 mg/kg (vertical marker lines, see Fig. 4).

Figure 5 shows the relationship between water-soluble phosphorus and those parameters that are contained in DPS: total phosphorus (see Fig. 5a), sorption maximum (see Fig. 5b), and the quotient SP/TP (see Fig. 5c). In Figs. 5a, b, WSP is not correlated with TP and SP, particularly if the data are plotted disregarding the soil types. Here, the influence of soil type is evident. However, if WSP is plotted versus the quotient (SP/TP) , the large scatter of the data is confined significantly (see Fig. 5c).

4 Discussion

4.1 Relation between DPS and EPC_0

The parameter EPC_0 is of high significance regarding P leaching and represents the P concentration at which neither adsorption nor desorption of phosphorus occurs in soil. Up to this P concentration, soils exhibit their maximum buffer capacity (Bridgham et al. 2001). Since small changes in dissolved P are almost completely compensated by sorption or desorption of P, the EPC_0 values at $DPS < 60\%$ remain virtually unaffected (see Fig. 3). The average of all DPS

Table 2 Ranges of basic physiochemical properties of studied soils (minimum and maximum of each parameter in bold)

Parameter	Sandy soils	Loamy soils	Calcareous soils	Decomposed-peat soils
Total P (mg/kg)	1–1,815	40–2,330	72–1,560	68– 3,060
Total Fe (g/kg)	0.5 –14	5–57	3–36	3– 58
Total Al (g/kg)	0.1 –12	5– 71	2–24	3–51
Ca+Mg (g/kg)	0.01 –16	2–61	58– 340	1–75
Organic matter (%)	0.2 –5.3	0.7–8.5	1.2–8.3	8.2– 54
pH	3.9–8.1			

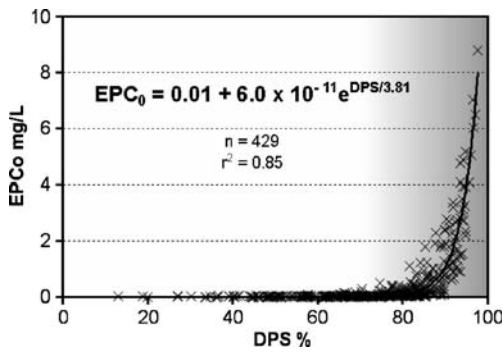


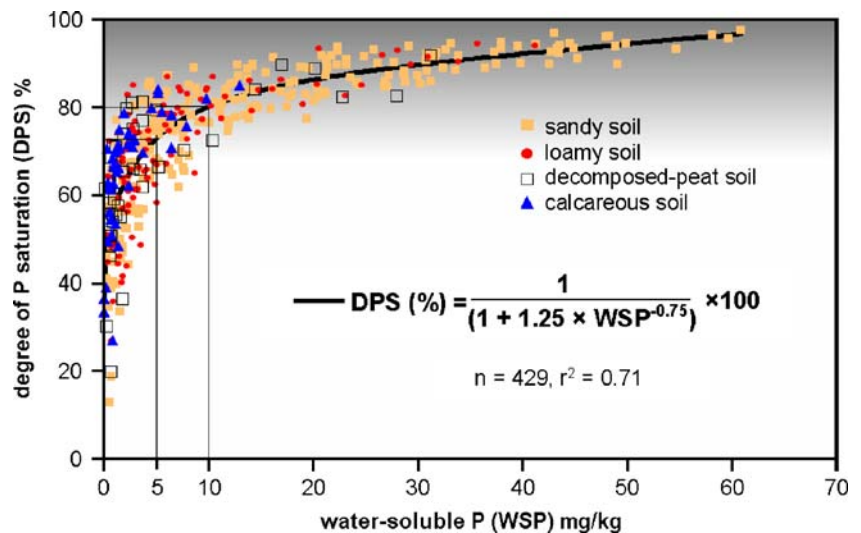
Fig. 3 Dependence of the equilibrium P concentration on the degree of P saturation. The range of environmental risk is *highlighted*

values <60% results from the average background concentration of EPC₀ in our samples of 0.01 mg P/L (ranging from 0.001 to 0.08 mg/L). This range is in good agreement with reported natural background concentrations of P in streams and rivers (0.006–0.08 mg/L) (Smith et al. 2003). The average background concentration is a required constant in the exponential function that describes the relationship between DPS and EPC₀ (see Fig. 3). However, both parameters, DPS and EPC₀, which are most suitable for a reliable risk assessment regarding P loss from soil, are laborious to measure.

4.2 Relation between DPS and WSP

The comparison of Figs. 3 and 4 reveals that DPS is reflected equally well by EPC₀ (see Fig. 3) and by WSP (see Fig. 4). Some experimental data show significant deviations from the saturation function curve mainly due to unavoidable heterogeneities within the soil samples. This is because each data point representing one soil sample on the curve requires the measurement of P in six to nine sample fractions (see also Sections 2.2.2 and 2.2.3). Nevertheless,

Fig. 4 Correlation between the degree of P saturation and water-soluble phosphorus of soils. The independent parameter, DPS, is plotted on the *y-axis* since DPS shall be calculated from WSP. The investigated soil types are labeled by *different symbols and colors*. The range of environmental risk is *highlighted*



high WSP values are always caused by a high degree of soil P saturation. These findings are in good agreement with the results of other authors, who found that the risk of P loss from agricultural soil to surface and ground water generally increases with the degree of P saturation in soils (Börling et al. 2004; Nair et al. 2004; Penn et al. 2006; Beck et al. 2004; Ulen 2006).

However, the most important insight of Fig. 4 is the fact that all investigated soil samples react similarly regardless of the differences in soil type. The result is a coherent relation between DPS and WSP, which can be described by one single saturation function. This function is based on the definition of DPS:

$$DPS(\%) = \frac{TP}{PSC} \times 100 \tag{1}$$

Where PSC, the phosphorus sorption capacity, is

$$PSC = TP + SP \tag{2}$$

The combination of Eqs. 1 and 2 yields

$$DPS(\%) = \frac{1}{1 + SP/TP} \times 100 \tag{3}$$

The term SP/TP can be substituted by a function of WSP

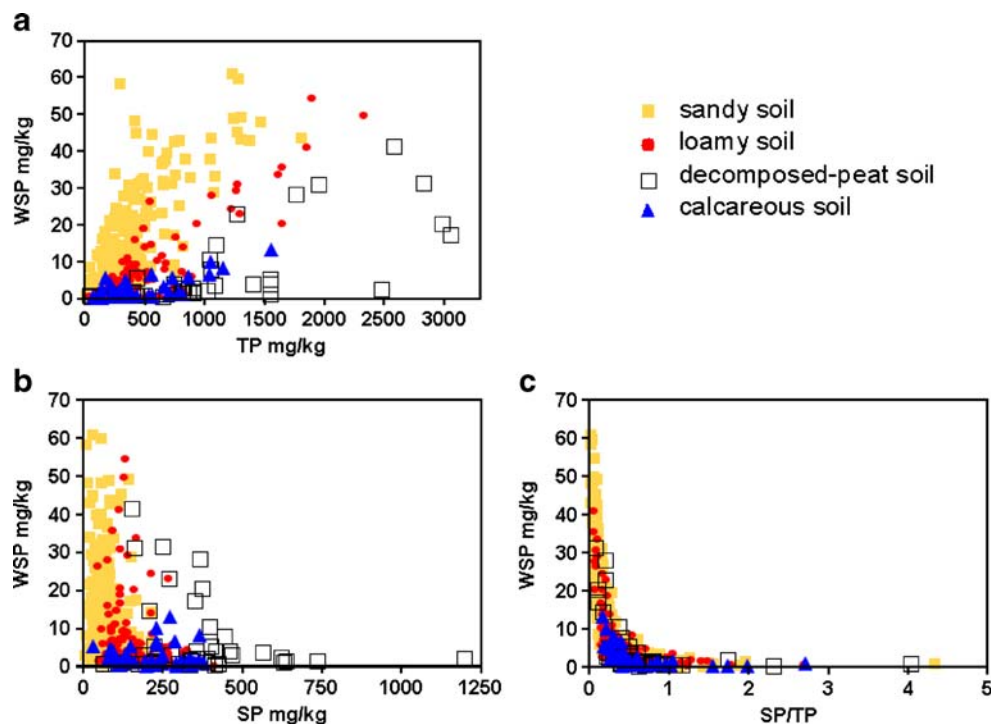
$$DPS(\%) = \frac{1}{1 + f(WSP)} \times 100 \tag{4}$$

The dependence of DPS on WSP, shown in Fig. 4, results in

$$DPS(\%) = \frac{1}{1 + 1.25 \times WSP^{-0.75}} \times 100 \tag{5}$$

Thus, the degree of soil P saturation is quite simply to be determined by calculation from WSP using Eq. 5. Having defined a threshold WSP value, which preferably should be

Fig. 5 Dependencies of water-soluble phosphorus on total phosphorus (a), sorption maximum (b), and on the quotient SP/TP (c)



lower than 10 mg/kg (see Fig. 4), the risk assessment can be based reliably on WSP by calculating the corresponding DPS value.

The independence of the relation between DPS and WSP from soil type, which is evident from Fig. 4, can be seen also in Fig. 5c that shows the relationship between WSP and SP/TP (compare with Eq. 3). The influence of soil type on the relation between WSP and SP/TP is eliminated due to the mutual compensation of the parameters SP and TP. If the amount of accumulated P (TP) is relatively low with respect to the total capacity (PSC), the amount of P that can be further sorbed (SP) is higher and vice versa. The degree of P saturation is a function of the quotient SP/TP (Eq. 3) that can be substituted by $f(WSP)$ (Eq. 4). Therefore, the relationship between DPS and WSP has been found to be independent of soil type (see Fig. 4).

In contrast, the influence of soil type is evident in Fig. 5a, b. This means that WSP is not correlated with TP or SP if the results of different soil types are plotted in the same diagram. The influence of soil type becomes apparent when TP is examined at distinct DPS values (Table 3). The range of 70% to 80% DPS, at which the potential P loss becomes critical, is reached for the individual soil types at values that differ significantly. Hence, the soil type certainly affects its capacity of phosphorus accumulation.

4.3 Soil type, land use, and DPS

The degree of P saturation, which is determined by P sorption isotherms, includes all P sorption and binding sites. The

binding forms of phosphorus and their relative quantities are different in all soil types. They vary from loosely sorbed P on organic matter, over chemically sorbed P on hydroxides and oxides, to strongly bound P in phosphates and complex solids. In all soil types, the strongest P sorption and binding sites are occupied preferentially, and the sites with the smallest affinity to P are used up only at high degree of P saturation. Vice versa, the weakly bound P reacts more readily with water causing high values of WSP.

Table 3 reveals that soils with small quantities of P sorption and binding sites, like sandy soils, can be highly saturated with P already at relatively low TP. On the other hand, soils with high quantities of P sorption and binding sites, like decomposed-peat soils, are able to accumulate high amounts of P before DPS becomes critical. Consequently, soils of different type reach a distinct degree of P saturation at different levels of absolute P accumulation.

But in all soil types, the P sorption and binding sites of different affinity are occupied in the same sequence. This means that, at distinct degree of P saturation, the occupied

Table 3 Average TP values of different soil types at a degree of P saturation of 70–80%

Soil type	Average TP (mg/kg)
Sandy soil	260
Loamy soil	500
Calcareous soil	530
Decomposed-peat soil	1,320

P sorption and binding sites exhibit similar binding strength and consequently similar water solubility. Therefore, the term SP/TP in Eq. 3 can be substituted by $f(\text{WSP})$, resulting in a correlation between DPS and WSP. This function is independent of soil type (see Fig. 4).

As mentioned above, the investigated soil samples not only varied in soil type but have been sampled from areas which also varied highly in land use. But, neither the differences in soil type nor in land use show a significant diversion from the saturation function in Fig. 4. The degree of P saturation of soils is the crucial factor for the amount of water-soluble phosphorus in soils and therefore for the risk of P loss from soils to waters. A study of the effect of land use on some soil properties related to the risk of loss of soil phosphorus (Troitino et al. 2008) revealed a similar result. In all soils, independently of their use, the amount of P desorbed was closely related to the degree of P saturation.

5 Conclusions

Coherent relationships between DPS and EPC_0 (see Fig. 3) as well as between DPS and WSP (see Fig. 4) were obtained from systematic studies on the potential of P loss from soil, which are based on P sorption isotherms, equilibrium P concentration and water-soluble phosphorus. Furthermore, it was shown that these relationships are independent of soil type and land use. Thus, it is possible to specify the risk of phosphorus loss from soil to water by a general relation for all soils. The complex parameter DPS, which characterizes the actual state of P fertilization of soil, can be calculated from WSP using Eq. 5. The parameter WSP is easily accessible by a standard measurement of extractable soil phosphate. Values of WSP, which exceed 5 mg/kg, signify a degree of soil P saturation of 70–80% and, thus, a high risk of P loss from soil to water.

6 Recommendations and perspectives

The proposed method of risk assessment for the potential of P loss from soils is highly advantageous because of its simplicity and cost effectiveness. Therefore, it can be applied widely in both industrialized and developing countries. The method can be carried out by soil test laboratories or directly by farmers using a suitable test set for measuring phosphate in soil extracts as described above. We like to emphasize that the use of such a method by no means substitutes in-depth investigations and the measurement of parameters such as DPS or EPC_0 . But the calculation of DPS from measured WSP (Eq. 5) is adequate to routine monitoring of agriculturally used soils and could also be implemented in the techniques of precision farming.

Because it could take aquatic ecosystems a thousand years or longer to recover from eutrophication caused by phosphorous pollution from overfertilized soils (Carpenter 2005), a simple method of risk assessment preventing the P loss from soils is highly important. The rigorous application of risk monitoring yields ecological and economical profits: the prevention of soil and water eutrophication by phosphorus with the result to maintain the world's vital freshwater ecosystems and to save P resources as an essential nutrient necessary for life.

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