Identification and characterization of phosphorus-rich sandy soils

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Abstract

For the identification of phosphorus-rich and phosphorus-leaky soils, various extraction methods have been proposed as indicators to estimate the risk of phosphorus (P) losses. In this study we compare and discuss the extractability of P from sandy soils, using various modifications of mild extractants (water and $CaCl_2$), FeO-impregnated filter-paper strips (Pi-test), and ammonium oxalate (P-ox).

In the soils studied, the amounts of water- and $CaCl_2$-extractable P were (much) smaller than the amounts of P extracted with FeO-strips or with ammonium oxalate. With the water-based extraction method Pw (1:60 v:v soil:solution ratio), end-over-end shaking (Pw-2) compared with reciprocative shaking (Pw-1) resulted in increased amounts of extractable P in all soils. Because in the original Pw procedure reciprocative shaking and end-over-end shaking were implicitly treated as being exchangeable, the shaking method needs further standardization. Exponential relationships were found between *P-1:2* (water-extractable P at a 1:2 w:v soil:solution ratio; roughly comparable with P in the soil solution) on the one hand, and *Pw-1* ($R^2 = 0.99$; $P < 0.001$) and *Pw-2* ($R^2 = 0.96$; $P < 0.001$) on the other. The non-linearity of such relationships must be taken into account if Pw is used as an indicator to estimate the risk of P leaching, i.e., at high values of *Pw*, leaching may be underestimated if a linear instead of a non-linear relationship is used. A similar exponential relationship was observed between *P-1:2* and the P saturation degree (*PSD*) for soils sampled from the same site ($R^2 = 1.00$; $P < 0.001$). The relationship was not valid for soils from other sites, suggesting that the PSD as such cannot be used as an indicator for the risk of leaching dissolved P. Based on both PSD and P-1:2, a simple alternative scheme is proposed to provide guidance for selecting P-leaky soils and for evaluating the effectiveness of measures to restore such soils.

Keywords: phosphorus, P extractability, $CaCl_2$-extractable P, water-extractable P, Pw, Pi-test, P saturation degree, risk indicators, leaching, sandy soils.

Introduction

In the course of the 20th century, intensively managed agricultural soils have become enriched with phosphorus (P) as the result of P applications in the form of chemical fertilizers and animal manure that exceeded the P taken up by the harvested crops. The enrichment has been excessive in areas with intensive livestock farming, where heavy applications of animal manure have caused a near saturation of the soil with P (e.g. Breeuwsma *et al.*, 1995; Lexmond *et al.*, 1982; Pautler & Sims, 2000). As the leaching of P from P-rich soils to surface water contributes to eutrophication and associated adverse effects, these soils are now a menace to surface waters (e.g. Hosper, 1997; Sharpley *et al.*, 1994). The main routes of P losses from agricultural soils to surface water are through runoff, especially on sloping land, and through leaching of drainage water. The latter is relevant especially in flat areas with shallow groundwater.

In the period 1950–2000, the average annual P surplus of agricultural land in the Netherlands ranged from 25 to 45 kg ha^{-1} (e.g. Smaling *et al.*, 1999). Regionally, surpluses have been much larger, especially in the sandy areas of the east and south of the country, where intensive livestock farming systems predominate. From 1986 onwards, a series of policies and measures has been implemented to reverse the trend of increased P loading of agricultural soils (e.g. Hotsma, 1997; Oenema & Roest, 1998). As from 2003, the net loading of the soil has been limited to a maximum of 8.7 kg P ha^{-1} per year for all agricultural land. Despite these efforts, P leaching from agricultural soils to surface water is expected to further increase, as the enrichment of the already P-rich agricultural soils continues, although be it at a decreased rate. Estimates indicate that agricultural soils contribute on average 30% to the total P load of surface water in the Netherlands, but in some watersheds this contribution can be as high as 90% (Coppoolse & Kersten, 1992). Evidently, to effectively decrease P leaching from agricultural soils to surface water, regionally additional measures are needed.

Agricultural soils are generally considered to be 'diffuse' sources of P leaching whereas P-saturated soils are considered to be 'hot spots'. So restoration measures should focus on these hot spots. Various indicators have been proposed as suitable for assessing the risk of P leaching from agricultural soils to surface waters. One of the first proposals has been the P saturation degree (PSD) as described by Van Der Zee *et al.* (1990). Using this indicator, Reijerink & Breeuwsma (1992) estimated that 70% of the agricultural land on sandy soils in the Netherlands – amounting to 400,000 ha – might contribute to (excessive) P enrichment of surface waters. However, the PSD is only indicative for the potential risk of P leaching. Evidently, P in the soil solution draining from the soil to the surface water determines the actual leaching of P from P-enriched sandy soils. The P concentration in the soil solution and the transport of P from the soil to the surface water depend on soil- and site-specific conditions, and on soil management (Lemunyon & Gilbert, 1993; Sharpley, 1995). Important soil characteristics are soil-P level, P-sorption capacity, pH, water-infiltration capacity and permeability, and groundwater level (e.g. Beauchemin & Simard, 1999). Important site-specific conditions are geography (distance between site and water body), surface topography and climate (rainfall). Important manage-

ment factors are land use (arable land or grassland), soil cultivation and P application (type of chemical fertilizer and animal manure, timing and method of application). Evidently, the release of P from soil to surface water depends on a complex of interacting factors, so best-management practices need to be taken into account for these interacting factors to be effective in decreasing P losses to the environment.

The purpose of this paper is to refine the identification of P-leaky sandy soils, so as to improve the effectiveness of restoration measures. We accept the PSD as a robust indicator for the potential risk of P leaching, but to assess the actual risk of P leaching, a P intensity indicator should be used. We propose that a combination of soil characteristics that are indicative of both the potential and the actual risks of P release, are helpful in identifying the soils that most urgently need restoration measures and adapted best-management practices (e.g. Chardon *et al.*, 1996b; Oenema & Roest, 1998). In this paper we (i) compare and discuss the extractability of P from a selected number of sandy soils varying in *PSD*, using various mild extraction methods that are indicative of readily dissolved P in the soil, (ii) evaluate the relationships between these extraction methods, and (iii) propose a simple scheme for establishing priorities in the implementation of measures for the restoration of P-leaky soils.

Materials and methods

Soils

Samples were taken from the topsoil (0–30 cm) of four experimental sites in the northern part of the Netherlands, i.e., Emmer Compascuum (abbreviated as Emmer C.), Giethoorn, Wijster and Haren, representing soils with a wide range in organic matter and extractable Fe, Al and P contents (Table 1). Although these sites are not in the centre of intensive livestock farming, the soils selected can be considered as representative for sandy soils throughout the Netherlands. In Haren, the samples were taken from three treatments in a long-term field experiment (Del Castilho *et al.*, 1993). Treatments Haren 7 and Haren 11 had received 40 and 160 tons of pig slurry

Table 1. Physical and chemical characteristics of the soils studied. Means with sample standard deviation of [Fe+Al]-ox and PSD in brackets (n = 3).

Soil	Clay	Silt	Sand	$[Fe+Al]$-ox (mmol kg^{-1})	pH-H$_2$O	Organic matter (%)	Total P content (mg P kg^{-1})	PSD[1]
	--------- (%) -----------							
Emmer C.	3.0	7.7	89.3	52.9 (2.1)	5.0	14.4	327	0.28 (0.004)
Giethoorn	3.9	12.3	83.7	135.7 (6.8)	5.3	7.3	830	0.34 (0.006)
Wijster	4.0	17.0	79.0	90.3 (0.8)	5.9	4.8	734	0.44 (0.002)
Haren 1	4.1	17.3	78.6	65.2 (1.4)	5.3	3.6	593	0.46 (0.005)
Haren 7	3.6	21.3	75.1	64.5 (1.8)	5.2	3.6	614	0.52 (0.010)
Haren 9	3.8	23.0	73.2	71.7 (0.3)	6.0	3.7	917	0.66 (0.004)
Haren 11	3.6	17.3	79.2	63.6 (1.0)	5.7	3.7	978	0.85 (0.003)

[1] $\alpha = 0.5$.

per ha per year, respectively, for 11 consecutive years. Treatment Haren 9 had received P in the form of only superphosphate, equivalent to 80 tons of pig slurry per ha per year over the same period. The Haren 1 soil was sampled from a field in the vicinity of the site of the long-term field experiment. The Haren 1, Emmer C., Giethoorn and Wijster soils had received variable mixtures of animal manure and superphosphate in amounts corresponding with those used in common agricultural practice.

Soil samples were dried at 40 °C, and passed through a 2-mm sieve. Particle-size distribution, pH-H_2O, organic matter (Houba *et al.*, 1997) and total P content (Houba *et al.*, 1993) were determined using standard analytical procedures. Table 1 shows the selected physical and chemical characteristics of the soils studied.

P-extraction methods

The extractability of P from the selected soil samples was characterized using 8 methods denoted as P-1:2, P-$CaCl_2$, P-1, P-2, Pw-1, Pw-2, Pi and P-ox (Table 2). The first 6 procedures include mild extractants (water and $CaCl_2$) commonly used in agriculture and horticulture to determine the content of readily available P in soil samples (e.g. Tunney *et al.*, 1997). Pi and P-ox are indicative of the amounts of total plant-available P and of P adsorbed to amorphous Fe- and Al-(hydr)oxides, respectively.

A modification of the method of Sonneveld *et al.* (1990) was used to determine water-extractable P at a 1:2 w:v soil:solution ratio (P-1:2). Water-based soil suspensions were shaken reciprocatively (130 strokes per minute, spm) for one hour. After centrifugation (1800 g for 10 minutes), supernatants were filtered through a 0.45 μm filter, and P was determined in the filtrates. $CaCl_2$-extractable P (P-$CaCl_2$) was determined in 0.01 M $CaCl_2$ according to Houba *et al.* (1986). The $CaCl_2$-based soil suspensions were shaken reciprocatively at 165 spm. In the original Pw procedure of Sissingh (1971), reciprocative and end-over-end shaking of the 1:60 v:v water extracts were implicitly treated as being exchangeable. To evaluate the effect of the shaking method, the water extracts were either shaken reciprocatively at 165 spm with the bottles placed upright (Pw-1) or end-over-end at 30 rotations per minute (rpm) (Pw-2). Houba *et al.* (1986) recommended the use of 0.01 M $CaCl_2$ as an extractant for determining the content of readily available P in soil samples, because of the high reproducibility of the results. To evaluate the effect of the use of 0.01 M $CaCl_2$, water was replaced with 0.01 M $CaCl_2$ in the Pw method of Sissingh (1971) for determining *P-1* and *P-2*. Comparable with Pw-1 and Pw-2, $CaCl_2$-based soil suspensions were shaken either reciprocatively (P-1) or end-over-end (P-2). A slightly modified method of Sissingh (1983) was used for FeO-strip extractable P (Pi). Filter papers were immersed in a 0.37 M $FeCl_3$ solution for 5 minutes, and then neutralized in a 2.7 M NH_4OH solution for 45 seconds. The 0.01 M $CaCl_2$-based soil suspensions (1:40 w:v) were shaken end-over-end at 4 rpm for 16 hours with one FeO-strip in a fixed position. Adhering soil particles were removed using an airbrush as recommended by Chardon *et al.* (1996a). Subsequently, shaking end-over-end at 30 rpm with 0.1 M H_2SO_4 dissolved the FeO with adsorbed P, which was then determined in the extracts. Ammonium oxalate extractable P (P-ox) was determined by the method of Schwertmann (1964). Soil suspensions were shaken reciprocatively at

Table 2. Procedures of the extraction methods used for the characterization of the P-rich sandy soils.

Extraction method	Extractant	Soil:solution ratio	Shaking procedure[1]	Shaking time (h)	Reference
P-1:2	H_2O	1:2 w:v	130 spm rec.	1	modified after Sonneveld et al. (1990)
P-CaCl₂	0.01 M CaCl₂	1:10 w:v	165 spm rec.	2	Houba et al. (1986)
P-1	0.01 M CaCl₂	1:60 v:v	165 spm rec.	1	modified after Sissingh (1971)
P-2	0.01 M CaCl₂	1:60 v:v	30 rpm eoe	1	modified after Sissingh (1971)
Pw-1	H_2O	1:60 v:v	165 spm rec.	1	Sissingh (1971)
Pw-2	H_2O	1:60 v:v	30 rpm eoe	1	Sissingh (1971)
Pi	FeO-strip in 0.01 M CaCl₂	1:40 w:v	4 rpm eoe	16	modified after Sissingh (1983)
P-, Fe- and Al-ox	Ammonium oxalate	1:20 w:v	165 spm rec.	2	Schwertmann (1964)

[1]rpm: rotations per minute; spm: strokes per minute; eoe: end-over-end; rec.: reciprocative.

165 spm. The *PSD* was calculated as follows:

$$PSD = \frac{P\text{-}ox}{\alpha * [Fe + Al]\text{-}ox} \tag{1}$$

where
P-ox and *[Fe+Al]-ox* are the amounts of P, Fe and Al (mmol kg^{-1}) extractable with ammonium oxalate, and α denotes the saturation factor, i.e., affinity of *[Fe+Al]-ox*.

In acidic sandy soils, Van Der Zee et al. (1990) reported α values ranging from 0.4 to 0.6 with an average of 0.5. This means that 1 mmol of [Fe+Al]-ox sorbs a maximum amount of 0.5 mmol of P. Although the value of α depends on experimental conditions such as equilibration time and initial P concentration – and may thus be somewhat variable – we have used $\alpha = 0.5$ to calculate the PSD of our soils.

The extractions were carried out in triplicate. In all extracts, except ammonium oxalate, P was determined according to Murphy & Riley (1962). Concentrations of P, Fe and Al in ammonium oxalate extracts were determined using inductively coupled plasma atomic emission spectroscopy (ICP-AES).

Results and discussion

Soil-extractable P

The amounts of P extracted ranged from less than 1 mg P kg^{-1} (*P-1:2*) to more than 800 mg P kg^{-1} (*P-ox*) of soil, depending on extraction procedure and soil sample

Table 3. Amounts of P extracted (mg P kg^{-1}) from the soil samples studied, using 8 extraction methods, i.e., P-1:2, P-CaCl$_2$, P-1, P-2, Pw-1, Pw-2, Pi and P-ox. Means with sample standard deviation in brackets (n = 3). Table 2 shows the procedure of these extraction methods.

Soil	P-1:2	P-CaCl$_2$	P-1	P-2	Pw-1	Pw-2	Pi	P-ox
Emmer C.	3.75 (0.01)	10.0 (0.19)	10.3 (0.55)	15.8 (0.22)	17.1 (0.93)	23.1 (0.11)	48.0 (4.64)	232 (5.6)
Giethoorn	1.13 (0.01)	2.8 (0.04)	2.5 (0.29)	4.9 (0.09)	6.3 (0.77)	10.3 (0.12)	30.9 (1.15)	706 (34.1)
Wijster	2.46 (0.02)	3.2 (0.12)	4.5 (0.54)	6.8 (0.02)	13.2 (0.58)	22.3 (1.11)	63.5 (0.57)	614 (3.7)
Haren 1	0.41 (0.00)	1.0 (0.04)	1.1 (0.09)	2.1 (0.05)	2.8 (0.21)	6.0 (0.22)	19.2 (0.26)	461 (5.1)
Haren 7	0.61 (0.00)	1.7 (0.03)	2.4 (0.07)	3.9 (0.11)	5.9 (0.57)	11.3 (0.60)	33.0 (0.52)	522 (5.4)
Haren 9	1.71 (0.01)	3.3 (0.05)	4.7 (0.13)	7.3 (0.07)	11.5 (0.35)	20.1 (0.67)	52.2 (0.54)	731 (4.2)
Haren 11	7.40 (0.03)	8.9 (0.09)	9.2 (0.57)	14.7 (0.26)	22.8 (0.54)	33.9 (0.12)	69.7 (3.47)	833 (9.8)

(Table 3). Relative differences among soil samples were more pronounced with the mild extractants (water and CaCl$_2$) (factor 10) than with the Pi and P-ox procedures (factor 4). With water and CaCl$_2$, the largest amounts were extracted from the Haren 11 and Emmer C. soils, and the smallest amount from the Haren 1 soil. With P-ox, the largest amount was also extracted from the Haren 11 soil, but the smallest from the Emmer C. soil. The ratio between mild extractants and P-ox was lowest in the soil samples from Haren 1, Haren 7 and Giethoorn and highest in the Emmer C. soil. This suggests that the relative P extractability with mild extractants was largest for the soil sample from Emmer C. Generally, amounts of P extracted increased in the following order:

$$P\text{-}1{:}2 < P\text{-}CaCl_2 < P\text{-}1 < P\text{-}2 < Pw\text{-}1 < Pw\text{-}2 < Pi \ll P\text{-}ox.$$

The coefficient of variation was ≤ 0.01 for *P-1:2* and ranged from < 0.01 to 0.05 for *P-CaCl$_2$*, *P-2*, *Pw-2* and *P-ox*, and from 0.01 to 0.12 for *P-1*, *Pw-1* and *Pi*, suggesting that P-1:2 is the most robust procedure whereas P-1, Pw-1 and Pi are least robust.

Shaking procedures

Currently, the Pw procedure is being used for determining the soil-P status in arable farming and horticulture in the Netherlands, Belgium and Switzerland (Tunney *et al.*, 1997). In the original Pw method, end-over-end and reciprocative shaking were implicitly treated as being exchangeable (Sissingh, 1971). However, reciprocative shaking (*P-1* and *Pw-1*) extracted substantially less P from all soils than end-over-end shaking (*P-2* and *Pw-2*), whilst the standard deviations of *P-1* and *Pw-1* were larger (Table 3). The ratio between the amount of P extracted by reciprocative shaking and the amount of P extracted by end-over-end shaking was similar for all soils. In the water extracts (*Pw-1* and *Pw-2*), the ratio was 0.65 ± 0.03 (ratio ± standard error). In Figure 1, *Pw-1* is plotted against *Pw-2* ($R^2 = 0.96$; $P < 0.001$). In comparison, the ratio in the CaCl$_2$ extracts (*P-1* and *P-2*) was 0.64 ± 0.01 ($R^2 = 0.99$; $P < 0.001$). Apparently, more vigorous end-over-end shaking increases the mixing of the soil
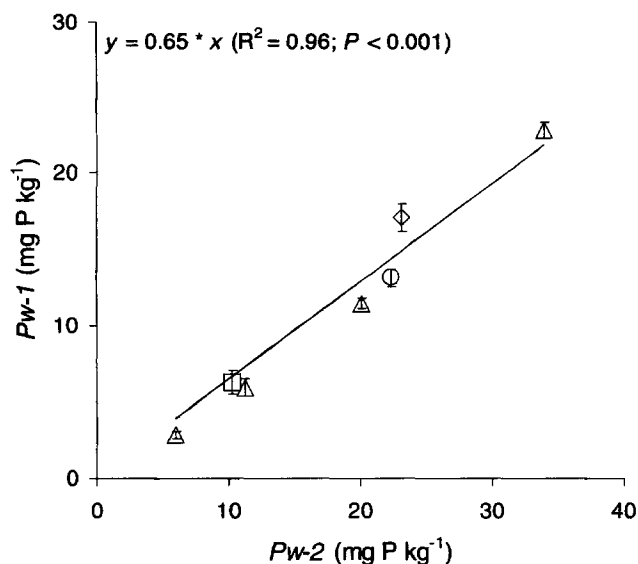
Figure 1. Pw-1 (water-extractable P at a soil:solution ratio of 1:60 v:v, reciprocative shaking) versus Pw-2 (idem, but end-over-end shaking) for the soils studied. Means with sample standard deviation of Pw-1 ($\Diamond$: Emmer C.; $\square$: Giethoorn; $\triangle$: Haren; $\bigcirc$: Wijster).

suspension and the P extraction from soil. An additional explanation may be the breakdown of soil particles leading to the exposure of new desorption sites, which in turn results in an increase of P desorption. From our results we conclude that end-over-end shaking is to be preferred to reciprocative shaking, because of the lower variation coefficients. Furthermore, comparing Pw results from different studies, our results suggest that the shaking method should be taken into account.

Water versus CaCl$_2$ as a P extractant

The replacement of water (*Pw-1* and *Pw-2*) by 0.01 M CaCl$_2$ (*P-1* and *P-2*) in the Pw method of Sissingh (1971) resulted in less P extraction for all soils (Table 3). With the exception of Emmer C., the ratio between the amount of P extracted by CaCl$_2$ and the amount of P extracted by water was similar for all soils. In the extracts shaken end-over-end (*P-2* and *Pw-2*), the ratio was 0.39 ± 0.03. In Figure 2, *P-2* is plotted against *Pw-2* ($R^2 = 0.93$; $P < 0.001$). The Emmer C. soil clearly did not fit this relationship. In the extracts shaken reciprocatively (*P-1* and *Pw-1*), the ratio was 0.39 ± 0.01 ($R^2 = 0.99$; $P < 0.001$; Emmer C. excluded). Desorption of P is known to decrease with an increase in the CaCl$_2$ concentration (Barrow & Shaw, 1979). The use of CaCl$_2$ as an extractant results in an exchange of H$^+$ from the soil with Ca^{2+} from the solution, and causes a decrease of the solution pH (Barrow & Shaw, 1979). So the net positive charge of the soil surface increases, and subsequently P retention increases (Barrow, 1989). Furthermore, the release of dissolved organic carbon (DOC) and the dispersion of soil colloids in solution decrease with increasing Ca^{2+} concentration (Chardon *et al.*, 1996a; Römkens & Dolfing, 1998). So the release of P from DOC or soil colloids in CaCl$_2$ extracts – which contributes to P measured in water extracts (Sinaj *et al.*, 1998) – decreases accordingly.
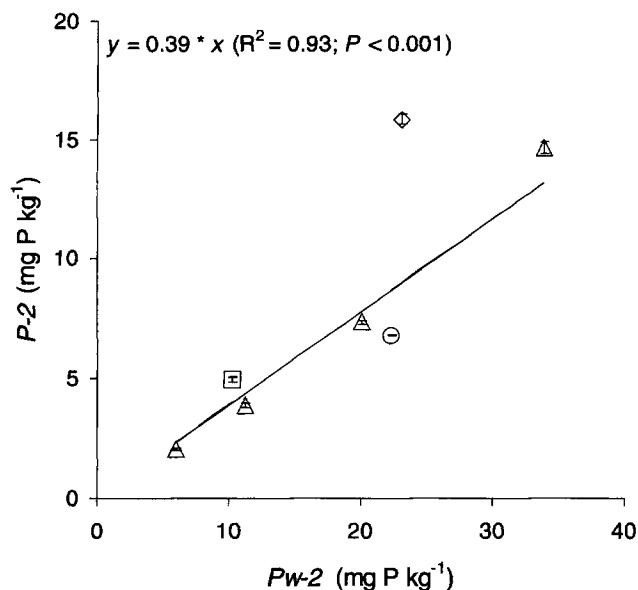
$$y = 0.39 * x \ (R^2 = 0.93; \ P < 0.001)$$

Figure 2. *P-2* (0.01 M Ca-Cl$_2$-extractable P at a soil:solution ratio of 1:60 v:v, end-over-end shaking) versus *Pw-2* (water-extractable P at a soil:solution ratio of 1:60 v:v, end-over-end shaking) for the soils studied (line fitted for the results of all soils excluding Emmer C.). Means with sample standard deviation of *P-2* (◇: Emmer C.; □: Giethoorn; △: Haren; ○: Wijster).

Water-extractable P

Lowering the soil:solution ratio from 1:2 w:v (*P-1:2*) to 1:60 v:v (*Pw-1*) resulted in an increased P extraction from all soils, owing to the larger volume of extractant (Table 3) (Chardon *et al.*, 1996a). In Figure 3, *P-1:2* is plotted against *Pw-1*. The results fitted an exponential relationship very well ($R^2 = 0.99$; $P < 0.001$). The non-linear character of P adsorption (Van Der Zee *et al.*, 1987) explains why non-linear relationships are found between the results of two methods that extract different fractions of the total amount of desorbable P when applied on a range of soils in increasing stages of P accumulation. Results of *P-1:2* and *Pw-2* showed a comparable pattern ($R^2 = 0.96$; $P < 0.001$). Similarly, Chardon & Van Faassen (1999) found a non-linear relationship between dissolved P in centrifuged soil solutions – which is roughly comparable with water-extractable P at a high soil:solution ratio (Sonneveld *et al.*, 1990) – and *Pw* in 284 soil samples (clay, loess, reclaimed peat, and sand). The non-linearity of such relationships is to be taken into account if the Pw extraction method is used as an indicator to estimate the potential of a soil to release dissolved P to the soil solution. At high *Pw* values, this potential may be underestimated if a linear instead of a non-linear relationship is used.

Pi and P-ox

FeO-strips act as an infinite P sink and maintain a negligible P concentration in the soil suspension, facilitating continuous P desorption from soil during incubation (Van Der Zee *et al.*, 1987). So from all soils (much) more P was extracted with the Pi procedure than with the mild extraction methods (Table 3). The average amount of
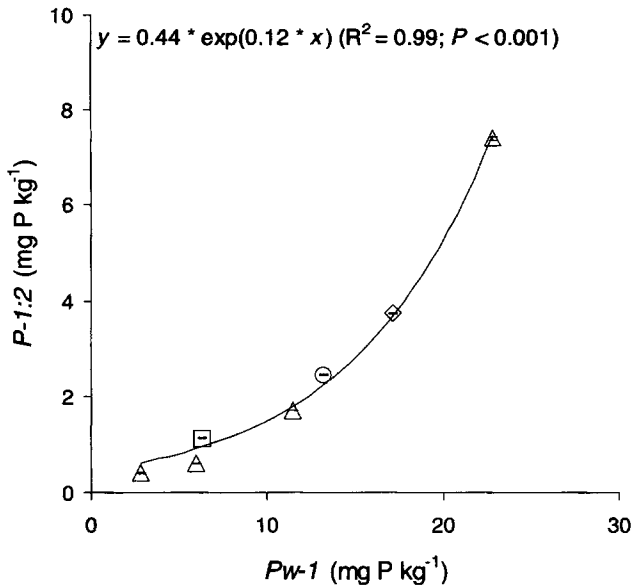
Figure 3. $P-1:2$ (water-extractable P at a soil:solution ratio of 1:2 w:v) versus $Pw-1$ (water-extractable P at a soil:solution ratio of 1:60 v:v) for the soils studied. Means with sample standard deviation of $P-1:2$ ($\diamond$: Emmer C.; $\square$: Giethoorn; $\triangle$: Haren; $\circ$: Wijster).

FeO-strip extractable P for all soils was 6.3% of the average P content whereas average amounts of water- and $CaCl_2$-extractable P ranged from 0.4% ($P-1:2$) to 2.5% ($Pw-2$). Largest amounts of P (on average 82.1% of the average P content) were extracted with ammonium oxalate. This extractant dissolves amorphous Fe- and Al-(hydr)oxides from the soil, which are mainly responsible for P sorption in acidic sandy soils (Beek, 1979). So P in our soils may have been associated for a large part with Fe- and Al-(hydr)oxides. However, $P-ox$ does not exclusively represent inorganic P. Polyvalent cations such as Fe and Al are able to form cation-bridges between the negatively charged sites of organic matter and the sorbing solid phase (Römkens & Dolfing, 1998). Because of the dissolution of Fe and Al by ammonium oxalate, organic P bound to the solid phase through these cation-bridges dissolves too, and thus contributes to P-ox.

The ratio between Pi and $P-ox$ [0.07 ± 0.01 ($R^2 = 0.46$; $0.05 < P < 0.10$)] was more or less the same for all soils except the Emmer C. soil, where a much higher ratio (0.21) was found. The Pi procedure provides an indication of the total amount of desorbable P in the soil (Van Der Zee et al., 1987). So although the amount of $P-ox$ in the Emmer C. soil was small (smallest of all soils), the potential to release P was high (Table 3).

Water- and $CaCl_2$-extractable P versus the PSD

In the four soils sampled from the Haren site, the amounts of P extracted with $P-1:2$ were exponentially related to the PSD ($R^2 = 1.00$; $P < 0.001$) (Figure 4). Chardon (1994) and Sims (1998) found similar non-linear relationships between water-extractable P and the PSD. Soils have a finite capacity for P sorption, and with an in-
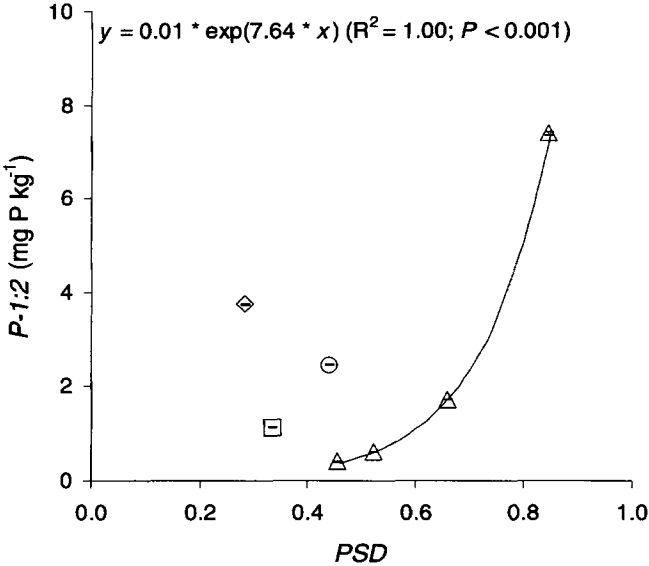
Figure 4. *P-1:2* (water-extractable P at a soil:solution ratio of 1:2 w:v) versus *PSD* ($\alpha = 0.5$) for the soils studied (line fitted for the results of the Haren soils only). Means with sample standard deviation of *P-1:2* ($\Diamond$: Emmer C.; $\square$: Giethoorn; $\triangle$: Haren; $\bigcirc$: Wijster).

crease in the degree of P saturation the P concentration in the soil solution increases non-linearly owing to the non-linear character of P adsorption. However, results from the other sites did not fit the exponential relationship for the Haren site (Figure 4). For the calculation of the PSD the affinity of the soil to sorb P was assumed to be similar in all soils, i.e., $\alpha = 0.5$ (Equation 1), although α ranges from 0.4 to 0.6 (Van Der Zee *et al.*, 1990). Differences in α may partly explain the observed differences among our soils in their potential to desorb P. The value of α may differ because of variability in physical and chemical soil characteristics, such as organic matter content, pH, and the particle size distribution (Beauchemin & Simard, 1999). For the Haren site the following exponential relationship was used to fit the results of *P-1:2* and the *PSD* (Figure 4):

$$P\text{-}1\text{:}2 = a * \exp(b * PSD) \tag{2}$$

or:

$$\ln P\text{-}1\text{:}2 = \ln a + b * PSD \tag{3}$$

where
P-1:2 is expressed in mg P kg^{-1}, and
a and b are constants.

With multiple regression analysis we determined the relationship between ln *P-1:2* and the *PSD* extended with either organic matter content, pH, the clay, silt or sand fraction or a combination of these variables (Table 1). The variability in the re-

sults of ln *P-1:2* was explained best by the following combination of the *PSD* and organic matter content (*OM*; %):

$$\ln P\text{-}1{:}2 = -3.76 + 5.41 * PSD + 0.26 * OM \qquad (4)$$

For this equation $R^2 = 0.71$ ($0.05 < P < 0.10$). In comparison, applying Equation 3 to all soils gave an R^2 value of only 0.13. The pH and particle size distribution did not contribute significantly to the explained variability in the results of ln *P-1:2*. Apparently, the *PSD* and *OM* accounted for a large part of the P desorption characteristics of our soils. So the value of α may differ among our soils, which could explain the deviation of the Emmer C., Giethoorn and Wijster soils from the exponential relationship between *P-1:2* and the *PSD* for the Haren soils (Figure 4). However, the release of organic P from the Emmer C. soil, and to a lesser extent from the Giethoorn and Wijster soils, could also have contributed to the amounts of P measured in the 1:2 w:v water extracts. The acidic molybdate-solution may cause hydrolysis of organic P so that the molybdate-blue colour reaction of Murphy & Riley (1962) does not exclusively represent inorganic P (Haygarth & Sharpley, 2000).

In conclusion, the PSD by itself may not be a reliable indicator for P leaching. If the organic matter content is included a much better indication is obtained. On the other hand, Sharpley (1995) and Pote *et al.* (1999) found that results of dissolved P in simulated runoff and the *PSD* in soils sampled from different sites could be described well by a single relationship. Soils in their experiment may have been more homogeneous with respect to P sorption behaviour than the sandy soils in our study.

Synthesis and conclusions

Characterization of phosphorus-rich sandy soils

In the course of the 20th century, numerous extractants and procedures have been examined for determining the P status of the soil. The procedures with mild extractants (water and $CaCl_2$) examined in this study are commonly used in arable farming and horticulture for the determination of P fertilizer recommendations. The basic philosophy is that extraction procedures should mimic the action of plant roots in the soil. But plants differ in root activity and soils differ in P desorption characteristics. Furthermore, climate, soil cultivation, crop management and nutrient management can affect both root activity and sorption characteristics. Consequently, many extractants appeared to be suitable, although relationships between soil-P test and crop response (to P fertilizer application) often showed a large variation. Currently, a large number of extractants and procedures are used in Europe as soil-P tests for P fertilizer recommendations, but most procedures do not assess possible risks of P leaching (Tunney *et al.*, 1997). Owing to the excessive P enrichment of soils in intensively managed agricultural areas, emphasis has now shifted from refining P fertilizer re-

commendations to the identification of P-leaky soils that pose a menace to surface waters. The focus shifted also somewhat from the topsoil to the whole soil profile down to at least the upper groundwater level.

Large areas of sandy soils in the Netherlands have been identified as 'P saturated soils' (Reijerink & Breeuwsma, 1992), on the basis of the PSD concept developed by Van Der Zee et al. (1990). If the average *PSD* value of the soil profile down to the average upper groundwater level exceeds 0.25, the soil is considered 'P saturated', which means that the total P concentration in the upper groundwater exceeds or will exceed the critical level of 0.15 mg total P l^{-1}. Although the location of these soils in the Netherlands has been roughly identified, restoration is costly (Chardon et al., 1996b) and no site-specific policies and measures have been implemented yet. The lack of such policies and measures is partly because of the large economic consequences for intensive livestock farming systems, and partly also because of the lack of tools to identify the urgency of these measures.

The urgency of measures depends on the actual leaching of P from the soil to surface waters that are sensitive to eutrophication. The major pathway of P losses from agricultural land to surface waters in flat areas – such as in the Netherlands – is through leaching of P-containing drainage water. Evidently, the amount of dissolved (and colloidal) P in the soil solution draining from the soil to the surface water is a critical factor. This amount can be assessed easily through extraction of soil with water using the P-1:2 procedure (Sonneveld et al., 1990). For the Haren soils this amount is related exponentially to the *PSD*, but this relationship was not valid for the other soils (Figure 4). Lowering the soil:solution ratio – as in the Pw procedure – increased the amount of P extracted and an exponential relationship with *P-1:2* was again found (Figure 3).

Our results also show that small modifications in the extraction procedure had significant effects on the amounts of P extracted. In all soils, end-over-end shaking extracted more P than reciprocative shaking during the Pw method. Evidently, the Pw method – in which both shaking procedures have been treated as being exchangeable (Sissingh, 1971) – needs to be standardized. The replacement of water by 0.01 M $CaCl_2$ in the Pw method decreased the amount of P extracted from all soils, as shown before by Barrow & Shaw (1979), although the decrease was not the same for all soils (Figure 2).

In conclusion, the amount of readily available P in sandy soils can be assessed with mild extractants such as water and $CaCl_2$, but small modifications in soil:solution ratio and shaking method can have a large impact on the amount of P extracted. Furthermore, for the Haren soils the amount of P extracted by the P-1:2 procedure is exponentially related to the PSD, but this relation was not valid for the other soils. If the PSD is to be solely used as an indicator for the risk of leaching dissolved P, α needs to be determined separately for each soil. However, as the determination of α is rather laborious this is not feasible.

Establishing priorities for restoring P-leaky soils

Restoring P-leaky soils requires that the P enrichment of the soil is reversed into a P

depletion to decrease the concentration of dissolved P in the soil solution. This could be achieved by phytoremediation, which has been proposed as an effective restoration method (Chardon *et al.*, 1996b). Phosphorus is withdrawn from the soil by plant uptake and crop harvesting. If no replenishment of P takes place, the (readily) available P content decreases rapidly (Sharpley, 2000). Possible additional measures include increasing the P-sorption capacity of the soil by lowering the groundwater level or by incorporating Fe- or Al-(hydr)oxides into the soil (Chardon *et al.*, 1996b). Such measures are expensive, especially in flat areas with intensive livestock farming and surpluses of animal manure. A first step to an effective and efficient restoration is the identification of the soils that are most sensitive to P leaching.

We propose that the PSD (with $\alpha = 0.5$) in combination with an assessment of the dissolved-P concentration in the soil solution, is suitable for the identification of P-leaky soils, and subsequently for prioritizing restoration measures. For the assessment of dissolved-P concentrations in the soil solution, we propose P-1:2, because it is a straightforward and robust procedure (low variation coefficient). The PSD is an indicator for long-term monitoring, whereas P-1:2 is an indicator for immediate action. The simple scheme presented in Figure 5 provides some guidance, but needs further development and calibration. It should be applied to the whole soil profile down to the upper groundwater level.

Although our study was limited to samples from the topsoil, the results will be used here to further illustrate the case. As follows from Tables 1 and 3, the soil from Haren 11 is high in both *PSD* and *P-1:2*, whereas Haren 1 is medium in *PSD* and low in *P-1:2*. Evidently, immediate action (restoration measures) and long-term monitoring are required for Haren 11, whereas no action seems to be needed for Haren 1. Soil from Emmer C. is low in *PSD* and medium to high in *P-1:2*, suggesting that immediate or short-term actions are required.

The scheme may also be helpful for monitoring the effectiveness of restoration

P-1:2	PSD		
	low	medium	high
low			
medium			
high			

Figure 5. Scheme for prioritizing the restoration of P-leaky soils in relation to *PSD* and *P-1:2* class. Soils with a high *PSD* and a high *P-1:2* require immediate action and long-term monitoring (black). Soils with a low or medium *PSD* and a high *P-1:2* may require immediate but short-term action (light grey). Soils with a high *PSD* and a low or a medium *P-1:2* require long-term monitoring (dark grey). Soils with a low or medium *PSD* and a low or medium *P-1:2* may not require any action (white).

measures. Often, the readily available P content decreases rapidly when the withdrawal of P through the harvested crop exceeds the P input through additions of animal manure and chemical fertilizer (Sharpley, 2000), i.e., in the case of a net P depletion even if the *PSD* is high (Koopmans *et al.*, 2001). This would suggest that measures are effective. If in the case of a net soil-P depletion, *P-1:2* does not decrease rapidly – for instance, because the desorption process is faster than the P uptake rate of the crop – additional measures are required.

In conclusion, a combination of the PSD and P-1:2 as indicators (Figure 5) may provide guidance for selecting P-leaky soils that require immediate action or long-term monitoring. The scheme may also be helpful for evaluating the effectiveness and efficiency of policies and measures that aim at restoring P-leaky soils. Further development and testing of the scheme are foreseen, however.

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