The use of indicators for the identification of phosphorus transfer from agricultural land to surface waters

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ABSTRACT

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Increased loading of agricultural soils with phosphorus (P) has been directly associated with P transfer from soil to surface waters, contributing to eutrophication. Policies and measures have been implemented to decrease the P loading. To evaluate the effectiveness of these policies and measures, we propose indicators, selected from literature, which are suitable for the assessment of the potential risk of P transfer at the field level. Our study focuses mainly on simple 'soil' indicators of the potential risk of P transfer only. The indicators were qualitatively assessed on basis of the selection criteria purposive, measurable and reactive. Based on these criteria, P in soil solution and Pw have been selected for testing in a field experiment.

Keywords: phosphorus, phosphate, literature study, soil chemistry, indicator, soil test, soil water test, risk assessment, losses, leaching

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Contents

Preface

The enrichment of intensively managed agricultural land with phosphorus (P) has been directly associated with transfer of P from soil to surface waters, contributing to eutrophication and adverse effects. In our report, some potential 'promising' indicators are proposed and discussed for evaluating the effectiveness of policies and measures implemented to decrease P loading of agricultural soils and the associated potential for P transfer. Our study was conducted within the framework of the program 398 III 'Assessment, monitoring and evaluation of policies on animal manure and nutrients' and the former program 317 'Nutrient management on a local and regional scale', financed by the Dutch Ministry of Agriculture, Nature Management and Fisheries.

Summary

Intensively managed agricultural land has been enriched with phosphorus (P), as the result of animal manure and P fertilizer applications exceeding crop demand. The increased loading of agricultural soils with P has been directly associated with transfer of P from soil to surface waters, contributing to eutrophication and adverse effects. In the Netherlands, where flat areas predominate, the main hydrological pathways of P transfer to surface waters are leaching of water with mobile P forms through the topsoil, followed by transport of P through drainage pipes or directly through the soil by subsurface runoff. Policies and measures have been implemented to decrease P loading of agricultural soils and the associated potential for P transfer. To evaluate the effectiveness of these policies and measures, we propose indicators, which are suitable for the assessment of the potential risk of P transfer in the soil at the field level. The actual P transport from agricultural land to surface waters depends on (i) the degree of P enrichment of the soil in relation to soil physical-chemical characteristics, such as P sorption capacity and pH, and (ii) the presence of a hydrological connection between the source of P in the field and surface waters. However, the estimation of actual P loading rates of surface waters is rather complicated, since it requires the input of many factors. Therefore, our study focuses mainly on simple 'soil' indicators of the potential risk of P transfer only.

To select suitable indicators, understanding of the behavior of P in different soil types is important. Based on the reactions of P in noncalcareous sandy soils, a concept including two P pools can be proposed: a pool which contains reversibly adsorbed P and another pool which contains P that can be desorbed only on the long term, denoted as absorbed P. The FeO-strip method (filter paper impregnated with FeO) can be used to measure the size of the reversibly adsorbed P pool. Due to desorption of reversibly adsorbed P, P transfer to ground- and surface waters may occur. The acid ammonium oxalate method can be used to extract total sorbed inorganic P (P_{ox}). Since absorbed P is released only on the long-term, it is less relevant for the estimation of the risk of potential P transfer. The latter is generally considered as a process controlled by the fast ad- and desorption reactions of P with the solid phase of the soil. Thus, a method indicative of the reversibly adsorbed P pool may be more relevant for monitoring purposes. The understanding of the behavior of P in other soil types than noncalcareous sandy soils is poor to moderate. Therefore, mainly knowledge on the behavior of P in these soils is used to select an indicator.

Our study gives an overview and a description of indicators frequently studied in literature:

- agricultural indicators (the P balance at the farm level, Pw, and P-AL), and
- other indicators (the degree of phosphorus saturation [DPS], FeO-strip method, P_{ox}, and P in soil solution and drainage water).

With the exception of the P balance at the farm level, all of these methods are so-called 'soil' indicators.

The indicators were qualitatively assessed on basis of the following selection criteria: *purposive*, *measurable* and *reactive*. The term *purposive* refers to the relation between the indicator and the purpose of policies and measures. If an indicator is not directly related to the purpose of policies and measures, the purpose may not be entirely reached. The criterion *measurable* refers to the *costs* and *accuracy* of the indicator. The *costs* should be low whereas the *accuracy* of an indicator should be high. The criterion *reactive* refers to the connectivity between an indicator and policies and measures involving a change of P management. An indicator should respond to changes in P management, i.e., a criterion referred to as *sensitivity*. Based on an insensitive indicator, effects of changes in P management cannot be monitored. On the other hand, an indicator should be *independent* of other factors, such as variability in soil physical-chemical characteristics and weather conditions. Obviously, for monitoring purposes, effects of other factors than a changing P management are highly undesirable.

Based on these criteria, P in soil solution and Pw have been selected for testing in a field experiment. Furthermore, it is recommended to include P-AL. To obtain a thorough understanding of the behavior of these selected indicators, the following soil conditions have to be measured in the field experiment: the size of the reversibly adsorbed P pool and physical-chemical characteristics, such as the P sorption capacity, pH, $CaCO_3$ and organic matter content. We restrict the use of these indicators to the so-called 'wet' soils, exhibiting shallow groundwater levels and directly draining to surface waters. In addition to a high potential risk, these possible 'hot spots' are likely to exhibit a high actual risk of P transfer, because of the high probability of a hydrological connection between these 'hot spots' and surface waters.

Samenvatting (Dutch Summary)

Intensief beheerde landbouwgronden zijn verrijkt met fosfor (P), omdat de hoeveelheid P, als gevolg van het toedienen van grote hoeveelheden dierlijke mest en kunstmest, groter is dan de hoeveelheid P die wordt opgenomen door, en afgevoerd met het gewas. Verliezen van P uit dergelijke landbouwgronden leiden tot een verhoogde P-concentratie in het oppervlaktewater, en uiteindelijk tot eutrofiëring met de daarbij behorende nadelige effecten. In het hoofdzakelijk vlakke Nederland vindt transport van P uit landbouwgronden naar het oppervlaktewater voornamelijk plaats door middel van verticale uitspoeling van bodemoplossing met daarin opgeloste P-vormen door de bovengrond, gevolgd door transport door drainagebuizen of ondiepe horizontale uitspoeling. Verschillende beleids- en aanvullende maatregelen zijn geïmplementeerd om het verrijken van landbouwgronden met P, en het daaraan gerelateerde risico op P-verliezen, te verminderen. In deze studie worden mogelijke indicatoren geselecteerd voor het evalueren van de effectiviteit van deze beleids- en aanvullende maatregelen op perceelsniveau.

De werkelijke P-verliezen van landbouwgronden naar het oppervlaktewater worden bepaald door (i) de mate van P-verrijking in relatie tot fysisch-chemische bodemeigenschappen, zoals de sorptiecapaciteit van de grond voor P en de pH, en (ii) de aanwezigheid van een hydrologische verbinding tussen de bron van P in het perceel en het oppervlaktewater. Het schatten van de werkelijke P-verliezen is echter gecompliceerd, omdat hierbij informatie van veel verschillende factoren nodig is. Onze studie richt zich als gevolg hiervan voornamelijk op het gebruik van eenvoudige 'bodem'-indicatoren voor het schatten van het potentiële risico op P-verliezen.

Kennis van het gedrag van P in verschillende grondsoorten is zeer belangrijk om een geschikte indicator te selecteren. Gebaseerd op de reacties van P in kalkloze zandgronden wordt een concept voorgesteld, waarbij twee P-pools worden onderscheiden: een pool met reversibel geadsorbeerd P en een pool met geabsorbeerd P. Fosfor komt vrij uit de eerstgenoemde pool als gevolg van een desorptiereactie. De FeO-strip methode (filterpapier geïmpregneerd met FeO) kan worden gebruikt om de omvang van de pool met het reversibel geadsorbeerde P te schatten. De relatief sterke extractievloeistof zure ammonium oxalaat kan worden gebruikt voor het schatten van de totale hoeveelheid anorganisch gebonden P (P_{ox}). Het geabsorbeerde P komt pas vrij op de lange termijn; hierdoor lijkt deze P pool minder geschikt voor het schatten van het risico op potentiële P-verliezen. De snelle ad- en desorptiereacties van P met de vaste fase van de bodem bepalen in sterke mate het optreden van potentiële P-verliezen. Een indicator waarmee het reversibel geadsorbeerde P (deels) wordt geëxtraheerd lijkt voor het schatten van het risico op potentiële P-verliezen van landbouwgronden naar het oppervlaktewater een geschikte methode. Er is echter nauwelijks of slechts in beperkte mate kennis voorhanden van het gedrag van P in andere grondsoorten. Hierdoor wordt, voor het selecteren van

een geschikte indicator, voornamelijk gebruik gemaakt van de kennis van het gedrag van P in kalkloze zandgronden. In onze studie wordt een overzicht gegeven van indicatoren welke veelvuldig zijn bestudeerd in de literatuur, namelijk:

- landbouwindicatoren (P balans op bedrijfsniveau, Pw en P-AL), en
- andere indicatoren (P-verzadigingsgraad [PVG], FeO-strip methode, P_{ox} en P in bodemoplossing en drainagewater).

Het merendeel van deze methoden zijn 'bodem'-indicatoren. De indicatoren zijn kwalitatief beoordeeld op basis van de volgende selectiecriteria: *doelgerichtheid, meetbaarheid* en *reactiviteit.* Onder *doelgerichtheid* wordt verstaan de relatie tussen de indicator en het doel van de desbetreffende beleids- en aanvullende maatregelen; het doel wordt waarschijnlijk niet gerealiseerd als een indicator hieraan niet direct is gerelateerd. Onder *meetbaarheid* worden de *kosten* en *accuratesse* van de indicator verstaan; de *kosten* moeten laag zijn, terwijl de *accuratesse* van de resultaten van een indicator hoog moet zijn. Met reactiviteit wordt bedoeld de mate waarin een indicator samenhangt met wijzigingen in het mineralenbeheer; een indicator dient een hoge mate van *responsiviteit* te bezitten. Een indicator met een lage mate van *responsiviteit* is niet geschikt voor het evalueren van het effect van beleids- en aanvullende maatregelen gericht op het verminderen van potentiële P-verliezen. Een indicator dient echter onafhankelijk te zijn van andere factoren, zoals de variatie in fysisch-chemische bodemeigenschappen en weersomstandigheden. Voor het monitoren van de effecten van een gewijzigd mineralenbeheer zijn de effecten van dergelijke factoren op de resultaten van een indicator zeer ongewenst.

Op basis van deze criteria zijn P in bodemoplossing en Pw geselecteerd om te worden getest in een veldexperiment. Bovendien wordt geadviseerd om P-AL mee te nemen. Er wordt tevens geadviseerd om een aantal condities van de bodem te meten om een goed begrip van het gedrag van deze indicatoren te verkrijgen, namelijk: de omvang van de pool met reversibel geadsorbeerd P en fysisch-chemische bodemeigenschappen, zoals de P-sorptiecapaciteit, pH, $CaCO_3$-gehalte, en organische stof. We beperken het gebruik van de indicatoren tot de zogenaamde 'natte' gronden met een hoge grondwaterstand en een hydrologische verbinding met het oppervlaktewater via ondiepe uitspoeling of door transport van met P verrijkte bodemoplossing door drainagebuizen. Bij deze mogelijke 'hot spots' bestaat naast het potentiële risico eveneens een actueel risico op P-verliezen door de aanwezigheid van een hydrologische verbinding.

1 Introduction

In the course of the 20th century, intensively managed agricultural land has been enriched with phosphorus (P), as the result of large P applications exceeding crop demand. From 1950 to 2000, the average P surplus of agricultural land in the Netherlands ranged from 25 to 45 kg of P ha^{-1} yr^{-1} (Smaling et al., 1999). Regionally, P surpluses have been much higher in areas with noncalcareous sandy soils in the middle, east and south of the Netherlands, where intensive livestock farming systems predominate. Large applications of animal manure have caused a near saturation of the soil with P (Breeuwsma et al., 1995). Consequently, the soil P status in these areas, measured as Pw (water extractable P with a soil to solution ratio of 1:60 [v/v]) (Sissingh, 1971), increased to values exceeding optimum crop demand 2 to 3 times (Neutel, 1994). Increased loading of intensively managed agricultural land with P has been associated directly with transfer of P from soil to surface waters, contributing to eutrophication (Sharpley et al., 1994; Foy et al., 1995; Hosper, 1997). The main hydrological pathways of P transfer from agricultural land to surface waters are surface runoff and erosion, especially on sloping land, and leaching of soil solution followed by subsurface runoff or transport through drainage pipes. In the Netherlands, where flat areas predominate, the latter pathways are most important, especially in areas with shallow groundwater. On average, agricultural soils contribute 30% of the total P load of surface waters, but in some watersheds, the contribution can be as high as 90% (Coppoolse and Kersten, 1992). These areas are considered as 'hot spots' of P losses. For the identification of these 'hot spots', van der Zee et al. (1990) developed the degree of P saturation (DPS). Based on the DPS, an estimated 70% of the Dutch noncalcareous sandy soils, covering an area of about 400,000 ha, is likely to contribute to (excessive) P enrichment of surface waters (Reijerink and Breeuwsma, 1992). The DPS method was developed for noncalcareous sandy soils, since intensive livestock farming systems with high application rates of animal manure predominate in these areas; thus, the use of the DPS is restricted to these soils only (van der Zee et al., 1990).

From 1986 onwards, a series of policies and measures has been implemented to decrease P loading of agricultural soils and the associated potential for P transfer to surface waters (Hotsma, 1997; Oenema and Roest, 1998). The net loading of the soil has been set to be a maximum of 8.7 kg of P ha^{-1} yr^{-1} for all agricultural land to be reached in 2003. To evaluate the effectiveness of these policies and other regional measures (e.g., in 'hot spot' areas), the potential of the soil for P transfer needs to be monitored at the field level. For these purposes, indicators can be used (Chardon and van Faassen, 1999; Schoumans and Groenendijk, 2000). Many indicators only give an indication of potential risk, implicating some transfer of P out of the root zone of the soil or field is likely to occur (Schoumans et al., 2000). The actual P transfer via (sub)surface runoff to surface waters (i.e., the actual risk) depends on many more factors: soil type, land use, soil P status, mean highest groundwater level (MHW) and annual P surplus (Schoumans et al., 2000). However, estimation of actual P loading rates of surface waters requires the input of many factors, and is thus rather complicated. Therefore, our study mainly focuses on simple 'soil' indicators of potential risk of P transfer to surface waters.

In literature, various indicators have been studied, so apparently no agreement has been reached on an appropriate method. Therefore, the objective of our study is to select indicators, which are suitable to evaluate the effectiveness of policies and measures aiming to decrease potential P transfer at the field level. The selected indicator has to be tested in a field experiment. To select a suitable indicator, understanding of the behavior of P in soil and water is important. In chapter 2, we describe a concept and definitions of P in soil and water. Moreover, understanding of the hydrological pathways of P transport from the source in the field to surface water is needed; in chapter 3 we describe these pathways. Then, in chapter 4, we give an overview and description of the indicators studied in literature and of some new indicators. In chapter 5, the indicators are qualitatively assessed and discussed on the basis of some selection criteria. We select indicators suitable for evaluating the effects of policies and measures aiming to decrease potential P transfer.

2 Phosphorus in soil: Concepts and definitions

2.1 Introduction

The first step in transfer of P from soil to surface waters is solubilization of P from the solid phase of the soil to water (e.g., soil solution or runoff); the solid phase acts as a source for P and water acts as a 'carrier' for P (Haygarth and Jarvis, 1999). For selecting an indicator, a thorough understanding of the P speciation in the solid phase of the soil is important, since not all P forms exhibit the same solubility. Hence, an indicator should be indicative of soluble soil P. Similarly, understanding of different P forms occurring in water is important, since not all P forms contribute to P enrichment of surface waters to the same extent. In the following, some concepts and definitions of P forms in water and the solid phase of the soil are discussed in combination with analytical (extraction) methods proposed for measuring these P forms.

2.2 Forms of phosphorus in soil water

Mobile P forms solubilized in water can be divided into different fractions defined in terms of analytically determined methodologies (Haygarth et al., 1998). Fractionation is important for the understanding of potential P transfer, as it provides more insight in the quantitative importance of the different processes, e.g., inorganic versus organic P transfer. Hens and Schoumans (2002) proposed to define P forms by physical (size) and chemical fractionation. Physical fractionation reflects the concept of dissolved and particulate P forms; a 0.45 μm filter is commonly used to separate these P forms. However, if P containing colloids are present, part of it may pass a 0.45 μm filter resulting in an overestimation of the dissolved P concentration. Haygarth et al. (1997) and Sinaj et al. (1998) demonstrated the importance of colloidal P in soil solution and leachate. However, some laboratories use other sized filters to separate dissolved P from particulate P which complicates comparison between different studies on P mobility, so filter size should always be specified. Chemical fractionation reflects the concept of total P (TP) and inorganic P. The molybdate blue color reaction of Murphy and Riley (1962) can be used to measure inorganic P. However, the P measured does not exclusively represent inorganic P. Hydrolysis of organic P may occur, due to the acid molybdate solution, resulting in an overestimation of the inorganic P concentration (Haygarth and Sharpley, 2000). Therefore, Hens and Schoumans (2002) proposed the definition reactive P (RP) for the P measured according to Murphy and Riley (1962). Total P can be determined by Inductive Coupled Plasma (ICP) or after digestion of TP into inorganic P. Table 1 shows the terminology for mobile P forms. To give an idea of the relative size of the dissolved reactive P (DRP) concentration, 50 to 70% of the total dissolved P (TDP) concentration in soil solution of the root zone of noncalcareous sandy soils was present as DRP (Chardon et al., 1997).

Table 1 Terminology for P forms in water (Hens and Schoumans, 2002)

chemical fractionation	physical fractionation		
	unfiltered water sample	filtered water sample (0.45 μm)	by difference
reactive P (RP)	total reactive P (TRP)	dissolved reactive P (DRP)	particulate reactive P (PRP)
total P (TP)	total P (TP)	total dissolved P (TDP)	total particulate P (TPP)
by difference	total unreactive P (TUP)	dissolved unreactive P (DUP)	particulate unreactive P (PUP)

2.3 Phosphorus pools in the solid phase

2.3.1 Reactions of phosphorus in soil

In animal manure, P is mainly present as inorganic P (Gerritse, 1981; Dou et al., 2000; Sharpley and Moyer, 2000). For example, 80 to 90% of total P in pig slurry (a mixture of feces, urine and cleaning water) was found to be inorganic P (Gerritse, 1981). Thus, in soils of intensively managed agricultural land, P may be expected to be mainly present as inorganic P. Indeed, long-term field experiments indicate a tendency to support a larger fraction of inorganic P rather than organic P, probably reflecting long-term application of animal manure and P fertilizer (Hawkes et al., 1984; Sharpley et al., 1984). This was confirmed in a study of Koopmans et al. (2003); in a noncalcareous sandy soil, which received large applications of NPK fertilizer or different animal manures for 11 consecutive years, on average 70% of total P in the soil (0-5 cm) was found to be inorganic P. In soil, inorganic P can react with various soil constituents, such as amorphous or crystalline Al- and Fe-(hydr)oxides, complexes of Al- or Fe-(hydr)oxide and organic matter, calcium carbonates and edges of clay minerals (Schoumans, 1995). The following reactions of P are distinguished: adsorption, sorption, and precipitation. Because of these reactions, P is distributed among different forms in the solid phase. Furthermore, P can be immobilized in organic matter. Based on the reactivity of different P forms, different P pools can be distinguished. Due to chemical and biological reactions, P can be released from these pools to soil solution (solubilization) and become mobile. Overall, the pH is the main soil characteristic controlling the distribution of P between the different P forms in soil, but the previously described soil constituents determine the amounts being formed (Sharpley, 2000). The reactions of P with the solid phase in soil (Table 2), a concept of P pools in the solid phase and the analytical extraction methods needed to measure the size of these pools (Table 3) are discussed here.

2.3.1.1 Noncalcareous soils

In noncalcareous soils sandy soils, amorphous Al- and Fe-(hydr)oxides and complexes of Al- and Fe-(hydr)oxides with organic matter are the main reactive constituents (Beek, 1979). The overall reaction of inorganic P with Al- and Fe-(hydr)oxides is the result of a fast adsorption reaction at surface sites (<1 day) and a slow one: diffusion through the solid phase or micropores of Al- and Fe-(hydr)oxides followed by precipitation or adsorption inside the aggregates (van Riemsdijk and Lyklema, 1980a, b; van Riemsdijk and de Haan, 1981; Barrow, 1983; van Riemsdijk et al., 1984a, b; Bolan et al., 1985; Madrid and De Arambarri, 1985; Willett et al., 1988). The fast reaction was described as a ligand exchange reaction between phosphate anions and OH^-- or H_2O-groups at the surface of Al- and Fe-(hydr)oxides (van Riemsdijk and Lyklema, 1980a). Similarly, the reaction of P with complexes of Al- and Fe-(hydr)oxides and organic matter is described as a ligand exchange reaction with OH^--groups at the surface of the complexed Al- and Fe-(hydr)oxides (Appelt et al., 1975). In noncalcareous peaty soils, P adsorption was highly positively correlated with Al and Fe content, whereas correlation with organic matter was poor or negative (Cuttle, 1983). In these soils, the adsorption reaction may dominate overall P sorption (Schoumans, 1999). In soils with a high clay content, Al- and Fe-(hydr)oxides may be associated with the negatively charged surface of clay minerals, and P may adsorb at surface sites of these Al- and Fe-(hydr)oxides. It is unclear whether a slow reaction occurs in peat soils (Schoumans, 1999). The adsorption reaction is considered to be completely reversible (Schoumans, 1995, 1999). Hence, due to a fast desorption reaction of adsorbed P, P may become available again in soil on the short-term (<1 day).

The slow reaction of P is still not completely understood. It was described as a slow diffusion process through the solid phase to the zone where a fast precipitation reaction occurs: the conversion of Al- or Fe-(hydr)oxides to Al- or Fe-P precipitates leading to a shrinking core of unreacted parts (van Riemsdijk and Lyklema, 1980a, b; van Riemsdijk and de Haan, 1981; van Riemsdijk et al., 1984a, b). In contrast, in studies of Madrid and De Arambarri (1985) and Willett et al. (1988), the reaction was described as a slow diffusion through the micropores of synthetic aggregates of Fe-(hydr)oxides followed by fast adsorption inside the aggregates. Nevertheless, all studies agree on (reactive) diffusion as transport for P into the aggregates as the rate-limiting step in the slow reaction. However, the exact reaction mechanism is probably not relevant, since all studies agree on diffusion as the main time dependent step (Schoumans, 1997). Phosphorus can be released by desorption of adsorbed P, or dissolution of precipitated P inside the aggregate, followed by diffusion to the soil solution. Since diffusion is slow, absorbed P becomes available again only on the long-term. Therefore, the reaction is considered to be 'irreversible' under common agricultural conditions (Schoumans, 1995). The term P fixation has often been used to indicate P absorption, which is then treated as an irreversible reaction.

Besides adsorption and desorption, precipitation of P can occur in noncalcareous sandy soils. At a low pH (<4), Al- and Fe-(hydr)oxides may dissolve, resulting in high Al and Fe concentrations. In combination with a high P concentration, Al and Fe may precipitate with P (e.g., strengite and variscite). Furthermore, in soils saturated with P, that are unable to retain additional P by sorption, precipitation of Ca-P minerals may occur after application of animal manure (pH >5.5). De Haan and van Riemsdijk (1986) found indications for the existence of dicalcium phosphate (i.e., brushite, DCP) in noncalcareous sandy soils receiving large applications of pig slurry. Depending on the solubility of the P mineral, P can become available in soil due to dissolution.

2.3.1.2 Calcareous soils

In calcareous soils, calcium carbonate is the main reactive constituent. At a low P concentration in soil solution (up to 10 mg P L^{-1}), the reaction of P with calcite ($CaCO_3$) can be considered as a fast adsorption reaction (Cole et al., 1953; Griffin and Jurinak, 1973, 1974; Schoumans and Lepelaar, 1995). However, the reaction is not completely understood. Kuo and Lotse (1972) proposed a ligand exchange reaction between phosphate anions and CO_3^{2-}- and OH^--groups at the surface of $CaCO_3$. With time (>1 day), adsorption of P did not increase, indicating there is no slow formation of Ca-P compounds at a low P concentration. Hence, Schoumans and Lepelaar (1995) consider the adsorption reaction to be completely reversible. In contrast, precipitation of P is the main process at a higher P concentration (up to 100 mg P L^{-1}) (Cole et al., 1953; Griffin and Jurinak, 1973, 1974). The reaction was described as a slow nucleation process, where precipitation of P with Ca on nuclei of adsorbed P at the $CaCO_3$ surface results in the 'three dimensional growth' of a Ca-P mineral (5-8 μm) (Schoumans and Lepelaar, 1995). As the Ca-P precipitate covers the calcite surface, the Ca-P precipitate is referred to as a 'surface precipitate' (Fig. 1). In the beginning, DCP may be formed, but within three months, DCP may be slowly transformed into octacalcium phosphate. If the P concentration is >100 mg P L^{-1}, a fast process may occur: nuclei can cluster into large Ca-P minerals (about 500 μm) (Freeman and Rowell, 1981; Schoumans and Lepelaar, 1995). The pH and Ca concentration in the solution considerably affect the precipitation reaction (Lindsay, 1979). Depending on the solubility of the Ca-P mineral, P can dissolve in the soil solution.

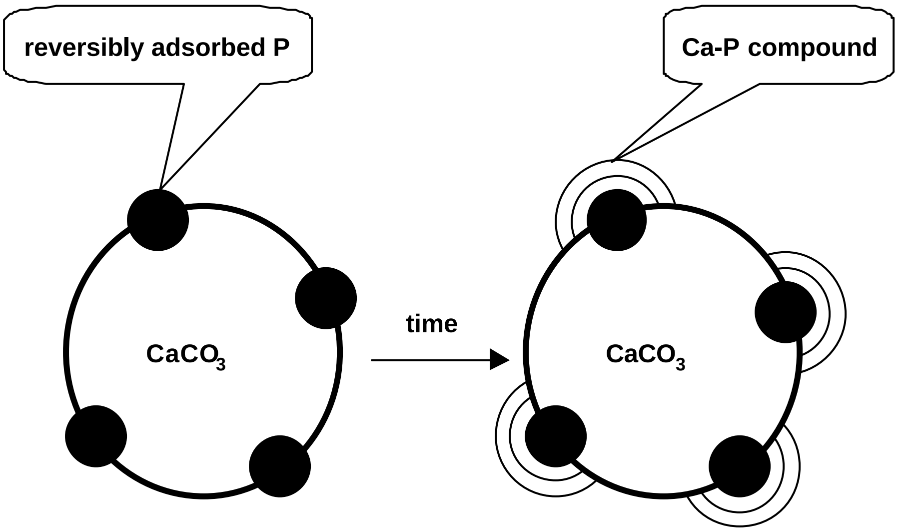

Figure 1 Concept of P retention by $CaCO_3$ *(Schoumans and Lepelaar, 1995)*

Table 2 Overview of the reactions of P in soil (Schoumans, 1995)

soil constituents	reversible adsorption	absorption	precipitation
Al- and Fe-(hydr)oxides	+	+	+
complexes of Al- or Fe-(hydr)oxides and organic matter	+		
calcium carbonate	+		+
edges of clay minerals	+		
Al- and Fe-(hydr)oxides associated with clay minerals	+	?	

2.3.2 Definition of phosphorus pools in the solid phase

Based on the previously described reactions of P in soil, P can be divided into different pools. A concept including two P pools is proposed: a pool containing reversibly adsorbed P and another pool containing absorbed P (Fig. 2). Depending on the solubility of precipitated P minerals and the persistence of P immobilized in organic matter to mineralization, P can contribute to either of these P pools. The sum of all reactions involving the release of P to soil solution is termed solubilization. The concept of Fig. 2 has frequently been applied to intensively managed agricultural land on noncalcareous sandy soils amended with large amounts of animal manure (van der Zee et al., 1988; van Noordwijk et al., 1990; Lookman et al., 1995; Schoumans and Groenendijk, 2000). For agricultural purposes, the P pool concept was interpreted in terms of availability for plant uptake: reversibly adsorbed P and absorbed P have been defined as labile and stable P, respectively (Kuo, 1996). In a laboratory experiment, Lookman et al. (1995) and Maguire et al. (2001) studied P desorption from P-rich noncalcareous sandy soils in the presence of an 'infinite' P sink. The latter maintains a very low P concentration in soil suspension facilitating continuous P desorption from soil. They demonstrated desorption of absorbed P under conditions where the soil P status becomes very low. Using a model including a reversibly adsorbed and an absorbed P pool, Lookman et al. (1995) accurately described their desorption results supporting the concept presented in Fig. 2. However, since the P concentration in the shaking solution was maintained at a very low level, the latter was not included in the model. Consequently, the model of Lookman et al. (1995) cannot be used for estimating P potentially available for P transfer.

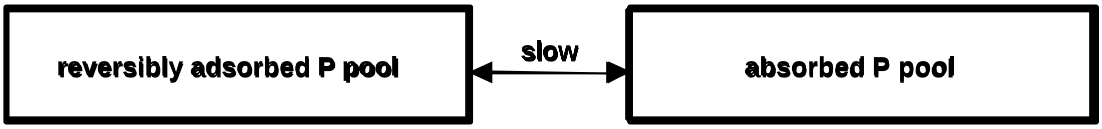

Figure 2 Concept of the P chemistry of heavy manured and fertilized land on noncalcareous sandy soils (van Noordwijk et al., 1990; Lookman et al., 1995; Schoumans and Groenendijk, 2000)

2.3.3 Analytical methods

Table 3 Analytical methods for measurement of pools of P in soil

analytical method	P pool
1. FeO-strip method	reversibly adsorbed P
2. acid ammonium oxalate	reversibly adsorbed P + absorbed P
3. digestion with concentrated acids	reversibly adsorbed P + absorbed P + mineral P = total inorganic P
4. digestion with concentrated acids after dry or wet oxidation	total inorganic P + organic P = total P
5. by difference	total P - total inorganic P = organic P (4 – 3)

2.3.3.1 Reversibly adsorbed phosphorus FeO

The use of impregnated filter paper strips (FeO-strip method) has been proposed to determine the amount of reversibly adsorbed P (van der Zee et al., 1987). The method was introduced by Sissingh (1983): one FeO-strip is incubated with one g of soil in 40 mL 0.01 M $CaCl_2$ and shaken for 16 h. The FeO-strip acts as an 'infinite' sink for P and maintains a negligible P concentration in soil suspension facilitating continuous P desorption from soil during incubation. However, in many other studies (van der Zee et al., 1987; Lepelaar and Schoumans, 1999), the surface area of the FeO-strip, the number of FeO-strips, the amount of soil and the incubation time were different. These differences have a significant effect on P desorption (Chardon et al., 1996). For example, after a 16 h incubation period, as recommended by Sissingh (1983), P desorption continued with time, reflecting the continuous character of P desorption rather than the presence of a reversibly adsorbed and absorbed P pool. According to Schoumans et al. (1991), within 48 h, reversibly adsorbed P was to a large extent desorbed from soil, since P desorption continued only very slowly. The use of FeO-strips in calcareous soils, where P may precipitate with Ca, may introduce errors: due to the dissolution of Ca-P minerals, Ca dissolves as well. Since Ca is not retained by the FeO-strip, the Ca concentration in the solution increases, thus inhibiting the further dissolution of Ca-P minerals. In calcareous soils, a combination of anion and cation exchange membranes may be an alternative method (Kuo, 1996).

2.3.3.2 Total sorbed inorganic phosphorus

In noncalcareous sandy soils, the total amount of sorbed inorganic P (F) has been interpreted to be the sum of reversibly adsorbed P (Q) and slowly sorbed P (S), i.e., $F=Q+S$ (van der Zee et al., 1988; Schoumans and Groenendijk, 2000). The term absorbed P is used here to indicate slowly sorbed P. The acid ammonium oxalate extraction method (Schwertmann, 1964) was used to determine F (P_{ox}) as well as the sum of amorphous Al- and Fe-(hydr)oxides ($[Al+Fe]_{ox}$) which determines the total sorption capacity for inorganic P in noncalcareous sandy soils (Beek, 1979; van der Zee and van Riemsdijk, 1988). In noncalcareous sandy soils, the maximum amounts of reversibly adsorbed P (Q_{max}; mmol P kg^{-1}) and absorbed P (S_{max}; mmol P kg^{-1}) depend on $[Al+Fe]_{ox}$ (van der Zee et al., 1988; Schoumans and Groenendijk, 2000):

$$Q_{max} = \frac{1}{6} \times [Al + Fe]_{ox} \qquad (1)$$

$$S_{max} = \frac{1}{3} \times [Al + Fe]_{ox} \qquad (2)$$

Consequently, the maximum amount of inorganic P (F_{max}; mmol P kg^{-1}) sorbed, or the maximum sorption capacity, in noncalcareous sandy soils can be calculated according to Eq. (3) or (4):

$$F_{max} = Q_{max} + S_{max} \qquad (3)$$

$$F_{max} = \frac{1}{6} \times [Al + Fe]_{ox} + \frac{1}{3} \times [Al + Fe]_{ox} = a \times [Al + Fe]_{ox} \qquad (4)$$

The saturation factor α (=0.5) denotes the affinity of Al- and Fe-(hydr)oxides for P sorption. In noncalcareous sandy soils, van der Zee et al. (1990) reported α values ranging from 0.4 to 0.6 with an average of 0.5, implicating 1 mmol of $[Al+Fe]_{ox}$ sorbs a maximum amount of 0.5 mmol of P. In calcareous soils, $CaCO_3$ may buffer the acid mixture of ammonium oxalate and oxalic acid decreasing the effectiveness of the extractant. So in these soils, an alternative method has to be used. Also, the use of concentrated acids may cause the dissolution of otherwise slightly soluble Ca-P minerals, i.e., a fraction of P in soil which is not relevant for transfer to surface waters (Hartikainen, 1982). So for calcareous soils, Turtola and Yli-Halla (1999) proposed the use of NH_4F and NaOH to extract P sorbed by Al- and Fe-(hydr)oxides, respectively, and the acid ammonium oxalate method (Schwertmann, 1964) to extract Al and Fe.

2.3.3.3 Total inorganic phosphorus

In addition to the reversibly adsorbed and absorbed P pool (Fig. 2), a discrete mineral P pool can be distinguished in soil, containing P associated with Al, Fe or Ca in a crystalline form. Mineral P can be calculated as the difference between total inorganic P and P_{ox}. Various methods have been developed for measuring total inorganic P in soil. These methods often make use of concentrated acids to dissolve total inorganic P, e.g., HCl or H_2SO_4 (Kuo, 1996; Lepelaar and Schoumans, 1999).

2.3.3.4 Organic phosphorus

The organic P pool can be calculated as the difference between total P and total inorganic P. To measure total P, organic P has to be made available as inorganic P, which can be achieved by either dry or wet oxidation. Kuo (1996) used a combustion step in a muffle furnace at 550°C to oxidize organic matter; organic P is calculated as the difference between the amounts of H_2SO_4-extractable inorganic P for the ignited and unignited soils. Lepelaar and Schoumans (1999) used a wet oxidation step (H_2O_2) to oxidize organic matter; organic P is calculated as the difference between the amounts of HCl-extractable P for the oxidized and unoxidized soils.

3 Hydrological pathways of phosphorus transport

3.1 Introduction

Soil hydrology is one of the most important factors in determining the actual P transfer, because water transported from the field to surface waters acts as a 'carrier' for P (Haygarth and Jarvis, 1999). For example, a grassland soil with a high P status can be considered to have a high potential risk of P transfer, but P transport will not occur if there is no surface or subsurface runoff of water enriched with P to surface water. Hence, P transfer is associated with vertical and horizontal hydrological pathways. Here some definitions of the hydrological pathways of P transfer from topsoil to ground- and surface waters are described. For more detailed information on soil hydrology, the reader is referred to an extensive review by Haygarth and Jarvis (1999).

3.2 Vertical transport of phosphorus through the soil profile

Due to leaching, dissolved P is transported from the topsoil to deeper soil layers. Leaching is a general term in soil science referring to the downward movement of water with solutes through the soil. It is the sum of more or less independent hydrological pathways, such as saturated (or piston) and preferential (or macropore or bypass) flow (Haygarth and Jarvis, 1999). Consequently, P can be horizontally transported to surface water via subsurface runoff or through drainage pipes. Figure 3 shows a concept of the hydrological pathways. Saturated flow refers to the uniform movement of water through the soil after pores have become saturated with water, and is most common in sandy soils. During saturated flow, P in soil solution can be sorbed in deeper soil layers. Preferential flow involves the rapid and direct transport of a relatively large volume of water through a small part of the soil (Simard et al., 2000). Preferential flow occurs in soils with a locally low hydraulic conductivity forcing the water to flow through parts with a higher conductivity or in soils exhibiting a high conductivity. A low conductivity can be due to a low porosity resulting from a high clay content or to the presence of organic matter causing water repellency of the soil (Dekker, 1998; Ritsema, 1998). A high conductivity can be due to the presence of macropores (>100 μm), originating from soil cracks occurring especially in clayey soils, which are particularly vulnerable to cracking during dry periods, or to root channels and earthworm holes (Edwards et al., 1993). Preferential flow through these pores only occurs during rainfall events with a high intensity exceeding the infiltration capacity of these soils. Stamm et al. (1998) demonstrated the importance of P transfer from grassland soils due to preferential flow through earthworm holes. Furthermore, on arable land with conventional tillage P transfer was smaller than on arable land with reduced tillage, which was attributed to the destruction of macropores by tillage (Gaynor and Findlay, 1995). As stated by Stamm et al. (1998), instead of an exception, preferential flow may occur regularly, especially in permanent grassland soils and arable soils with reduced tillage. For the identification of 'hot spots', where preferential flow is the dominant hydrological pathway, only P in the topsoil should be monitored (Chardon and van Faassen, 1999). In contrast, under conditions where saturated and fingered flow are more important, P in the whole soil profile down to the upper groundwater should be considered. However, these criteria are difficult to apply in practice, because it is difficult to distinguish between these hydrological pathways.

3.3 Horizontal transport of phosphorus to surface water

Horizontal transport of P from soil to surface water comprises hydrological pathways such as surface runoff (or overland flow), subsurface runoff (or interflow or lateral flow), or transport of soil solution enriched with P through drainage pipes (Fig. 3). Surface runoff refers to the lateral movement of water across the surface of a sloping field in response to a rainfall event. The occurrence of surface runoff depends on the field slope and the permeability of the soil for infiltration of rainwater. The field slope determines the soil depth of interaction between surface runoff and soil P. For example, at a slope of 4%, the depth of interaction was calculated to be 0.2 to 0.3 cm (Ahuja, 1986). Phosphorus is mobilized in runoff water due to solubilization of P or detachment of P containing particles from soil, a process referred to as erosion (Hens and Schoumans, 2002). Erosion can mobilize P contained in both the reversibly and the absorbed P pool. The intensity and duration of the rainfall event are important factors, since they determine the volume of the runoff and erosion water. Subsurface flow refers to the lateral transport of soil solution below the soil surface along or above an impermeable deeper soil layer (e.g., clay). In sandy soils with a high water table subsurface flow is common. Furthermore, drainage pipes have been placed in the subsoil of many soils to facilitate lateral transport of soil solution. Consequently, the actual P load of surface water from a specific field can be calculated as the P concentration multiplied by the flux of surface or subsurface runoff or drainage water leaving the field.

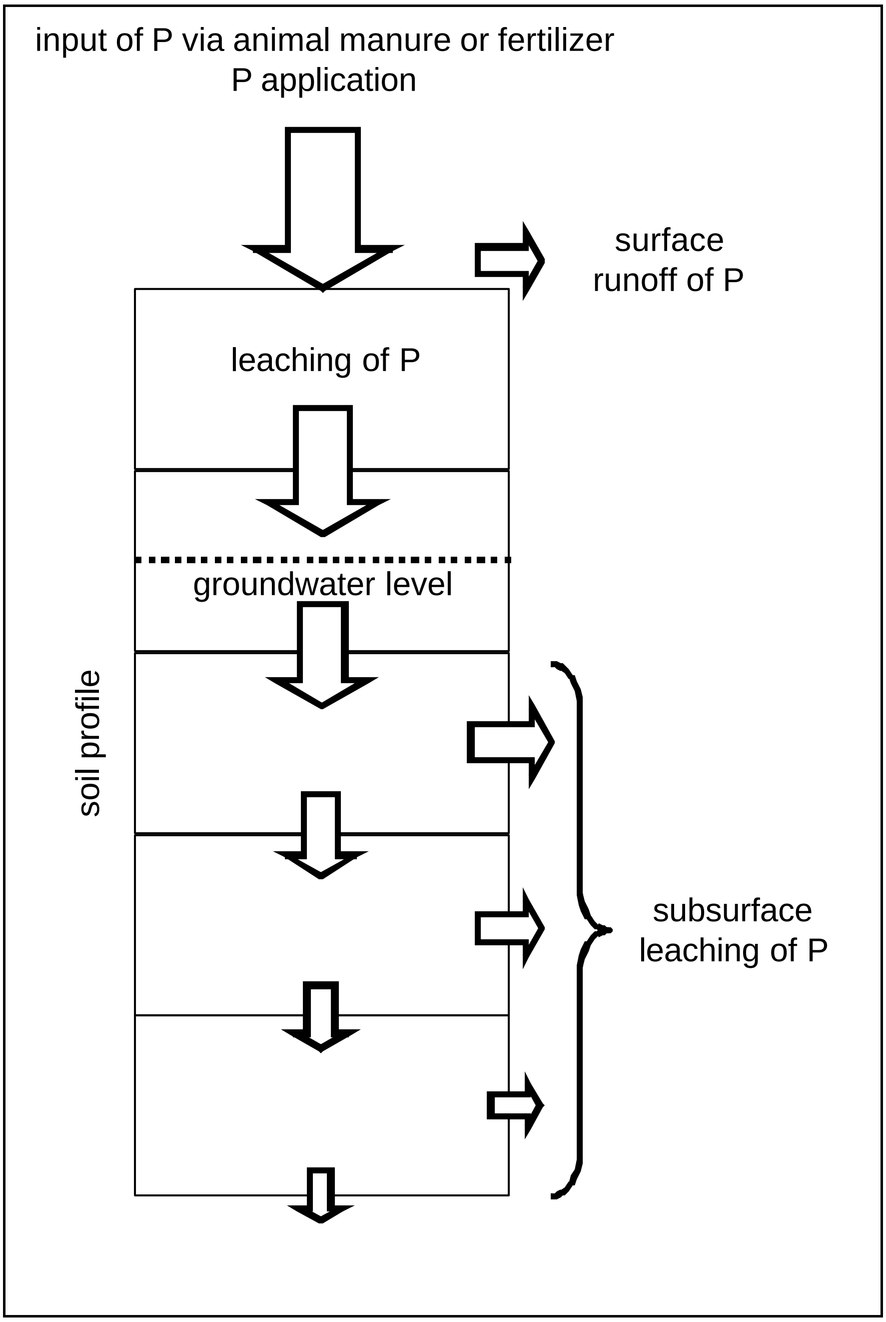

Figure 3 Concept of the hydrological pathways

4 Potential risk of phosphorus transfer

4.1 Introduction

Various indicators have been discussed and proposed in literature to estimate the potential risk of P transfer to surface water: a P balance at the farm level and ‘soil’ indicators (Table 4). The following ‘soil’ indicators are distinguished: agricultural, environmental and additional soil tests and soil water tests. The basic philosophy of using the P balance at the farm level is the following: due to a P surplus P accumulates in soil, and thus both the soil P status and the amount of P potentially available in soil for transfer to surface waters increase. Thus, a higher P surplus corresponds to a higher potential risk of P transfer. Simple relationships have been developed between agricultural, environmental and some additional soil tests on the one hand and P in soil water on the other, i.e., the so-called quantity (Q)-intensity (I) relationships. The Q-term refers to the amount of P potentially available in soil for transfer to surface water, whereas the I-term refers to P in soil solution, leachate, drainage water or runoff. Based on these relationships, a threshold for soil tests can be developed above which potential P transfer becomes unacceptable. However, these quantity-intensity relationships do not include a hydrological risk. Thus, the potential risk is separated from the actual risk. Soil water tests simulate P in soil solution or measure the P concentration directly in soil solution and drainage water closely approximating or representing actual P transfer from the field to surface waters. Here the P balance at the farm level and some 'soil' indicators are introduced.

Table 4 An overview of indicators proposed in literature to assess the risk of potential P transfer from agricultural soils to surface water

indicator	reference
P balance at the farm level	Chardon and van Faassen (1999)
P_{ox}	Pote et al. (1996)
DPS	van der Zee et al. (1990)
P-AL	Schoumans and Groenendijk (2000)
FeO-strip method	Pote et al. (1996)
Pw	Schoumans (1997), Chardon and van Faassen (1999), Schoumans and Groenendijk (2000)
soil solution	Chardon and van Faassen (1999)
drainage water	Chardon and van Faassen (1999)

4.2 Phosphorus balance at the farm level

The P balance at the farm level is the difference between the import and export of P. On an average dairy farm in the Netherlands, P is imported by purchased animal feed (61% of the total annual P import), P fertilizers (23%), animal manure (10%), animal products (2%) and other terms (2%). Exported takes place via animal products (77% of the total annual P export), animal manure (14%), plant products (5%) and other terms (5%) (Poppe et al., 1995). Differences can be expected between farm types; at an arable farm the P surplus is generally smaller than at a dairy farm, since the export of P via plant products is much higher than the export of P via animal products. Results of Poppe et al. (1995) indicated an average annual P surplus of 23 kg P ha^{-1} for an arable farm, 31 kg P ha^{-1} for a dairy farm, and 37 kg P ha^{-1} for a mixed livestock farm. Differences can be expected between individual farms as well. For example, Haygarth et al. (1998) compared the P balance of two grassland farming systems in the United Kingdom (UK), on an intensive dairy farm the annual P surplus was 26 kg P ha^{-1}, whereas on an extensive sheep farm it was only 0.28 kg P ha^{-1}. Thus, differences can be related to livestock density (Leinweber et al., 1997). In areas with noncalcareous sandy soils in the middle, east and south of the Netherlands where intensive livestock farming systems predominate, P surpluses have been much larger than the average P surplus of all agricultural land in the Netherlands; the average P surplus of arable land cropped with maize on these soils in the period between 1950 and 1990 ranged from 48 to 108 kg P ha^{-1} yr^{-1} (Reijerink and Breeuwsma, 1992), whereas the average P surplus of all agricultural land increased from 26 kg P ha^{-1} yr^{-1} in 1950 to 46 kg P ha^{-1} yr^{-1} in 1980, but decreased to 35 kg P ha^{-1} yr^{-1} in 1995 (Smaling et al., 1999).

4.3 Dutch standard agricultural soil fertility test methods

In the course of the 20th century, various agricultural soil tests have been examined to determine the availability of P for plant uptake, referred to as the soil P status. Relationships between soil P status and crop response (to P fertilizer application), established in (long-term) field experiments, are now widely used as a basis for P fertilizer recommendations. The basic philosophy of using soil tests is to mimic P uptake by plant roots under different soil conditions. This is rather complicated, because plants differ in root activity and soils differ in P desorption characteristics. Furthermore, climate, soil cultivation, crop management and nutrient management may affect both root activity and (ad)sorption characteristics. Many soil tests appeared to be suitable, although relationships between soil test P and crop response often showed a large variation. Currently, many different soil tests are used for P fertilizer recommendations (Tunney et al., 1997). Due to the enrichment of soils with P in areas where intensive livestock farming systems predominate, emphasis has shifted from P fertilizer recommendations to the identification of 'hot spots' of potential P transfer.

Pw and P-AL

Chardon and van Faassen (1999) and Schoumans and Groenendijk (2000) discussed the use of the Dutch agricultural soil tests Pw and P-AL as indicators for the potential risk of P transfer. The advantages of using these soil tests are the availability of extensive data sets and routine analytical methods. Furthermore, the use of these indicators facilitates communication between scientists, policy makers and farmers (Schoumans et al., 2000). The Pw method, introduced by Sissingh (1971) and van der Paauw (1971), is used in the Netherlands as a soil test for arable land. The Pw value is determined at a soil to solution ratio of 1 to 60 (v/v): 1.2 mL of soil is preequilibrated with 2 mL of water for 22 h at 20°C. After pre-equilibration, 70 mL of water is added and the soil is shaken for 1 h, and the DRP concentration is determined after filtration. Normally, Pw is expressed in mg P_2O_5 L^{-1} of soil. The P-AL method is used as a soil test for grassland. The DRP concentration is determined after extraction of 2.5 g soil with 50 mL of a mixture containing ammoniumlactate and acetic acid solution (pH=3.75) for a period of 4 h (Egnér et al., 1960). Normally, P-AL is expressed in mg P_2O_5 100 g^{-1} of soil. Due to the wide soil to solution ration, Pw represents P in soil solution and part of the reversibly adsorbed P (Schoumans and Groenendijk, 2000). On average, Pw represented 15.4% of FeO-strip-P in 71 noncalcareous sandy topsoil samples, (Schoumans et al., 1991). In the study of Schoumans et al. (1991), P-AL was on average 2 times higher than FeO-strip-P. Thus, P-AL represents P contained in the reversibly adsorbed P pool and a part of P contained in the absorbed pool (Schoumans and Groenendijk, 2000). Chardon and van Faassen (1999) found a good experimental nonlinear relationship between DRP in the centrifuged soil solution and Pw of 284 soil samples (clay, loess, reclaimed peat and noncalcareous sand) (Fig. 4). Apparently, Pw extracts a part of P from soil indicative for the potential P transfer via leaching of soil solution. In noncalcareous sandy soils, Schoumans and Groenendijk (2000) accurately estimated the Pw from calculations based on the time dependent P desorption from the reversibly adsorbed P pool, assuming the contribution of absorbed P to P desorption was negligible. Furthermore, Schoumans and Groenendijk (2000) derived a model to calculate the P equilibrium concentration in soil solution from the Pw value of a specific soil layer. Using an annual precipitation surplus of 300 mm yr^{-1}, the amount of P potentially leaching from the topsoil can be estimated.

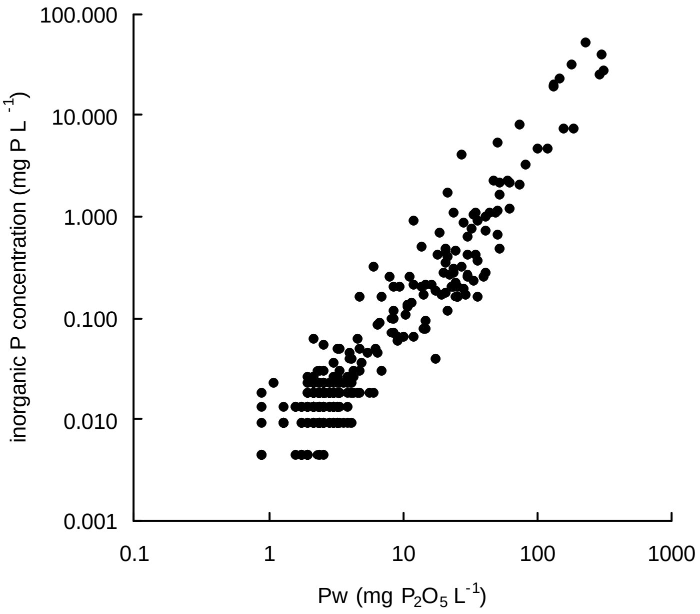

Figure 4 Experimental non-linear relationship between DRP in centrifuged soil solutions and Pw of 284 soil samples (clay, loess, reclaimed peat and sand). The results are plotted on a double log scale (Chardon and van Faassen, 1999)

4.4 Dutch standard environmental soil test: The degree of phosphorus saturation

To prevent contamination of groundwater, a critical degree of P saturation (DPS), was defined in the Netherlands, as described in the protocol on phosphate saturated soils (van der Zee et al., 1990). This protocol was developed exclusively for noncalcareous sandy soils, because intensive livestock farming systems with high application rates of animal manure predominate in areas on these soils. In noncalcareous sandy soils, P reacts mainly with Al- and Fe-(hydr)oxides (Beek, 1979). The maximum sorption capacity of the soil (F_{max}) can be calculated from the amounts of Al and Fe extracted by the acid ammonium oxalate method of Schwertmann (1964) according to Eq. (3) and (4) (see 2.3.4.). Consequently, the degree of saturation of F_{max} with P (DPS), can be calculated:

$$\mathrm{DPS} = \frac{P_{ox}}{F_{max}} \times 100 \tag{5}$$

where DPS is expressed as a percentage and P_{ox} is the P extracted by acid ammonium oxalate expressed in mmol P kg^{-1}. The basic philosophy of preventing groundwater contamination is that the P equilibrium concentration in soil solution at the MHW should not exceed 0.10 mg inorganic P L^{-1}. The value of 0.10 mg P L^{-1} has been set as the upper limit for inorganic P in surface waters to prevent eutrophication and associated adverse effects (TCB, 1990). Chardon and van Faassen (1999) and Schoumans and Groenendijk (2000) derived a nonlinear relationship between the DPS of the soil profile between the soil surface and the MHW and the P equilibrium concentration in soil solution leaching out of the soil profile on the long-term:

$$\mathrm{P\ concentration} = \frac{\frac{1}{6}}{0.5 \times K} \times \frac{\mathrm{DPS}}{100 - \mathrm{DPS}} \tag{6}$$

where the P concentration is expressed in mmol P L^{-1}, K (expressed in L $mmol^{-1}$), is a constant of the Langmuir adsorption equation describing the soil adsorption strength of the fast reaction (Q), and DPS is expressed as a percentage. Figure 5 shows the nonlinear relationship between the DPS and the P equilibrium concentration for a noncalcareous soil sandy soil with an average K value. At a DPS>25%, the P equilibrium concentration leaching out of the soil profile above the MHW exceeds 0.10 mg P L^{-1} on the long-term. Thus, already before the soil becomes completely saturated with P, the limit for P in surface waters in the Netherlands would be exceeded at the MHW.

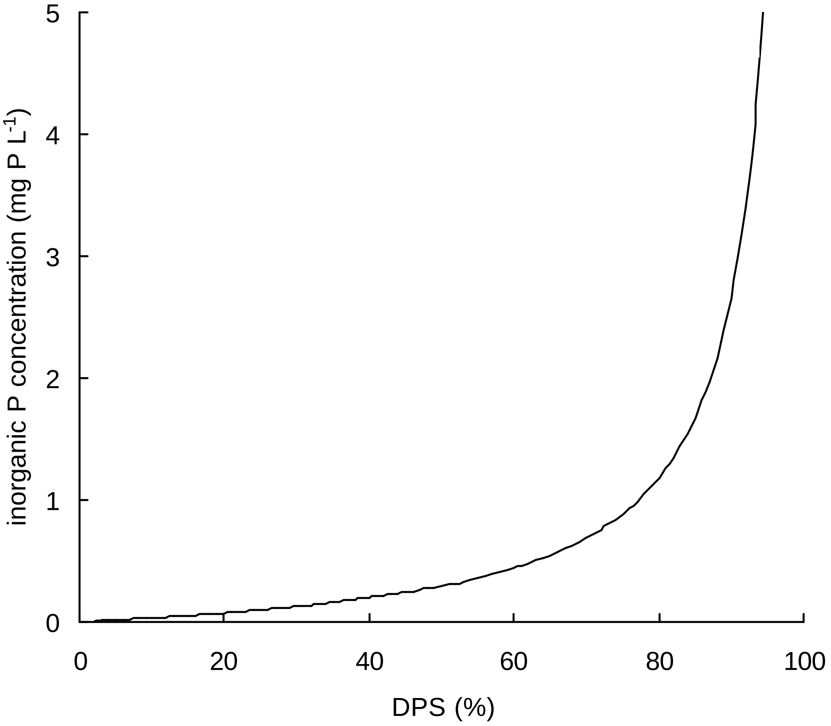

Figure 5 The nonlinear relationship between the DPS of the soil and the P equilibrium concentration in soil solution (Chardon and van Faassen, 1999; Schoumans and Groenendijk, 2000)

The DPS concept has already been used intensively to define the extent of P saturated noncalcareous soils in the Netherlands (Reijerink and Breeuwsma, 1992), Belgium (Lookman, 1995) and Germany (Leinweber et al., 1997). In the Netherlands, the P concentration in the upper groundwater exceeds the surface water limit of 0.10 mg P L^{-1} in an estimated 70% of the noncalcareous sandy soils, covering an area of about 400,000 ha (Reijerink and Breeuwsma, 1992).

The unfamiliarity of the DPS concept to farmers may complicate communication between scientists and policy makers on the one hand, and farmers on the other hand. Farmers only work with agricultural soil tests such as Pw and P-AL (Schoumans et al., 2000). For communication purposes, it should be possible to convert the DPS to Pw or P-AL. Based on the experimental results of a large number of noncalcareous sandy topsoil samples, Schoumans et al. (1991) derived some simple linear regression models between DPS on the one hand, and Pw and P-AL on the other. These models may be suitable for converting DPS to Pw and P-AL in the topsoil. Fraters and Boumans (1997) used the same approach for results obtained from the 'mestmeetnet'. Moreover, based on some assumptions (e.g., P status below the topsoil), Schoumans et al. (1991) and Fraters and Boumans (1997) derived threshold values for Pw and P-AL in 'wet' noncalcareous sandy topsoils which correspond to the critical DPS value of 25% of the soil profile between the soil surface and the MHW. The ‘wet’ noncalcareous sandy soils are defined as soils exhibiting shallow groundwater levels. For the use of the DPS concept in calcareous soils, Turtola and Yli-Halla (1999) developed an alternative method (see 2.3.4.). This method needs further studying as it has not been applied yet in the Netherlands.

4.5 Inventory of other ‘soil’ indicators

4.5.1 Soil tests

The FeO-strip method has frequently been used as an indicator for estimating 0.01 M $CaCl_2$-extractable P (Pautler and Sims, 2000), water-extractable P (Hooda et al., 2000) and the DRP concentration in runoff (Pote et al., 1996). Pautler and Sims (2000) found a good nonlinear relationship between FeO-strip-P and 0.01 M $CaCl_2$-extractable P over 127 soil samples of differing physical-chemical characteristics. Hooda et al. (2000) found a good linear relationship between FeO-strip-P and water-extractable P. The FeO-strip method had a good correlation with the DRP concentration in runoff over 54 silt loam soil samples with different levels of soil P (Pote et al., 1996). In the studies of Pote et al. (1996) and Hooda et al. (2000), P_{ox} was used as an indicator as well. Pote et al. (1996) found a good correlation between P_{ox} and the DRP concentration in runoff, but Hooda et al. (2000) found a very poor correlation between P_{ox} and water-extractable P over 11 soil samples of differing physical-chemical characteristics. For the purpose of estimating potentially soluble P in soil samples with increasing levels of soil P of one specific soil type, as in the study of Pote et al. (1996), P_{ox} is expected to give a good correlation with P in runoff. However, for soils with different physical-chemical characteristics (pH, organic matter content, $[Al+Fe]_{ox}$ and clay content), the correlation between P_{ox} and potentially mobile P becomes much worse, as these physical-chemical characteristics affect the distribution of P over the solid phase and soil solution; P_{ox} provides an indication of the total amount of inorganic sorbed P instead of potentially soluble P (Schoumans et al., 1991; Hooda et al., 2000).

4.5.2 Soil water tests

Many experimental and model based relationships between soil tests on the one hand, and P in soil solution and drainage water on the other have been developed for estimating actual P losses. Instead of using these approaches, the P concentration in soil solution and drainage water can be measured directly as well. These methods, referred to as soil water tests, are introduced here. To estimate the contribution of a specific field to the total P load of surface water, the measured P concentration has to be multiplied by the flux of soil solution or drainage water leaving the specific field. Thus, still additional measurements or model calculations of water fluxes have to be conducted to obtain an estimate of the actual P transfer.

4.5.2.1 Soil solution

The amount of P in the soil solution generally represents less than 1% of total P in the soil. Indeed, the P-1:2 method (water-extractable P at a soil to solution ratio of 1:2 [w/v]) of Sonneveld et al. (1990), which can be used to simulate P in soil solution, represented on average 0.4% of the total P content in 7 noncalcareous sandy topsoil samples (Koopmans et al., 2001). The P concentration in the soil solution depends on plant uptake of P and applications of animal manure and P fertilizer (Chardon and van Faassen, 1999). Due to the removal of P from soil solution by plant uptake, a fast desorption reaction of P adsorbed to surface sites of Al- and Fe-(hydr)oxides is expected (van der Zee et al., 1987). On the other hand, after an application of animal manure or P fertilizer a fast adsorption reaction is expected. Since the fast adsorption and desorption reactions vary both in space and time, due to spatial and temporal variability of important soil physical-chemical characteristics (e.g., Al- and Fe-[hydr]oxide content, background electrolyte, pH, redox potential and temperature) (Schoumans, 1995), so does the P concentration in soil solution. Soil solution can be collected using porous cups placed in the field or by centrifugation of field-sampled moist soil in the laboratory followed by filtration (0.45 μm). A porous cup has an effective pore size of 0.1 μm (unpublished results). Thus, filtering is not necessary. The DRP and TP concentrations can then be measured.

There are some methodological problems with regard to the use of porous cups and the centrifugation technique. Results obtained by using both methods are often not comparable (personal communication, C. van der Salm, 2003). Generally, the DRP and TP concentrations in soil solution obtained from porous cups are (much) lower than those in a 0.45 μm filtered centrifugate, due to the larger filter size of porous cups. Furthermore, the vigor of the centrifugation method may result in the release of soil solution with a high P concentration from very small soil aggregates and of P containing colloidal soil particles, causing a further increase of the DRP and TP concentrations. As an alternative method for measuring P directly in soil solution, P-1:2 can be used as an approximation (Sonneveld et al., 1990). The P-1:2 method is determined in pretreated soil samples (drying at 40°C and sieving through a 2 mm sieve), implicating that soils can be stored until analysis.

In a lysimeter experiment with a silty clay loam soil (Broadbalk experiment, Rothamsted, UK), Thomas et al. (1997) measured P in soil solution which was collected from porous cups placed at drainage depth at a distance of 0.6 m from the drainage pipes. The DRP concentration in the soil solution at drainage depth was much lower than the RP concentration in the drainage water. However, a good correlation was found between the latter and the DRP concentration in soil solution obtained by centrifugation of moist soil samples from the plough layer. This was explained by the occurrence of preferential flow. For the identification of 'hot spots' where preferential flow is the dominant hydrological pathway, only the DRP and TP concentration in the topsoil should be monitored (Chardon and van Faassen, 1999). In practice, however, it is very difficult to assess whether preferential flow occurs.

4.5.2.2 Drainage water

Drainage water can be collected at the outlet of drainage pipes. After filtration (0.45 μm), the DRP and TDP concentrations can be measured. The P concentration in drainage water can have a high spatial variability (Chardon and van Faassen, 1999). The P concentration measured at an individual drainage pipe reflects only P losses at a specific part of the field, and cannot be considered as representative for a whole field. Hartmann et al. (1997) measured the RP concentration in water sampled at the outlet from drainage pipes placed in the subsoil of arable land (noncalcareous sandy and sandy loam soil) within the watershed of the river the Poekebeek (Belgium); it varied from 0.01 to 0.27 mg P L^{-1}. Hartmann et al. (1997) explained differences between RP concentrations by spatial variability of the DPS at the field level. Furthermore, a high temporal variability of the P concentration in drainage water has been found. Beauchemin et al. (1998) measured the TP concentration in drainage water collected at 27 sites in the province of Quebec in Canada, the Quebec water quality standard of 0.03 TP L^{-1} was exceeded in 14 out of 27 sites in 1994, but only in 6 out of 25 sites in 1995. In 1994, drainage water samples were collected after a high intensity rainfall event following a dry period. This resulted in a flush of inorganic P from the crop residues and preferential flow in dry clayey soils (Beauchemin et al., 1998). In Belgium, the VLM (1997) determined the RP concentration in drainage water leaving a field with a high P status; at the beginning of a rainfall event, the RP concentration was similar to the P concentration in soil solution at drainage depth. After several weeks of rainfall, the groundwater level between the drainage pipes increased to a level near the soil surface, resulting in a large increase of the RP concentration of the drainage water.

5 Discussion

5.1 Introduction

To evaluate policies and measures implemented to decrease P loading of agricultural soils and the associated soil potential for P transfer, P loss to surface waters should be monitored. However, the estimation of actual P loss is rather complicated, since it requires the measurement or model estimates of water fluxes leaving a specific field in combination with measurement of the DRP and TP concentration in soil solution in different soil layers or drainage water. Instead, we will propose simple methods indicative of the potential mobility of P in soil, excluding the hydrological risk. We restrict the use of these indicators to the so-called 'wet' soils exhibiting a shallow groundwater level and directly draining to surface waters. These possible 'hot spots' are likely to exhibit a high actual risk of P transfer, because of the probability of a hydrological connection between these 'hot spots' and surface water. Here the indicators, which were previously introduced in Chapter 4, are discussed on the basis of some selection criteria.

5.2 Selection criteria

An indicator suitable to evaluate changes in P management should satisfy the following three criteria: *purposive*, *measurable* and *reactive*.

Purposive
The term *purposive* refers to the relation between the indicator and the purpose of the implemented policies and measures. When there is no relation between an indicator and the purpose of the policies and measures, the purpose may not be entirely achieved, because the implemented policies and measures are evaluated and governed using irrelevant information.

Measurable
The term *measurable* refers to the *costs* and *accuracy* of the indicator. The *costs* refer solely to the analytical method without sampling of the soil in the field. In general, the *costs* are lower if a routine analytical method is available. Obviously, the *costs* of a large-scale monitoring program will not be acceptable for society if they are not in proportion to the economical importance of the agricultural sector. Thus, the *costs* of conducting an analytical method have to be as low as possible. The term *accuracy* refers to the error associated with an analytical method. If an analytical method has a large error, assessment of the potential risk of P transfer becomes less accurate. For policy makers, policies and measures cannot be based and governed on information with a low *accuracy*. In turn, farmers do not comply with such policies and measures, since application of a monitoring program may have serious consequences for P management of 'hot spots' exhibiting a very high potential risk of P transfer. For example, on these locations the application of animal manure and P fertilizer can be

largely restricted or even forbidden. Hence, indicators used for assessment of the potential risk need to have a high *accuracy*.

Reactive

The term *reactive* refers to the connectivity between an indicator and policies and measures involving a change of P management. An indicator should respond to changes in P management. In that case, the indicator is referred to as *sensitive*. Using an insensitive indicator, the effectiveness of policies and measures implemented to decrease the potential of agricultural soils for P transfer cannot be monitored or evaluated. Furthermore, an indicator should be *independent* of other factors, such as the variability in soil physical-chemical characteristics and weather conditions. To monitor the effects of a change in P management, effects of other factors are highly undesirable, a less *independent* indicator is expected to exhibit a higher spatial and temporal variability, due to the variability in soil physical-chemical characteristics (Schoumans, 1995). To encompass a higher variability of an indicator, a larger number of samples is required both in space and time, leading to higher *costs* of the monitoring program.

5.3 Qualitative assessment of the indicators

Based on the selection criteria explained before, the indicators are discussed and assessed qualitatively on a scale which varies from + to ++++. Ultimately, the overall score of each indicator can be calculated (Table 7). Not all of the criteria are considered to be equally important: the criteria *purposive* and *sensitive* are considered to be more important than the other criteria:

$$\text{Overall score} = 2*\textit{purposive} + \textit{costs} + \textit{accuracy} + 2*\textit{sensitive} + \textit{independent} \qquad (7)$$

5.3.1 Phosphorus balance at the farm level

Purposive

The basic philosophy of using the P balance at the farm level as an indicator is: due to the increase of the soil P status as a result of a P surplus, the amount of P potentially available in soil for transfer increases as well. Increased loading of the soil with P has been directly associated with P transfer to surface water leading to eutrophication (Foy et al., 1995). From the perspective of policies and measures implemented to decrease the loading of the soil with P, a less positive P balance at the farm level is expected to result in a decrease of the soil P status and the amount of P potentially available in soil for transfer. However, the use of the P balance at the farm level as an indicator on the field level has serious limitations. The soil P status not only depends on the recent P surplus, but also on the P surplus in the last decades. Therefore, a P balance at the farm level gives only a first indication of the potential risk of P transfer (Chardon and van Faassen, 1999). Also, the P balance at the farm level is not necessarily related to the soil P status of a specific field. For example, a specific field receiving large amounts of animal manure and P fertilizer has a positive P balance whereas the P balance averaged over all of the agricultural land of a farm can be much less positive if the other fields receive much less animal manure or P fertilizer. Furthermore, the P balance does not provide any understanding of the speciation of P sorbed to the solid phase of the soil (Fig. 2). For example, if all P is contained in the absorbed P pool, the actual risk of P transfer is very low, since desorption of absorbed P is very slow. Thus, a positive P balance does not necessarily result in a high potential mobility of P in soil. Concluding, the P balance at the farm level is not directly related to the purpose to decrease the potential P transfer and receives only one +.

Measurable
In the Netherlands, it should be possible to connect to the MINeral Accounting System (MINAS) for calculating the P balance at the farm level. In that case, the *costs* of collecting the information required to calculate the P balance are expected to be low. Therefore, the P balance received four +. In most cases, average values for the P content of the export terms of the P balance (e.g., animal manure, and animal and plant products) are used. Due to variation, the actual P content may differ from these average values, leading to a P balance with a low *accuracy*, so for this criterion the P balance at the farm level received two +.

Reactive
Obviously, effects of changes in P management are directly apparent on the P balance at the farm level implicating the latter is very *sensitive* to changes in P management, and the P balance received four +. Furthermore, the P balance at the farm level is *independent* and received four +.

5.3.2 Soil tests and soil water tests

Purposive
In contrast to the P balance at the farm level, soil tests provide direct insight of the actual soil P status and thus of the P potentially available for transfer. Thus, these indicators are more directly related to the purpose to decrease the potential P transfer. Some of these soil tests (P-AL and P_{ox}) are more indicative of (part of) total sorbed inorganic P than of the more readily soluble P forms; therefore, these methods received two +. Although the DPS has been shown to be an effective indicator for preventing contamination of the groundwater on the long-term (van der Zee et al., 1990), it is not necessarily indicative of readily soluble P on the short-term, since the DPS is based on the acid ammonium oxalate method which extracts total sorbed inorganic P; similar to P-AL and P_{ox}, the DPS received two +. A good relationship over different soil types has been demonstrated between Pw and FeO-strip-P on the one hand and 0.01 M $CaCl_2^-$ and water-extractable P and P in soil solution and runoff on the other hand (Pote et al., 1996; Chardon and van Faassen, 1999; Hooda et al., 2000; Pautler and Sims, 2000). Apparently, these soil tests are indices of potentially mobile P forms in soil and received three +. The soil water tests received four +, because P in soil solution represents the P actually at risk to

transfer whereas P in drainage water represents P actually being transferred from the field to surface waters. However, not all fields are drained by drainage pipes, implicating that P in drainage water is not generally applicable as an indicator on all fields. Furthermore, P in drainage water does not provide any information with respect to the possible enrichment of soil layers with P below the plough layer, if P has not been transported yet down to the depth where drainage pipes are present.

Measurable

Routine analytical methods are available for the Dutch standard agricultural soil fertility test methods Pw and P-AL, implicating *costs* of these analytical methods are low. Although a routine analytical method is available for P_{ox} and $[Al+Fe]_{ox}$ (the acid ammonium oxalate method of Schwertmann [1964]), *costs* are roughly two times higher than those of Pw and P-AL. Based on P_{ox} and $[Al+Fe]_{ox}$, the DPS can be calculated (Eq. [5]). For the FeO-strip method, a routine analytical method is currently being developed at ALTERRA. Nevertheless, the method remains laborious and costs are roughly three times higher than those of Pw and P-AL. Thus, Pw and P-AL received four +, P_{ox} and the DPS received three +, and the FeO-strip method received two +. The *costs* of the analytical method to measure the P concentration in soil solution and drainage water in the laboratory are low. However, *costs* to collect soil solution using porous cups are very high, implicating it is not feasible to use the latter in a large-scale monitoring program. Other less costly methods to collect soil solution have to be used, i.e., the centrifugation method, or the P-1:2 method, which has been used to simulate soil solution. The *costs* of these methods are expected to be comparable with those of P_{ox} and the DPS and received three +. The centrifugation method has a disadvantage: little experience is present to handle field-sampled moist soil in a large-scale monitoring program. Field-sampled moist soil has to be processed in the laboratory within a short period of time, because storage may affect the results. More research is needed on the comparability of P in soil solution with P in a 1:2 (w/v) water extract. The *costs* of P in drainage water are expected to be comparable to those of the centrifugation and P-1:2 extraction method and received three +. Table 5 shows the coefficient of variation (CV) of P-1:2, Pw, the FeO-strip method, P_{ox} and the DPS. The CV is considered to be indicative of the accuracy of these 'soil' indicators. The data were obtained from studies of Koopmans et al. (2001; submitted) in which a total number of 56 noncalcareous sandy soil samples were analyzed in triplicate. For each soil sample, the CV was calculated as the standard deviation divided by the average multiplied by 100%. The CV of the 'soil' indicators, averaged over the 56 soil samples, ranged from 1.42 (DPS) to 4.27% (FeO-strip method). In a limited number of soil samples, the maximal CV of P-1:2, Pw, and the FeO-strip method was above 10%. The CV of the FeO-strip method was in general somewhat higher than the CV of the other methods. Therefore, P-1:2, Pw, P_{ox}, and the DPS received four + whereas the FeO-strip method received 3 +. For P-AL, we expect an average CV similar to the one as was found for P_{ox}, as both methods are destructive soil tests; thus, P-AL received four +. For P in drainage water, we expect an average CV similar to the one as was found for P-1:2 and Pw; thus, P in drainage water received four +.

Table 5 Analytical error of the indicators, presented as the coefficient of variation (%), obtained from data-sets of Koopmans et al. (2001; submitted) in which a total number of 56 noncalcareous sandy soil samples were analyzed in triplicate

	P-1:2	Pw	FeO-strip-P	P_{ox}	DPS
average	2.41	2.44	4.27	1.98	1.42
median	1.34	2.18	3.69	1.46	1.26
minimum	0.08	0.22	0.72	0.38	0.17
maximum	14.12	10.24	10.81	6.76	3.19

Reactive: sensitive

Based on the results of the pot experiment of Koopmans et al. (submitted), where a noncalcareous P enriched sandy soil was depleted by intensive cropping of grass at zero P application for 2.7 yr in the greenhouse, the 'soil' indicators can be evaluated on the criterion *sensitivity*. The soil was sampled from the tillage layer of a site of a field experiment treated with 160 tons of pig slurry ha^{-1} yr^{-1} for a long period (Del Castilho et al., 1993). The pot experiment consisted of two 2 treatments: soil was placed in a layer of either 5 or 10 cm. In the soil samples obtained from the pot experiment, P was characterized using the following soil tests: Pw, the FeO-strip method, P-AL, P_{ox}, and the DPS. To estimate P in soil solution, the P-1:2 method was used. Table 6 shows the results of the pot experiment. The DPS of the initial soil was very high, i.e., 84% and exceeds the threshold of 25% corresponding to the surface water limit of 0.1 mg inorganic P L^{-1}. Hence, the P concentration in soil solution leaching from the 0-5 and 0-10 cm soil layers will exceed the P surface water limit on the long-term, demonstrating the necessity of measures aiming to decrease potential P transfer. From the 0-5 and 0-10 cm soil layers, 208 and 290 kg P ha^{-1} was removed within 2.7 years, respectively, via plant uptake and harvesting of the above ground plant parts. Phosphorus in soil solution showed the largest decrease, followed by Pw, FeO-strip-P, P-AL, P_{ox} and the DPS. Apparently, P in soil solution, Pw, and the FeO-strip method are more sensitive to changes in P management than P-AL, P_{ox} and the DPS. This can be understood from the perspective of a desorption isotherm which describes the equilibrium between total sorbed inorganic P and P in soil solution (Koopmans et al., submitted). The initial soil lies high on the desorption isotherm, but moves down the isotherm due to plant uptake of P. The desorption isotherm has a very strong nonlinear shape. Therefore, in the initial stage, the buffering of the soil is very low, explaining why the DRP concentration in soil solution (P-1:2) decreased very fast with plant uptake of P, whereas total sorbed inorganic P (P_{ox}) decreased much slower. Furthermore, from the strong nonlinearity of the desorption isotherm, it can be understood why Pw decreased at a higher rate than FeO-strip-P followed by P-AL. The FeO-strip method gives an estimate of the reversibly adsorbed P pool (van der Zee et al., 1987). The Pw method extracts both P in soil solution and part of the reversibly adsorbed P pool, whereas P-AL extracts both the reversibly adsorbed P pool and a large part of the absorbed P pool (Schoumans and Groenendijk, 2000). Consequently, because Pw resembles P in the soil solution more than FeO-strip-P and P-AL, Pw decreases at a higher rate (Koopmans et al., submitted). Summarizing, in the pot experiment P in soil solution was the most sensitive indicator to changes in P management in the topsoil and received four +. However, monitoring of P in soil solution in deeper soil layers may be less sensitive to changes in P management. During saturated flow of soil solution through the soil profile, soil solution can become enriched with P again, because of solubilization of P from deeper P enriched soil layers. Analogous to P in soil solution, P in drainwater may be less sensitive. Under conditions where preferential flow dominates P transport from the topsoil to deeper soil layers, P in drainage water can be a sensitive indicator. In practice, however, it is difficult to assess whether preferential flow occurs, so P in drainage water received two +. The Pw received three +, followed by the FeO-strip method receiving two +, and P-AL, P_{ox} and DPS receiving one +.

Table 6 Results of the pot experiment of Koopmans et al. (submitted)

indicator	unit	soil extractable P before depletion	soil extractable P after depletion		relative decrease of soil extractable P (%)	
			0-5cm	0-10cm	0-5cm	0-10cm
soil solution†	mg kg^{-1}	4.84	0.34	0.77	93	84
Pw	mg P_2O_5 L^{-1}	73.0	9.4	18.4	85	73
FeO-strip method	mg kg^{-1}	49.2	8.5	13.6	83	72
P-AL	mg P_2O_5 100 g^{-1}	91.3	35.2	50.1	61	45
P_{ox}	mg kg^{-1}	896	468	611	48	32
DPS (Eq. [6])	%	84	46	57	45	33

†Measured according to the P-1:2 extraction method

Reactive: independent

An indicator that is sensitive to changes in P management can also be sensitive to variability of soil physical-chemical characteristics, land-use changes, weather conditions, plant uptake of P, and animal manure and P fertilizer applications (Schoumans, 1995; Chardon and van Faassen, 1999). Such an indicator is not *independent.* Obviously, to evaluate changes in P management, effects of other factors are highly undesirable. Thus, an indicator has to be sensitive to changes in P management, but *independent* of other factors. Phosphorus in soil solution and drainage water can be highly variable both in space and time (e.g., Hartmann et al., 1997; Beauchemin et al., 1998). This is illustrated in Fig. 6, showing the average DRP concentration in solutions obtained from suction cups and its 95%-confidence interval as a function of time. The results were obtained from a field experiment where porous cups were placed 20 cm below the soil surface on four sites in a grazed pasture on a noncalcareous sandy soil (unpublished results, C. van der Salm). The export of P from the field was slightly higher than the import: the P balance was -2 kg P ha^{-1} yr^{-1} (van Middelkoop et al., in preparation). Thus, assuming equilibrium between the reversibly adsorbed P pool and the absorbed P pool, we would expect no change of the DRP concentration in soil solution due to P management. The average DRP concentration in soil solution showed a high spatial variability, as indicated by the wide 95%-confidence interval. To decrease the spatial variability, a higher number of porous cups should be used. For example, to decrease the width of the 95%-confidence interval of the average DRP concentration measured at day 14 from 0.8 to 0.2 mg P L^{-1} with a probability of 80% requires the use of more than 40 porous cups. To obtain a measure of the short-term temporal variation, we calculated the CV of the DRP concentration averaged over all days of the field experiment, which was 42%. Prummel (1974) reported results on the short-term temporal variation of Pw and P-AL in field experiments on calcareous clayey soils: for Pw and P-AL, a CV of 17 and 10% was calculated, respectively. Thus, P-AL may be a (much) better buffered 'soil' indicator than P in soil solution and Pw, and is thus more *independent.* The P_{ox} and DPS are very well buffered 'soil' indicators as well. Therefore, P-AL, P_{ox} and the DPS received four +. The FeO-strip method is expected to have a similar temporal variation as Pw, as both methods measure P from the same pools. The Pw and the FeO-strip method received three +, and the soil water tests received one +.

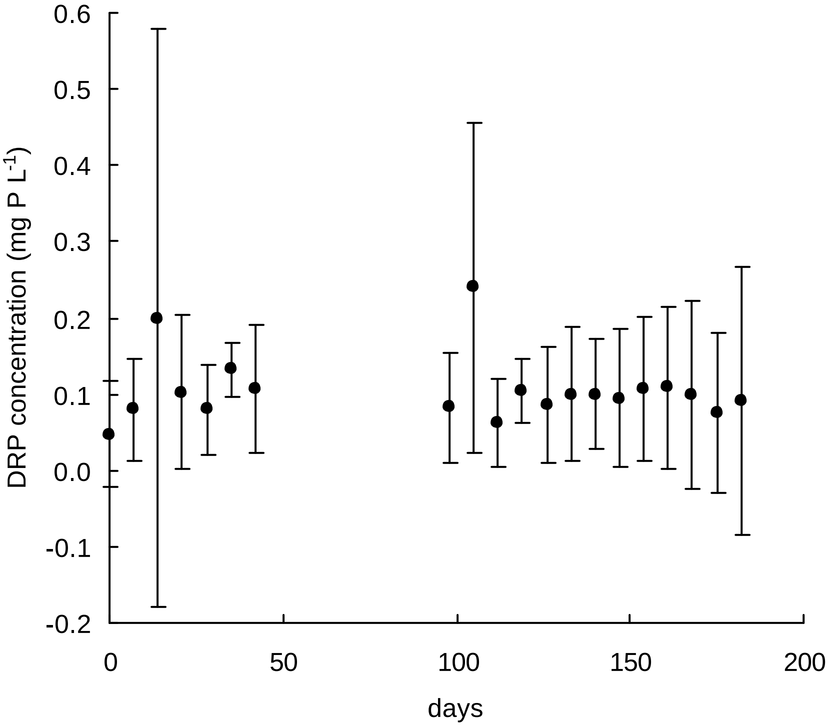

Figure 6 The average DRP concentration in soil solution and its 95%-confidence interval collected from porous cups placed 20 cm below the soil surface on four sites in a grazed pasture on a noncalcareous sandy soil plotted as a function of time (unpublished results, C. van der Salm)

5.4 Proposal for an indicator

The objective of our study was to select indicators that are suitable to evaluate the effectiveness of policies and measures aiming to decrease potential P transfer at the field level. The largest effects of changes in P management are expected to occur in the topsoil of intensively managed agricultural land. Therefore, only P in the upper soil layer of grassland and of the plough layer of arable land should be considered, irrespective of the hydrological pathway of P transport. Based on the overall score of the indicators, an indicator is selected that has to be tested in a field experiment. The overall score of the indicators was calculated according to Eq. (7), and results are given in Table 7. As mentioned before, not all criteria are considered to be equally important; the criteria purposive and sensitive are most important, so these criteria are multiplied by a factor 2 in Eq. (7).

Phosphorus in soil solution received the highest number of +, followed by Pw, and P in drainage water and the P balance at the farm level, whereas the FeO-strip method, P-AL, P_{ox} and the DPS received the lowest number of +. However, differences between the overall scores were small. The overall score of the indicators agreed with our expectations. The soil water tests, i.e., P in soil solution and drainage water, represent the P actually at risk to transfer and P actually being transferred from the field to surface waters, respectively, resulting in a high score on the criterion *reactive*. However, P in drainage water had a low score on the criterion *sensitive*; during the vertical transport of soil solution through the soil profile via saturated flow, soil solution can become enriched with P again, because of solubilization of P from deeper P enriched soil layers. Consequently, upon horizontal transport of P enriched soil solution via drainage pipes, monitoring of P in drainage water is not sensitive. Furthermore, not all fields are drained by drainage pipes, implicating P in drainage water is not generally applicable as an indicator to all fields. Therefore, P in drainage water is not a suitable indicator. The Pw method represents both directly soluble P and part of the reversibly adsorbed P, i.e., the more readily soluble P forms in soil, so Pw has a good relation with in soil solution. From our understanding of the behavior of P in soil, we are able to model Pw in noncalcareous sandy soils. Furthermore, the use of Pw has the advantage of facilitating communication between scientists, policy makers and farmers. The P balance at the farm level also received a high number of +. Nevertheless, in our perception, it is not directly related to the soil potential for P transfer at the field level. This resulted in a very low score on the criterion purposive implicating it is not suitable to use as an indicator. The P-AL method, P_{ox} and DPS are less indicative of readily soluble P forms and responded slowly to P depletion in the pot experiment of Koopmans et al. (submitted). This explains the low overall score of these indicators. We had relatively little quantitative information on the criteria *purposive*, *measurable*, and *reactive*. Consequently, assessment of the indicators on the basis of these criteria may have been uncertain.

We propose to test more than one indicator, because the differences between the overall scores of the indicators were small. Based on Table 7, we selected P in soil solution and Pw. Phosphorus in soil solution can be assessed by measurement of P in a solution obtained with the centrifugation method, or in a 1:2 (w/v) water extract. However, it is unclear whether the results of both methods are comparable, so this requires further study. Because P-AL is used for P fertilizer recommendations on grassland in the Netherlands, we recommend including P-AL. The field experiments where the selected indicators will be tested should include both arable land and grassland on different soil types with a varying P status. To obtain a good understanding of the behavior of the selected indicators, the following soil conditions have to be measured: the size of the reversibly adsorbed P pool (FeO-strip method) and physical-chemical characteristics, such as the $[Al+Fe]_{ox}$ content, pH, $CaCO_3$ content, and organic matter.

Table 7 Qualitative assessment of the indicators†

indicator	*purposive*	*measurable*		*reactive*		overall score‡
		costs	*accuracy*	*sensitive*	*independent*	
P balance at the farm level	+	++++	++	++++	++++	20 +
P_{ox}	++	+++	++++	+	++++	17 +
DPS	++	+++	++++	+	++++	17 +
P-AL	++	++++	++++	+	++++	18 +
FeO-strip method	+++	++	+++	++	+++	18 +
Pw	+++	++++	++++	+++	+++	23 +
soil solution¶	++++	+++	++++	++++	+	24 +
drainage water	++++	+++	++++	++	+	20 +

†++++ = High and + = low, except for the criterion *costs* where ++++ = low *costs*, and + = high *costs*.

‡ The overall score was calculated according to Eq. (7).

¶ Measured according to the centrifugation or P-1:2 extraction method.

6 Summary and conclusions

- The actual P transfer from agricultural land to surface waters depends on (i) the degree of P enrichment of the soil in relation to soil physical-chemical characteristics, such as P sorption capacity and pH, and (ii) the presence of a hydrological connection between the source of P in the field and surface waters, i.e., the transport of water with soluble P forms from the field to surface waters. However, estimation of actual P loading rates of surface waters at the field level requires the input of results of many factors which is, therefore, rather complicated. Our study focuses on using simple 'soil' indicators of potential P transfer only.
- To select indicators that are suitable for monitoring purposes, it is important to understand the behavior of P in different soil types, the distribution of P among P pools in the solid phase of the soil, i.e., the reversibly adsorbed P pool versus the absorbed P pool, and the hydrological pathways of P transport from the field to surface waters.
- At present, the understanding of the behavior of P is good in noncalcareous sandy soils with a moderate to high P status and poor to moderate in other soil types. Therefore, the general idea to select indicators can only be based on the concept of P behavior worked out for noncalcareous sandy soils.
- In addition to the soil conditions (e.g., the degree of P enrichment, soil physical-chemical characteristics), the actual risk of P transfer depends on the specific location of the field in relation to the drainage conditions: the type of drainage (drainage pipes versus 'natural drainage' to ditches) and the existence of some artifacts (preferential or fingered flow of soil solution).
- Our study was focused on fields which drain directly to surface waters. Therefore, the selection of indicators has been limited to 'soil' indicators: soil tests and soil water tests in the topsoil. The P balance at the farm level and P in drainage water may be less suitable.
- Based on a qualitative assessment, 'soil' indicators have been proposed. The selection criteria were: purposive, measurable, and reactive. The indicators selected for testing the suitability of predicting the risk of P transfer in a field experiment are: P in soil solution and Pw. Furthermore, it is recommended to include P-AL. To obtain a good understanding of the behavior of these selected indicators, the following soil conditions have to be measured in the field experiment: the size of the reversibly adsorbed P pool and physical-chemical characteristics such as the pH, and $[Al+Fe]_{ox}$, $CaCO_3$ and organic matter content.

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