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Phosphate saturation degree and accumulation of phosphate in various soil types in The Netherlands

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Objective: The objective of this study is to quantify the potential risk of P leaching to groundwater in characteristic soil types in The Netherlands. In areas with shallow groundwater P losses via groundwater to surface waters is an important pathway.

Methods: The risk of P leaching to groundwater can be assessed by means of the phosphate saturation degree (PSD) methodology. The PSD is an index of the actual phosphate accumulation in the soil (P_{act}) in relation to the maximum phosphate sorption capacity (PSC_m) of the soil to a reference depth. To assess the risk of P leaching the actual PSD of soils has to be compared to the critical PSD (PSD_{crit}) of the soil type. The critical PSD is determined for characteristic soil types based on phosphate sorption and desorption characteristics, and a reference depth (L_{ref}) where a defined P concentration (C_p) in solution may not be exceeded. A stratified soil survey is used to determine the actual PSD of the soils.

Results: The critical phosphate saturation degree we determined for the main Dutch soil types varies from 5%–78%. The average P accumulation in agricultural soils in The Netherlands is about 2050 kg P ha^{-1} (4700 kg P_2O_5 ha^{-1}) and the 5‰ and 95‰ are approximately 850 and 4500 kg P ha^{-1}. Since maize can tolerate high manure application rates, more phosphate has been applied on maize in the past, and high P accumulations are measured. In about 43% of the agricultural land in The Netherlands the critical PSD value for the given soil type is exceeded.

Practice: Consequently, a large area of agricultural land contributes, or is expected to contribute to the P pollution of surface water in the nearby future. Especially from fields with a high PSD severe P losses can occur due to the convex relationship between the PSD and the P concentrations in soil solution.

Implementation: Strategies and additional measures are needed for fields with a high PSD in order to substantially reduce the P losses from agricultural land to surface waters within a catchment.

1. Introduction

In the mid-20th century, agricultural production in Europe was stimulated and intensified. As a result the national phosphorus (P) balance increased (OECD, 2008), since the amount of phosphorus imported in fertilizer and fodder became much higher than the amount exported in products (crops, dairy and meat). Manure production increased, especially in areas with high livestock densities, and consequently the manure application rates on agricultural land rose to levels far above plant requirements for phosphorus, and a potential environmental risk was born (Smit and Dijkman, 1987).

As phosphate accumulated in soil, emissions of phosphate to surface water increased and agriculture became a major source of nutrient enrichment of such waters (Lee, 1973; Vollenweider, 1968). Phosphorus loss from agricultural land in flat areas such as The Netherlands is mainly determined by the phosphate accumulation in soils in relation to the phosphate sorption capacity and hydrological conditions. Based on studies of the phosphate sorption capacity of sandy soil types (Schoumans et al., 1987; Van der Zee and Van Riemsdijk, 1986) and a simple regional phosphorus transport model (Schoumans et al., 1986), the first estimations of phosphate saturation of soils in The Netherlands were made for areas with non-calcareous sandy soils and high livestock densities (Breeuwsma and Schoumans, 1987).

In the early 1990s, a straightforward approach for non-calcareous sandy soils was developed to determine a critical value for the degree of phosphate saturation (known as phosphate saturation degree, abbreviated as PSD) in The Netherlands (Van der Zee et al., 1990a,b). The criteria required, namely the acceptable P concentration and reference soil depth that should be protected, were defined by a technical committee (TCB, 1990). As acceptable P concentration the natural background concentration was chosen (0.1 mg L^{-1} ortho-P) and as reference depth, the mean highest water level (MHW). In lowland countries like The Netherlands the groundwater is shallow and fluctuates during the year. In the summer period the lowest groundwater levels and during the winter period (autumn–spring) the highest groundwater levels are

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reached. In The Netherlands the mean highest and lowest groundwater level (MHW and MLW respectively) are defined as resp. the average of the three highest or lowest groundwater levels during a period of 8 successive years. In the wet areas the MHW varies between 0 and 0.4 m and the MLW between 0.6 and 1.4 m. During the year the groundwater levels can be above or below this level for a short period (<2 months). Using these criteria and the phosphate kinetics of non-calcareous sandy soils, a critical PSD of 25% was calculated, which means that the actual phosphate accumulation in the soil should be less than 25% of the total phosphate sorption capacity of the soil between the soil surface and the MHW. When this critical value for non-calcareous sandy soils was used in a modeling application it was found that about 70% of the agricultural land in non-calcareous sandy soils in areas with intensive husbandry in The Netherlands exceeded the defined critical PSD (Breeuwsma and Silva, 1992). At that stage it was not possible to define a critical value for the other soils in The Netherlands because no information was available on the phosphate sorption and desorption parameters and, moreover, the reference criteria had not been defined. Since then, the sorption and desorption processes in other Dutch soil types have been studied (Schoumans, in press; Van Beek et al., 2003) and the phosphate accumulation has been determined by measurements (Finke et al., 2001). The main aim of this paper is to derive indicative critical values of phosphate saturation for different soil types and estimate the phosphate-saturated area and phosphate accumulation in The Netherlands.

2. Materials and methods

The dataset of the national stratified soil survey (Finke et al., 2001) was used to estimate the degree of phosphate saturation of the Dutch soil types. The locations had been selected randomly within 95 strata (combinations of soil type and groundwater regime) that are presented in Fig. 1. The red area in Fig. 1 represents the location of one of the 95 strata: calcareous silty clay soils with a MHW between 0.4 and 0.8 m. This stratum, like other strata, is situated in different parts of The Netherlands. For the soil survey, the soil samples were collected from 1992 to 1998 by sampling the horizons of the soil to a depth of 1.20 m at about 1400 locations. If a horizon layer was thicker than 0.25 m, the horizon was subsampled in layers less than 20 cm each. The soil profiles were described and all horizons were sampled and their chemical characteristics were determined (pH, oxalate-extractable P, Al and Fe, for example). At each location the land use of the field and the mean highest water level (MHW) and mean lowest water level (MLW) were also determined.

Table 1 gives the number of locations sampled (n) and the area represented for combinations of soil type and land use. The average density is approximately one sampled location per 2000 ha agricultural land. Although the sample density is not high, it is the only statistical database available for the entire country that includes the parameters needed to determine the PSD. For each stratum the PSD of each location was calculated in order to produce a map of the average degree of phosphate

Fig. 1. Locations of the national stratified soil survey sampling (Finke et al., 2001). The red area is an example of the location of one of the 95 strata (calcareous silty clay soils with a MHW between 0.4 and 0.8 m) that is distinguished in the national stratified soil survey.

Table 1
Number of the locations sampled (n) and the area represented (ha) for combinations of soil type and land use.

Soil type		Land use				Total
		Maize	Arable	Grass	Nature[a]	
Non-calcareous sandy soils[b]	n	64	82	312	218	676
	Area (ha)	168,540	185,774	748,136	441,866	1,544,316
Non-calcareous clay soils[c]	n	5	21	156	17	199
	Area (ha)	10,073	63,480	325,693	24,785	424,032
Calcareous clay soils[d]	n	8	113	98	15	234
	Area (ha)	27,230	355,066	227,116	10,493	619,904
Peat soils[e]	n		9	175	16	200
	Area (ha)		17,151	230,383	12,479	260,013
Calcareous sandy soils[f]	n	1	22	13	23	59
	Area (ha)	1362	39,800	22,821	27,203	91,186
Total locations		78	247	754	289	1368
Total area (ha)		207,205	661,271	1,554,149	516,826	2,939,451

[a] Nature is mainly forests.
[b] Non-calcareous sandy soils: histic en umbric gleysols, cambric en gleyic podzols, en fimic anthrosols, eutric cambisols (sand and silt loam).
[c] Non-calcareous clay soils: non-calcaric fluvisols (clay and sandy clay loam).
[d] Calcareous clay soils: calcaric fluvisols (clay and sandy clay loam).
[e] Peat soils in lower lying areas: histosols.
[f] Calcareous sandy soils: calcaric fluvisols (sand).

saturation for all strata. The phosphate-saturated area (abbreviated as PSA) of each stratum was determined by the number of locations where the PSD of the profile exceeded the critical PSD of the soil type, taking into account the total number of locations sampled within the stratum and the area of the stratum. The determination of the PSD and critical PSD is described hereafter.

3. Methodology: Definition of the critical phosphate saturation degree (PSD_{crit})

A soil is deemed to be phosphate-saturated if a critical P concentration in soil solution or groundwater (C_p) at reference depth (L_{ref}) is expected to be exceeded at some time due to the high phosphate accumulation in the top layer. This concentration will be exceeded if the phosphate accumulation is too deep and occurs below a certain depth (L_s) in the soil profile. The critical P concentration at L_{ref} will be exceeded if the phosphate sorption capacity (F) of the subsoil (from depth L_s to L_{ref} in equilibrium with the critical P concentration C_p) is too small when compared to the total amount of easily sorbed P, leached after desorption from the accumulated P in the top soil ($0–L_s$). Thus the critical condition of the PSD is based upon the condition that:

the excess amount of easily reversible bound P that will leach from the top layer ($0–L_s$) with a P concentration above the reference concentration (C_p) has to be bound in the layer below L_s and the reference depth (L_{ref}) at a maximum concentration of C_p. In formula:

$$\overline{\rho_{0-L_s}}\, L_s \left(\overline{Q_{m,0-L_s}} - \overline{Q_{C_p,0-L_s}}\right) = \overline{\rho_{L_s-L_{ref}}}\left(L_{ref} - L_s\right)\overline{F_{C_p,L_s-L_{ref}}} \tag{1}$$

where

$\overline{\rho_{0-L_s}}$	= average dry bulk density of layer $0–L_s$	(kg m^{-3})
$\overline{\rho_{L_s-L_{ref}}}$	= average dry bulk density of layer $L_s–L_{ref}$	(kg m^{-3})
L_s	= maximum phosphate penetration depth	(m)
L_{ref}	= reference depth where the critical P concentration (C_p) should not be exceeded	(m)
$\overline{Q_{m,0-L_s}}$	= average maximum amount of reversible bound P in layer $0–L_s$	(mmol kg^{-1} P)
$\overline{Q_{C_p,0-L_s}}$	= average amount of reversible bound P in layer $0–L_s$	(mmol kg^{-1} P)
$\overline{F_{C_p,L_s-L_{ref}}}$	= average phosphate sorption capacity at concentration C_p of layer $L_s–L_{ref}$	(mmol kg^{-1} P)

The left side of Eq. (1) gives the amount of reversible bound P (Q) above the reference concentration C_p in the top layer ($0–L_s$) and the right side of Eq. (1) gives the amount of P that can be sorbed (F) in the layer between L_s and L_{ref} at a concentration of C_p.

In Appendix A the chemical methods are mentioned and the critical phosphate saturation degree (PSD_{crit}) is derived, based on the conditions mentioned in Eq. (1), giving:

$PSD_{crit} = \frac{\gamma K C_p}{1+\gamma K C_p} * 100(\%)$		(see Appendix A, Eq. (13))
PSD_{crit}	= critical phosphate saturation degree of a soil type	(%)
K	= soil type specific Langmuir adsorption coefficient	(m^{-3} mol^{-1})
C_p	= maximum ortho-P concentration for a soil type at reference depth L_{ref}	(mol m^{-3})
γ	= soil type specific coefficient	(−)

This value has to be compared to the actual phosphate saturation degree (PSD) of the soil, which can be calculated by:

$PSD \equiv \frac{P_{act,0-L_{ref}}}{PSC_{m,0-L_{ref}}} * 100(\%)$		(see Appendix A, Eq. (14))
PSD	= phosphate saturation degree of the soil to depth L_{ref}	(%)
$P_{act,0-L_{ref}}$	= actual amount of phosphate accumulation in the soil in layer $0–L_{ref}$	(kg P_2O_5 ha^{-1})
$PSC_{m,0-L_{ref}}$	= maximum phosphate sorption capacity of the soil in layer $0–L_{ref}$	(kg P_2O_5 ha^{-1})

The actual amount of phosphate accumulated in the soils is based on the amount of oxalate extractable phosphate (P_{ox}) in the soil profile to L_{ref}. The maximum phosphate sorption capacity, expressed in kg P_2O_5 ha^{-1}, is based on the sum of the soil-specific phosphate sorption capacities of the soil layers to depth L_{ref}.

4. Results

4.1. Reference conditions of the soil types

In order to define critical values for the PSD for different soil types, values have to be chosen for the maximum acceptable concentration of P (C_p) and the reference depth (L_{ref}) and information is needed about the phosphate sorption and desorption characteristics (γ and K; see Appendix A). The depth used as the reference depth (L_{ref}) was the same depth as was defined for non-calcareous sandy soils, namely the mean highest groundwater level (MHW). In areas with tile drains, it would be better to use the depth of these drains for L_{ref}. As this information is not available for the entire country the MHW was used here too.

The maximum acceptable P concentration (C_p) for non-calcareous sandy soils has been defined as the natural background concentration

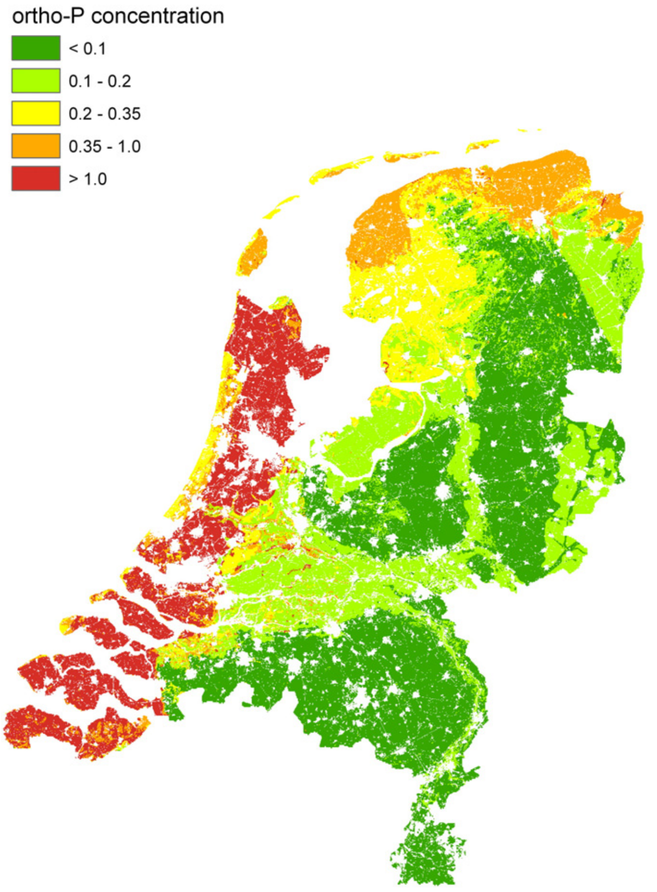

Fig. 2. Inorganic P concentrations (mg L^{-1} P) in deep groundwater in The Netherlands.

of inorganic P, which was determined at an average ortho-P value of 0.1 mg l^{-1} P (TCB, 1990). The background concentration of phosphorus varies across The Netherlands, especially in areas with marine sediments and in peat areas. The maps of the phosphorus background concentrations in the deep groundwater (>13 m) are based on the database that supplies model input data for the national evaluations of the Dutch manure policy (Wolf et al., 2003). The most recent mapped information is used (Griffioen et al., 2006; Groenendijk et al., 2013). It is assumed that inorganic P concentrations at those depths are not influenced by agricultural practices due to the high phosphate sorption capacity of the overlying soil. We used this dataset to calculate the background P concentration for five main soil types in The Netherlands. Fig. 2 shows that the highest ortho-P concentrations are measured in the areas with marine sediments (coastal area). These sediments consist of calcareous material (sand or clay) containing Ca/Mg–P precipitates. Due to chemical and physical weathering and precipitation of secondary (amorphous) minerals, relatively high P concentrations can occur. The average concentration of ortho-P of all soil types in this database is 0.36 mg P L^{-1} and the median concentration is 0.13 mg P L^{-1}, which is higher than the concentrations used for non-calcareous sandy soils by the TCB (1990). With respect to the definition of a phosphate-saturated soil, it is important that the natural background concentrations (C_p) that contribute to the diffuse losses to surface waters (trenches, ditches, brooks and rivers) at higher groundwater levels are accurately determined, because they directly affect the value of the critical PSD.

4.2. Soil chemical P characteristics of the different soil types

Information is needed not only about the reference conditions but also about the phosphate sorption and desorption parameters of the different soil types which determine the phosphate kinetics in soils.

In non-calcareous sandy soils and peaty clay soils, the maximum sorption capacity can be determined by Eq. (15), with a value of 0.5 for α (Schoumans, 2004, 2013; Van der Zee et al., 1990a,b). In clay soils different clay minerals can occur like kaolinite, illite, and montmorillonite. Under weathering conditions the primary clay minerals are dissolved and mixtures of Al- and Fe-sesqui(hydr)oxides (e.g. gibbsite $Al_2O_3 \cdot 3H_2O$; goethite $Fe_2O_3 \cdot 3H_2O$; $Al(OH)_x^{(3-x)+}$ and $Fe(OH)_y^{(3-y)+}$). These sesqui(hydr)oxides can be partly associated with the electric negative charged clay plates or organic complexes (Bolt and Bruggenwert, 1978; Rowell, 1994). It is well known that phosphate can be sorbed to the clay minerals and micro-crystalline Al- and Fe-sesqui(hydr)oxides beyond the adsorption maximum of the primary clay minerals due to phosphate adsorption and a diffusion precipitation reaction with micro-crystalline Al- and Fe-sesqui(hydr)oxides (Celi et al., 2000; Ler and Stanforth, 2003; Martin et al., 1988; Torrent et al., 1990; Van Riemsdijk and Lyklema, 1980). The micro-crystalline Al- and Fe (hydr)oxides (free, associated with the clay plates and/or organic complexes) which influences the phosphate sorption capacity, can be extracted with oxalate (Schwertmann, 1964). The amount of oxalate extractable Al and Fe is much higher in clay soils than in sandy soils (Finke et al., 2001), but the reaction mechanisms (fast adsorption reaction and slow diffusion/precipitation reaction) are similar, due to the role of micro-crystalline Al- en Fe-sesqui(hydr)oxides. When the phosphate sorption capacity of Dutch calcareous clay soils (3–12% $CaCO_3$; pH 7–8) was compared with non-calcareous clay soils (<3% $CaCO_3$; pH 5–7), no positive or negative influence was found of the $CaCO_3$ content on the P sorption capacity (unpublished data Schoumans), therefore, we decided to use Eq. (15) with a value of 0.5 for α. In calcareous sandy soils the amount of oxalate extractable Al and Fe (resp. Al_{ox} and Fe_{ox}) is low and the measured total sorption capacity was also found to be unrelated to the $CaCO_3$ content and/or to the contents of Al_{ox} and Fe_{ox} (Schoumans, in press). The lack of effect of $CaCO_3$ on P sorption has been shown by Frossard et al. (1992) and Holford and Mattingly (1975) and in the second paper it was shown that the specific area of $CaCO_3$ is a more important parameter in relation to the P sorption kinetics than the $CaCO_3$ content. In order to determine the critical PSD of calcareous sandy soils (Eq. (13)), the ratio of F_m and Q_m was used (Eq. (3); see Appendix A) to calculate the value of γ.

The phosphate desorption parameters were derived from the Langmuir equation (see Appendix A Eq. (2)) which was applied on desorption experiments. For non-calcareous sandy soils we used the parameters given in the protocol for non-calcareous sandy soils (Van der Zee et al., 1990a,b). Indicative parameters for calcareous sandy soils were based on experiments described in Schoumans (in press). The parameters for peat soils in The Netherlands were derived from experiments described in Schoumans (2013) and Van Beek et al. (2003). For this soil type the values of β and K differ between the soil horizons. As a result, the general equation for the critical PSD will not be constant but will depend on the characteristics of the soil horizons above the reference depth (L_{ref} = MHW). However, in low-lying peat soils the MHW always reaches the topsoil (<0.4 m below ground level) and in this part of the soil the parameters do not differ significantly.

4.3. Critical values of the PSD (PSD_{crit}) of different soil types

Table 2 shows the P sorption and desorption parameters of each soil type together with information of the critical background P concentration of each soil type (C_p). Eq. (13) was used to calculate PSD_{crit}.

The PSD_{crit} of peat soils is low when compared to the other soil types due to the low affinity to bind P (low K-value; Table 2), which means that phosphorus is relative mobile in peat soils. The range in P concentrations (5 and 95 percentile) mainly determines the range in critical phosphate saturation degree. Especially in the Western part of The Netherlands the range in P concentrations in deep groundwater is large (Table 2). The highest P concentrations are measured in geological formations containing marine sediments. It is questionable whether

Table 2
Parameters used to calculate critical phosphate saturation degree (PSD_{crit}).

Soil type	Parameters					Remarks and references
Al/Fe dominated soils	α (−)	β (−)	K ($mol\ m^{-3}$)	C_p[a] ($mg\ L^{-1}$)	PSD_{crit}[b] (%)	
Non-calcareous sandy soils	0.5	0.167	35	0.09 (0.03–0.31)	25	Van der Zee et al. (1990a,b)
Non-calcareous clay soils	0.5	0.167[c]	35[c]	0.13 (0.09–0.34)	31 (23–54)	Unpubl. data
Calcareous clay soils	0.5	0.167[c]	35[c]	1.06 (0.31–1.78)	78 (51–86)	Unpubl. data
Peat soils	0.5	0.10–0.15	1–2	0.25 (0.09–1.78)	5 (1–36)	Van Beek et al. (2003); Schoumans (2013)
Carbonate dominated soils	γ ($=F_m/Q_m$) (−)		K ($mol\ m^{-3}$)	C_p[a] ($mg\ l^{-1}$)	PSD_{crit} (%)	
Calcareous sandy soils	63–11.5		3.1	0.34 (0.34–0.52)	23 (18–37)	Schoumans (in press)

[a] Median ortho-P concentrations (C_p) based on the data of Fig. 2. Between brackets the 5 and 95 percentile values are mentioned.

[b] The critical PSD is calculated by means of Eq. (13) and based on the median ortho-P concentrations (C_p) (except non-calcareous sandy soils: values used for these soils were based on the official protocol for non-calcareous sandy soils). To obtain the concentration in mol m^{-3} the P concentrations must be divided by the mol mass (M) of P, which equals 31.

[c] Assumed same parameters values of β and K as for non-calcareous sandy soils.

these highest measured P concentrations in deep groundwater may be applied to the defined reference depth MHW, since it is unclear if these concentrations always represent the background concentration at this shallow depth. It is well known that phosphate in nutrient rich groundwater will be immobilized during aeration by co-precipitation with $CaCO_3$ or Fe(III) oxides, even in calcareous clay soils (Griffioen, 2006). In peat areas also high P concentrations can be measured in deep groundwater, but the median value is much lower than in calcareous clay soils. In shallow groundwater in peat areas total-P concentrations were measured between 0.17 and 0.57 mg L^{-1} P (Zwart et al., 2010), but also relative high ortho-P concentrations up to 1 mg L^{-1} P in soil solution (<4 m) were measured at a nutrient rich peat location (Van Beek et al., 2004).

4.4. Distribution of the phosphate saturation degree (PSD)

The PSD of each sampled location was calculated by Eq. (14) and for each stratum the average PSD was calculated based on the soil profile data. Fig. 3 shows the cumulative frequency distribution of the PSD calculated for the five soil types with agriculture as main land use. The sequence of the median PSD value is: calcareous sandy soils > non-calcareous sandy soils > calcareous clay soils > non-calcareous clay soils > peat soils. The high PSD of calcareous sandy soils is mainly caused by the relative low phosphate sorption capacity, because the lowest P accumulation in this soil type is measured in the layer 0–50 cm below surface (median value approximate 1350 kg P ha^{-1}). Fig. 4 shows the spatial distribution of the average PSD of the 95 sampled strata. Although each stratum can be found at various locations in The Netherlands (see example in Fig. 1), the differences between high P surplus regions (e.g. the intensive livestock areas in the central, southern and eastern part of the country) and lower P surplus regions are still clear. To assess the potential risk of P losses to the shallow groundwater levels (MHW) the measured PSD values of the individual profiles have to be compared with the critical PSD values of the specific soil type (Table 2).

4.5. Distribution of the phosphate-saturated (PSA)

For each stratum the phosphate saturated area (PSA) is calculated by means of the percentage of profiles exceeding the critical phosphate saturation degree. In Fig. 5 the PSA of agricultural land of each stratum is shown for two criteria: a PSD_{crit} of 25% and the PSD_{crit} specific to the soil type (Table 2). The critical PSD value of 25% represents the situation if the critical PSD value for non-calcareous soils (Van der Zee et al., 1990a) is applied to all soil types; consequently, differences in process parameters and background concentrations of the different soil types are not taken into account. If a PSD_{crit} of 25% is used, about 48% of the agricultural land is deemed to be phosphate-saturated. If the soil-specific PSD_{crit} is used, this percentage is lower (43%). If this PSD_{crit} is used the area of phosphate saturated clay soils is lower due to the higher

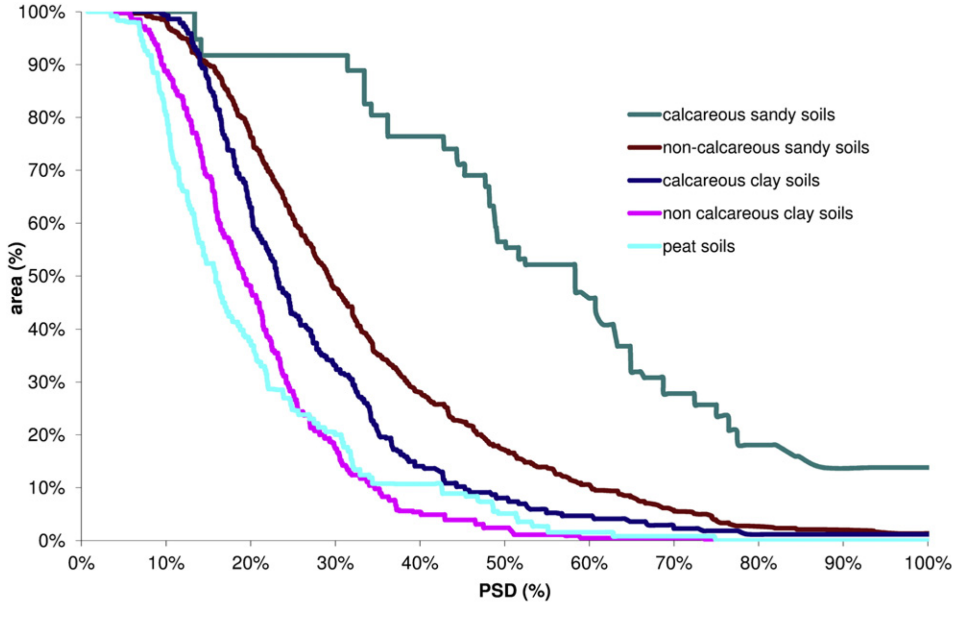

Fig. 3. Cumulative percentage distribution of the area agricultural land of the main soil types in The Netherlands in which a given PSD is exceeded.

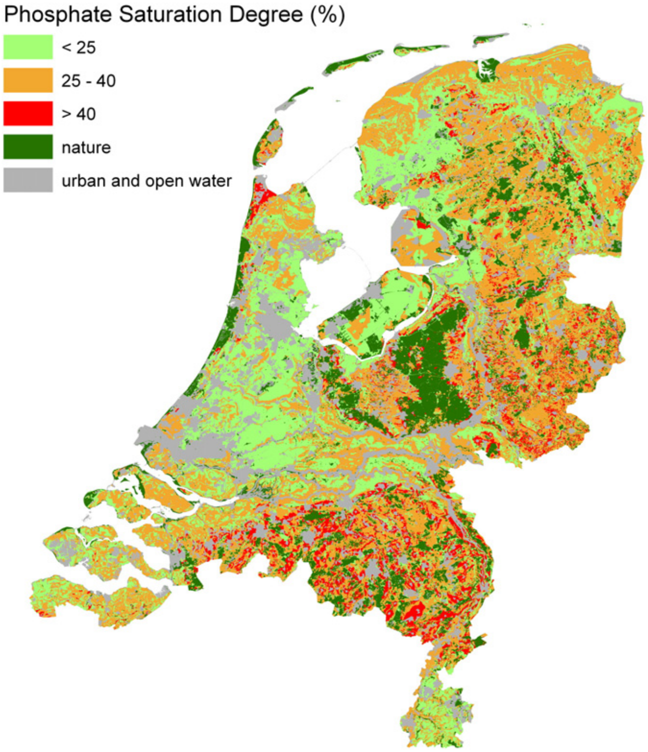

Fig. 4. Average PSD of the 95 sampled strata.

reference concentration (C_p; Table 2); many of the yellow areas (Fig. 5 left side) become green (Fig. 5 right side). On the other hand peat areas in the Western and North-western parts of The Netherlands become red, and seem to be vulnerable for P leaching to groundwater and subsequently to surface water.

4.6. Distribution of the P accumulation in soils

In addition to yielding information on the PSD and the PSA it is also possible to obtain an impression of the P accumulation of the main land uses (maize, grass, and other arable crops), because information on land use was collected during the sampling. In accordance with other measurements on P accumulation in soils (Lexmond et al., 1982), we found that maize land has the highest P accumulation (Fig. 6). The main reason for this high P content is that maize can tolerate high manure application rates, so more P has been applied on maize and thus more P has accumulated in these soils. Furthermore, in the past the legislation of the P application rates for maize was high in The Netherlands (about 350 kg P_2O_5 per ha; (Neeteson et al., 2001)). The measured average amount of P in agricultural soils in The Netherlands in the top layer (0.5 m) is about 2050 kg P ha^{-1} (4700 kg P_2O_5 ha^{-1}) and the 5‰ and 95‰ are approximately 850 and 4500 kg P ha^{-1} which equals to about 2000 and 10,000 kg P_2O_5 ha^{-1} (Fig. 6).

5. Discussion

Using the methodology to derive the critical phosphate saturation degree (PSD_{crit}) of non-calcareous sandy soils, we derived the PSD_{crit} of five soil types in The Netherlands. The method is based on the phosphate sorption and desorption characteristics of the soil and on the reference condition that should be protected, that is defined as no increase of the ortho-P concentration (C_p) at a certain reference depth (L_{ref}). Data from

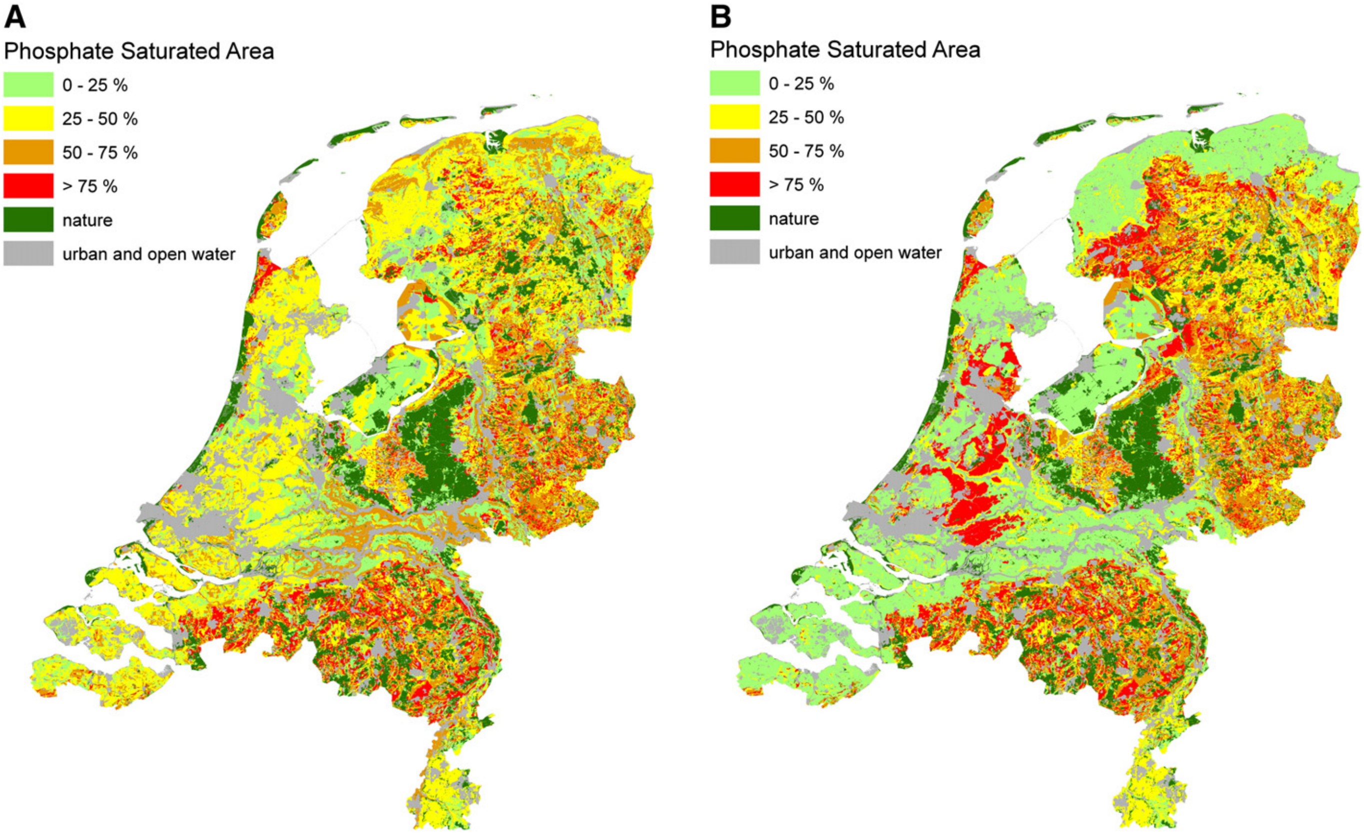

Fig. 5. Percentage of the area classified as phosphate-saturated soil for agricultural soil use: left-hand map, based on PSD_{crit} of 25%; right-hand map, based on the PSD_{crit} specific to the soil type (see Table 2).

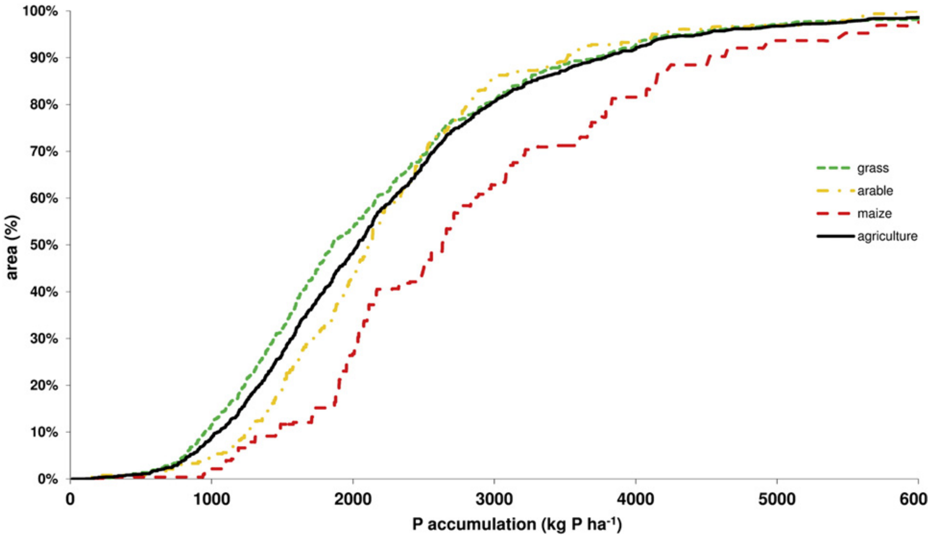

Fig. 6. Cumulative frequency distribution for the measured P accumulation in the topsoil (0–0.5 m) of various agricultural land uses.

a stratified sampling were used to determine the phosphate saturation in soils.

For all soil types and hydrological conditions the mean highest water level (MHW) was used as L_{ref} that should be protected. This approach has shortcomings. In the peat soils the groundwater level during autumn and spring in wet years will be close to the soil surface and the risk of P losses will be higher than those calculated on the basis of the MHW. Furthermore, reducing conditions can also lead to increased P release (Brand-Klibanski et al., 2007; Khalid and Patrick, 1974; Schärer et al., 2009; Shenker et al., 2005), which is not addressed by the methods used to assess PSD_{crit}. Furthermore, in clay soils where cracks are present also artificial P losses through preferential flow can occur (Svanbäck et al., 2014; Ulén and Persson, 1999; Uusitalo et al., 2001), also this is not taken into account in the methodology of the PSD_{crit}.

In areas with artificial drains, the depth of the drains would probably be more appropriate as L_{ref}, but we were unable to do so, as there is no nation-wide database with accurate information on the drained area and the depth of the artificial drains, obtained by soil survey.

For the natural background concentration of ortho-P we used the concentrations in deep groundwater (>13 m). It would be preferable to use background P concentrations from the upper part of the soil, but no such information was available for the soil types. It is likely that the P concentrations in the soil solution measured at MHW of unfertilized nature areas (mainly forests) of the distinguished soil types are more representative. If these concentrations have been determined, new values can be calculated for the critical PSD and the PSA.

The phosphate sorption and desorption characteristics were derived from other studies, but in most of these, only a few samples were subjected to the necessary time-consuming laboratory experiments. Therefore, the calculation of the critical PSD is only indicative for the soil types in question.

The P status of the soils (actual PSD and total P accumulation) was derived from data collected at about 1400 sampling locations (using stratified sample statistics). We found that in approximately 43% of the agricultural land in The Netherlands, the critical PSD value for the given soil type is exceeded. If the general value of $PSD_{crit} = 25\%$ (representative for non-calcareous sandy soils) is used, about 48% of the agricultural land in The Netherlands is above this critical value. Based on these findings it can be calculated that on about 1.0–1.2 million ha of agricultural land in The Netherlands the soil P accumulation is too high in relation to the phosphate sorption capacity. Consequently, the P concentration at MHW will exceed the natural background concentration at some time.

The PSD is an indicator for the potential risk of P losses to surface water. However, soils that are phosphate-saturated are not always the soils with the greatest P losses to surface waters. The actual risk of P leaching depends on the location and on the hydrological situation, e.g. the elevation of the field in relation to ditches, brooks and rivers, and drainage conditions. In addition, for many regions there is insufficient data on the contribution of background losses to total P losses at catchment scale. Furthermore, in practice the relationship between PSD and the actual P loss is not one to one because during excessive use of P fertilizers and manure, a major part of the P accumulation becomes strongly sorbed and the reversibility is poor (Koopmans et al., 2004a,b). When a P-rich sandy soil was depleted in the laboratory using a membrane filled with FeO, ortho-P measured in a 1:2 (w:v) water extract decreased much faster than the PSD and it was found that the relationship between P-1:2 and PSD for undepleted soil samples was not valid for the depleted soil samples (Koopmans et al., 2001). The consequence is that the soil PSD will remain high, whereas the P concentration in the soil solution decreases relatively fast (Koopmans et al., 2004b). This implies that at a certain PSD different P concentrations in soil solution can be observed which is visualized in Fig. 7 as example. The curve can be different for different soil types, but the principle is valid for all soil types. This is known as the hysteresis effect of P sorption and P desorption in soils (Barrow, 1983). These findings also imply that a relationship between soil test P and P loss via leaching or surface runoff that has been developed for field sites

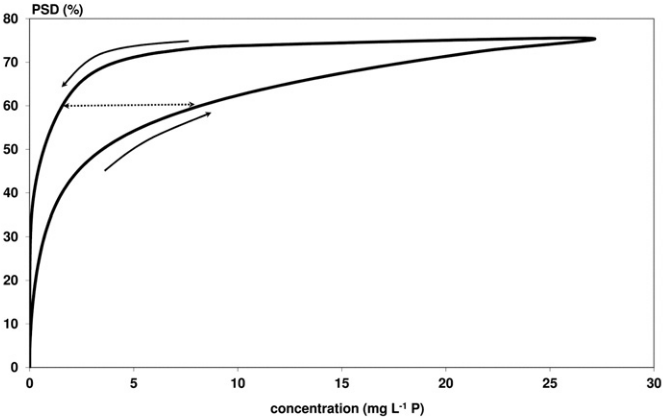

Fig. 7. Relation between the PSD and the ortho-P concentration in soil solution during loading of the soil with phosphate (upward line) and mining of the soil (backward line).

where P is accumulating may not be valid in situations where prolonged depletion of soil P has taken place; this hampers the interpretation of the PSD in relation to the actual risk of P losses. It is important that these aspects are taken into account with respect to the Water Framework Directive (WFD; EEC, 2000), because the areas and fields that contribute most to P losses to surface water should be identified. Nevertheless, despite these notices the PSD is a simple method to assess the potential risk of P loss to groundwater, and subsequently to surface water. Strategies and additional measures are needed for fields with a high PSD and shallow groundwater levels in order to reduce the P losses from agricultural land to surface waters within a catchment.

Alternative ways of calculating PSD

Instead of acid ammonium oxalate, other extraction methods have been used to calculate a P saturation degree to be used for risk assessment or plant uptake. Table 3 presents examples of various methods used for estimating the amount of P sorbed (instead of P_{ox}), and for the sorption maximum (instead of $Fe_{ox} + Al_{ox}$).

Uusitalo and Tuhkanen (2000) found that oxalate extracted the same amounts as those found in inorganic fractions subjected to the Chang & Jackson procedure (NH_4F, NaOH and H_2SO_4), and stated that “oxalate extraction estimates total inorganic P rather than the pool relevant in environmental risk assessment”. In order to measure a pool of P that is assumed to be more relevant, Beauchemin and Simard (1999) used colorimetry instead of ICP for measuring P in the oxalate extract, to avoid including organic forms of P. Sharpley (1996) used FeO strips for measuring the amount of reversibly sorbed P. Since oxalate may dissolve hardly mobile apatitic P, Turtola and Yli-Halla (1999) used the sum of NH_4F + NaOH extractable P instead of P_{ox}, in combination with $Fe_{ox} + Al_{ox}$. The presence of Ca–P compounds in manured soils has been demonstrated by various researchers (e.g. Beauchemin et al. (2002); De Haan and Van Riemsdijk (1986); Sharpley et al. (2004)).

Table 3
Examples of different indices for calculating degree of P saturation (sorbed P/sorption maximum).

Sorbed P, extractant	Sorption maximum	Ref.[a]
Oxalate	$a_m * (Al + Fe)$-oxalate	See text
Oxalate	(Al + Fe)-oxalate ($a_m = 1$)	[1]
Oxalate (MRP)	(Al + Fe)-oxalate	[2]
FeO-strip P	(Al + Fe)-oxalate	[3]
NH_4F (Al-P)	Al-oxalate	[4,20]
NaOH (Fe-P)	Fe-oxalate	[4]
NH_4F + NaOH	(Al + Fe)-oxalate	[5]
Mehlich I	(Al + Fe)-oxalate	[6]
Mehlich I	(Al + Fe)-Mehlich (molar)	[6,19]
Mehlich III	(Al + Fe)-Mehlich (molar)	[7,19]
Mehlich III	Al-Mehlich (molar)	[17]
FeO-strip P	Sorption max adsorption isotherm	[8]
Oxalate	Sorption max + P-oxalate	[9,10]
Mehlich III	Sorption max	[11]
Mehlich III	Sorption max + Mehlich III	[12]
Mehlich I	Sorption index + Mehlich I	[10]
Mehlich III	Sorption index	[13]
Water	Sorption index	[13]
0.1 N NaOH	Sorption index	[14]
Used for predicting plant-P		
Isotopic exchange	Sorption max	[15]
NaOAc or $NaHCO_3$	Sorption max	[16]
$NH_4OAc + NH_4F$	Al-NH_4Oac	[18]

[a] [1] Pote et al. (1996); [2] Beauchemin and Simard (1999); [3] Sharpley (pers. comm.); [4] Hartikainen (1979); [5] Turtola and Yli-Halla (1999); [6] Nair and Graetz (2002); [7] Maguire and Sims (2002); [8] Sharpley (1996); [9] Yuan and Lavkulich (1994);[10] Pautler and Sims (2000); [11] Sharpley (1995); [12] Sharpley (1997); [13] Pote et al. (1999); [14] Sallade and Sims (1997); [15] Thompson et al. (1960); [16] Kuo (1990); Kuo et al. (1988)); [17] Khiari et al. (2000); [18] Magdoff et al. (1999); [19] Nair et al. (2004); [20] Yli-Halla (1989).

As mentioned above, in The Netherlands the long-term P sorption maximum of non-calcareous soils is estimated as $\alpha_m * (Fe_{ox} + Al_{ox})$ with $\alpha_m = 0.5$. However, Beauchemin and Simard (1999) stated that “the factor 0.5 is empiric, and was obtained from a given set of soils and experimental conditions”. For this reason, some authors have simply used $\alpha_m = 1$ (see Table 3), whereas others have determined α_m themselves. Pautler and Sims (2000) calculated α_m by multiplying the sum of P_{ox} and Q_{max} of soils by 1.8, and found an average value of 0.61. By contrast, Van der Zee and Van Riemsdijk (1988) calculated α_m by $F_m = P_{ox} + 1.8F_r$, where F_r is the amount of P sorbed after 40 h.

In many countries, soil laboratories do not routinely apply the oxalate extraction as it is laborious. Much research has therefore been done on the suitability of a common soil test such as Mehlich-1 or Mehlich-3 for calculating a saturation index. Highly significant linear correlations have been found between PSD of a layer calculated using oxalate and Mehlich-1 or -3 (Esmaeilipour et al., 2012; Nair et al., 2004; Schiettecatte, 2006). Mehlich extractable P has been used either in combination with Mehlich-(Fe + Al), or with Mehlich-Al alone, or with other estimators of the sorption maximum of a soil (Table 3). The other estimators are the fitted maximum of the Langmuir isotherm, or a sorption index, calculated from P sorption to a soil at one initial P concentration (60 mg P L^{-1}) in solution (Pote et al., 1999), to which an initial amount sorbed can be added (P_{ox} or Mehlich-P; Table 3). However, although the correlation between PSD-oxalate and PSD-Mehlich-1,3 is high, the amounts extracted may differ considerably. For Fe, Maguire and Sims (2002) found that on average, Mehlich-3 extracted only 26% of the amount extracted with oxalate; for P the figure was 54% and for Al it was 80%. So, Mehlich-3 is not very effective in extracting amorphous iron oxides, and may thus underestimate P sorption capacity in iron-rich soils.

Summarizing: there is great variation in the methods used for calculating a PSD, both for determining the amount of P sorbed and for determining the P sorption capacity of a soil. All methods other than oxalate will extract less P and less (Al + Fe) from soils than oxalate, or will calculate a smaller sorption maximum if based on short-term sorption experiments. However, it may be expected that the fractions of P and (Al + Fe) not extracted by alternative methods will vary among soils, which makes it difficult to compare calculated values of PSD.

6. Conclusions

This study shows that it is technically possible to determine the potential risk of P leaching to groundwater by comparing the actual phosphate saturation degree of a soil with the soil type specific phosphate saturation degree. In order to determine the critical PSD values, information is needed about (1) the environmental conditions, (1a) the reference depth to protect and (1b) the natural background concentration, and (2) the phosphate characteristics of the soil types: (2a) maximum phosphate sorption capacity, (2b) fraction of easily available P and (2c) Langmuir adsorption constants. The critical PSD is indicative because there are still some uncertainties, mainly due to the natural background concentration. About 43% of the agricultural area in The Netherlands has a PSD above the soil-specific critical value and the measured average amount of P accumulated in the soil varies between approximately 850 and 4 500 kg P per ha (respectively 5‰ and 95‰).

However, the PSD is still only an indicator that gives information about the potential risk of P losses from land to groundwater, since e.g. prolonged anaerobic conditions and preferential transport in cracked soils are not taken into account. In order to predict the actual risk, more information is needed about the local conditions of a field, particularly about the hydrological conditions, like groundwater fluctuation during the year and amount of water discharges via different pathways (surface runoff, subsurface runoff, tile drains, deep groundwater flows) to adjacent surfaces waters. Nevertheless, the PSD, as defined in the protocol phosphate saturated soils, is a simple indicator to assess the potential risk of P loss to groundwater, and subsequently to surface water.

Parameters		
Q	= amount of adsorbed phosphate	(mmolkg^{-1} P)
Q_m	= maximum phosphate adsorption capacity	(mmolkg^{-1} P)
F	= amount of sorbed phosphate	(mmolkg^{-1} P)
F_m	= maximum phosphate sorption capacity	(mmolkg^{-1})
ρ	= dry bulk density	(kg m^{-3})
L	= depth	(m)
L_s	= maximum phosphate penetration depth	(m)
L_{ref}	= reference depth	(m)
K	= k_a/k_d = Langmuir adsorption coefficient	(m^{3}mol^{-1})
M	= molar mass of P (= 31)	(g mol^{-1})
c	= ortho-P concentration	(molm^{-3})
C_p	= maximum ortho-P concentration at reference depth (L_{ref})	(molm^{-3})
$\alpha, \beta, \gamma, \varepsilon, \lambda, \tau$	= defined coefficients	(−)
P_{ox}, Al_{ox}, Fe_{ox}	= oxalate-extractable P, Al and Fe	(mmolkg^{-1})
Z	= phosphate saturation fraction to depth L_{ref}	(−)
PSD_{crit}	= critical phosphate saturation degree to depth L_{ref}	(%)
PSD	= phosphate saturation degree of the soil to depth L	(%)
P_{act}	= actual amount of phosphate accumulation in the soil to depth L	(kg P_2O_5 ha^{-1})
PSC	= phosphate sorption capacity of the soil to depth L	(kg P_2O_5 ha^{-1})
PSC_m	= maximum phosphate sorption capacity of the soil to depth L	(kg P_2O_5 ha^{-1})

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Appendix A. Phosphate saturation degree (PSD)

The relationship between ortho-P concentration in soil solution and the amount of easily reversible bound P in the soil, as measured with the infinite sink method (Menon et al., 1989), can be described by the Langmuir equation (Van der Zee et al., 1987).

K	= k_a/k_d = Langmuir adsorption constant	(m^3 mol^{-1})
c	= ortho-P concentration	(mol m^{-3})
Q_m	= maximum phosphate adsorption capacity	(mmol kg^{-1})

$$Q = \frac{KcQ_m}{1 + Kc} \tag{2}$$

The maximum phosphate sorption capacity (F_m in mmol kg^{-1}) is defined as the amount of phosphate sorbed after which no substantial phosphate will be bound anymore. In most situations it takes years before the level is reached. The ratio between the maximum phosphate sorption capacity (F_m) and the maximum phosphate adsorption capacity (Q_m) is defined as:

$$\gamma = F_m/Q_m \tag{3}$$

It is assumed that for all phosphate concentrations this ratio is valid (Van der Zee et al., 1990a). So, the amount of total P sorbed can be assessed by the amount of P adsorbed:

$$F = \gamma Q \tag{4}$$

Further we define:

$$\lambda = \overline{\rho_{L_s - L_{ref}}}/\overline{\rho_{0-L_s}} \tag{5}$$

$$\tau = \overline{F_{m,L_s - L_{ref}}}/\overline{F_{m,0-L_s}} \tag{6}$$

The maximum phosphate penetration depth in relation to the critical concentration ($c = C_p$) at reference depth (L_{ref}) can then be calculated by substitution of Eqs. (2), (3), (4), (5) and (6) into Eq. (1) which leads to:

$$L_s = \frac{\gamma\lambda\tau KC_p}{1 + \gamma\lambda\tau KC_p} L_{ref} \tag{7}$$

The maximum phosphate saturation depth in a soil (L_s) can be calculated by Eq. (7) and depends on the (phosphate) soil characteristics, the reference depth (L_{ref}) and the maximum acceptable P concentration ($c = C_p$) at depth L_{ref}.

However, it is difficult to determine this maximum phosphate saturation depth in soil. Therefore, a relationship is derived based on the total phosphate accumulation in the soil to reference depth L_{ref}. In practice, this means that the actual phosphate accumulation (P_{act} in kg P_2O_5 ha^{-1}) in the soil may not exceed the maximum phosphate sorption capacity (PSC_m in kg P_2O_5 ha^{-1}) to penetration depth (L_s). So, the phosphate accumulation is too high if:

$$P_{act,0-L_{ref}} \geq PSC_{m,0-L_s} \tag{8}$$

Dividing both sites by $PSC_{m,0-L_{ref}}$ results into:

$$\frac{P_{act,0-L_{ref}}}{PSC_{m,0-L_{ref}}} \equiv Z \geq \frac{PSC_{m,0-L_s}}{PSC_{m,0-L_{ref}}} = \frac{\overline{F_{m,0-L_s}}\ L_s\ \overline{\rho_{0-L_s}}}{\overline{F_{m,0-L_{ref}}}\ L_{ref}\ \overline{\rho_{0-L_{ref}}}} \tag{9}$$

where Z is defined as the phosphate saturation fraction of the soil to depth L_{ref}.

The value of $\overline{\rho_{0-L_{ref}}}\ \overline{F_{m,0-L_{ref}}}$ can be calculated from:

$$\overline{\rho_{0-L_{ref}}}\,\overline{F_{m,0-L_{ref}}} = \frac{L_s\ \overline{\rho_{0-L_s}}\,\overline{F_{m,0-L_s}} + (L_{ref} - L_s)\overline{\rho_{L_s-L_{ref}}}\,\overline{F_{m,L_s-L_{ref}}}}{L_{ref}} \tag{10}$$

Substitution of Eq. (10) in Eq. (9) results into:

$$Z \geq \frac{1}{\frac{L_{ref}}{L_s}(1 - \tau\lambda) + \tau\lambda} \tag{11}$$

By substitution of Eq. (7) into Eq. (11) the phosphate saturation fraction (Z; Eq. (9)) becomes:

$$Z \equiv \frac{P_{act,0-L_{ref}}}{PSC_{m,0-L_{ref}}} \geq \frac{\gamma KC_p}{1 + \gamma KC_p} \tag{12}$$

So, in general the critical phosphate saturation degree (PSD) of a soil to the reference depth (L_{ref}) is defined by:

$$PSD_{crit} = \frac{\gamma K C_p}{1 + \gamma K C_p} * 100(\%) \quad (13)$$

PSD =Phosphate saturation degree of the soil (%)

The PSD_{crit} value will be compared to the actual PSD of the soil, which can be calculated by:

$$PSD \equiv \frac{P_{act,0-L_{ref}}}{PSC_{m,0-L_{ref}}} * 100(\%) \quad (14)$$

The determination of the critical PSD is valid for all soil types, because it is based on the general phosphate kinetics in soils and independent of the type of soil particles P reacts with. The critical PSD is based on the condition that each soil type has a maximum total phosphate sorption capacity (F_m) and a maximum capacity of the soil to bind P in an easily soluble form (Q_m). The critical PSD value of a soil (Eq. (13)) depends only on the ratio of both parameters (γ as defined by Eq. (3)) and the affinity of the soil to bind the easily reversible sorbed P in soils (K value). By collecting these parameters the critical PSD of a soil type can be determined.

In the Dutch protocol on phosphate saturated soils, the soil-specific values have been set for non-calcareous sandy soils (Van der Zee et al., 1990a,b) and the reference ortho-P concentration was set by a technical committee (TCB, 1990). The used parameters are described hereafter.

The soil-specific value of γ is defined by the ratio of F_m and Q_m (Eq. (3)). In non-calcareous sandy soils, the maximum phosphate sorption capacity (F_m) is related to the sum of the amount of microcrystalline (amorphous) Al and Fe (Beek, 1979; Schoumans et al., 1986, 1987; Van der Zee and Van Riemsdijk, 1988) which can be extracted with oxalate (Schwertmann, 1964):

F_m =maximum phosphate sorption capacity (mmol kg^{-1})
α =maximum phosphate sorption coefficient (−)

β =maximum phosphate adsorption coefficient (−)

α =0.5 (−)
β =0.167 (−)
γ $= F_m/Q_m = \alpha/\beta = 3$ (−)
K = 35 (m^3 mol^{-1})

$$F_m = \alpha(Al_{ox} + Fe_{ox}). \quad (15)$$

C_p $=0.1$ mg P $L^{-1} = 0.1/31$ (mol m^{-3})

The maximum phosphate adsorption capacity of non-calcareous sandy soils (Q_m) is also related to the amount of amorphous Al and Fe (Van der Zee et al., 1987):

$$Q_m = \beta(Al_{ox} + Fe_{ox}). \quad (16)$$

For non-calcareous sandy soils the following parameters were set (Van der Zee et al., 1990a,b):

The reference ortho-P concentration set by a technical committee (TCB, 1990) was:

Substitution of these values in Eq. (13) leads to a PSD_{crit} of 24% but in practice often a value of 25% is used. Thus, a non-calcareous sandy soil is deemed to be phosphate-saturated if the phosphate accumulation in the soil up to depth L_{ref} is more than 25% of the maximum phosphate sorption capacity, calculated to this depth. At higher values of the PSD, the P concentration at depth L_{ref} will at some time exceed the defined critical P concentration (C_p) due to leaching of accumulated phosphate from the topsoil.

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