Phosphorus leaching from soils:

process description, risk assessment and mitigation

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Phosphorus leaching from soils: process description, risk assessment and mitigation

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ABSTRACT

Phosphorus (P) is an irreplaceable finite resource for all living species on Earth. For optimal crop production the P content in the soil should be sufficient and annual P application rates should be in equilibrium with the P offtake by harvest. Due to the rise of intensive husbandry in the 1970s in the Netherlands, the import of P via animal feedstuffs increased, and most of the P accumulated in manure. Consequently, in many regions in the Netherlands much more P has been applied to agricultural land than required, resulting in high P accumulations in the soil, increased P losses to groundwater and surface waters and severe deterioration of the surface water quality (eutrophication).

The main objectives of this study were to determine the behaviour of phosphorus in various Dutch soil types, to develop and evaluate tools for risk assessment of P loss to surface waters and finally, to evaluate management strategies for reducing P losses and to set up more sustainable P management strategies at national and European scale.

It was already well known that non-calcareous sandy soils are vulnerable to P leaching; this study shows that peat soils and calcareous sandy soils are also vulnerable. The potential risk of P pollution of surface water is high, because the critical degree of phosphate saturation of the soil is very low. Different tools have been developed to assess the current actual risk of P losses from agricultural land to the surface water (at field, regional and national scales). They help watershed managers and policy makers to distinguish hotspots of P losses within a region or catchment. The many measures for reducing P losses from land to surface water or to counteract the negative effects in surface waters can be distinguished into nutrient and livestock management (farm system), crop and soil management (field system), water, land use and landscape management (landscape and hydrological system) and surface water management (ecological system). Since Europe is highly dependent on the import of P for food production, it is necessary to recover P from waste streams and to re-use it in our food production system.

Key words: Phosphorus, phosphate, sorption, desorption, phosphate saturation degree, soil P status, environmental losses, risk assessment, P management strategies.

Contents

CHAPTER 1

General introduction

1.1   Background

Phosphorus is an essential element in the function of all living species, because it is used for reproduction (DNA, RNA), energy transfer (ATP; adenosine triphosphate), and for bone and teeth structure (calcium phosphate). Consequently, it plays a key role in our whole food production system, and should be sufficiently available to secure the growth and quality of crops and animals. The use of P fertilisers has greatly contributed to the increase of food production. In the Netherlands, the intensification of the agricultural production system after WW II led to livestock numbers increasing substantially in the period 1970 – 1990, though in recent decades numbers have somewhat declined due to restriction of production (Figure 1). Nevertheless, the agricultural P balance of the Netherlands is still positive (Table 1) mainly because of high imports of P-containing resources to feed the livestock.

The P surplus of the agricultural system mainly accumulates in farmland soil via the application of manure. The surplus has fallen sharply since 1995 (Table 1), for three reasons: (1) less use of mineral fertilisers, (2) a reduction of the P content in animal feed, achieved by adding phytase to feed to increase the digestibility of the P in the feed, and (3) an increase of the export of manure. Before the mid-1980s, most of the P surplus was applied on land. Since 1987 much stricter limits have been in place, as the Manure Act has restricted the maximum amount of P that may be applied via manure to farmland.
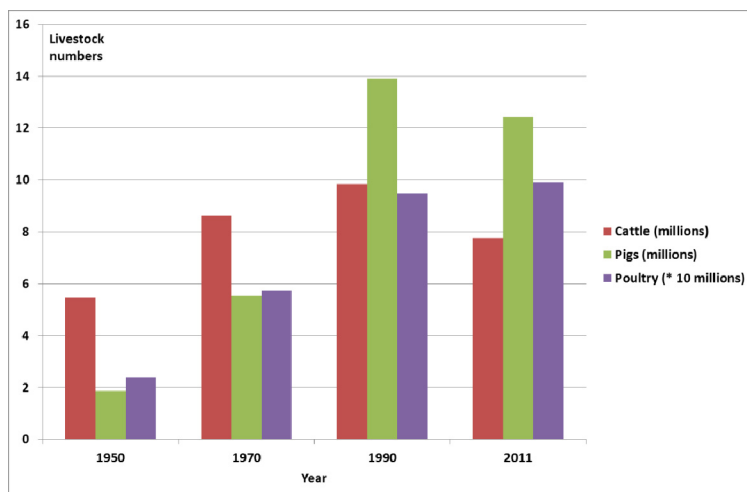

Figure 1. *Livestock numbers in the Netherlands in millions (cattle and pigs) and 10 million (poultry). (Source CBS-statline, 2014).*

Table 1. *The agricultural P balance of the Netherlands (Source CBS-statline, 2014).*

P balance (million kg)	1970	1986	1990	1995	2000	2005	2010
IN							
Feed	60	96	89	86	73	58	64
Fertilizer	47	37	33	27	27	21	13
Other	4	5	7	9	7	9	11
Total	111	138	129	122	107	88	88
OUT							
Export products	26	41	50	49	49	46	50
Export manure (net)	-	0	1	5	7	7	16
Total	26	41	51	54	56	53	66
Surplus	85	97	78	68	51	35	22

1.2   Phosphorus accumulation in soils

Over many decades more P has been applied to agricultural land than has been harvested in products from the land, resulting in an accumulation of P in the soil. In 1970 the average yearly P surplus in soil in the Netherlands was approximately 40 kg P ha^{-1} (surplus of 85 million kg P and 2.1 million ha agricultural land), which is equivalent to a surplus of about 93 kg P_2O_5 per ha. However, in the Netherlands the intensive livestock production is mainly located on the central, eastern and southern non-calcareous sandy soils and in the past most of the manure was applied in the region where it was produced. This resulted in very high annual P application rates: up to several hundreds of kg P_2O_5 ha^{-1} (Breeuwsma and Schoumans, 1987). Since the early 1980s more attention has been paid to the environmental side-effects of excessive P application rates on sandy soils. Many studies focussed on the quantification of the P sorption capacity of sandy soils, in order to assess the environmental risk of P leaching in areas with a high P content (Beek, 1979; Korzilius and Breeuwsma, 1983; Schoumans et al., 1987; Van der Zee and Van Riemsdijk, 1986; Van Riemsdijk and de Haan, 1981a). These finally resulted in a protocol to identify whether or not an acid sandy soil should be considered phosphate-saturated in terms of expected P emissions (Van der Zee et al., 1990a; Van der Zee et al., 1990b). A model application showed that based on the principles of the 'phosphate saturation degree' and the conditions defined by the Technical Committee on Soil Protection (TCB, 1990), there was a risk of P pollution in 70% of the soils in the non-calcareous sandy regions in the Netherlands (Breeuwsma and Silva, 1992). Since then, not much attention has been given to determining the degree of phosphate saturation and the risk of P pollution in regions with other soil

types. Because P is often one of the most important factors determining the ecological quality in inland surface water, and also because the water quality in other regions (than the non-calcareous sandy regions) in the Netherlands does not meet the objectives of the Water Framework Directive (EEC, 2000), information is also needed on the behaviour of P in other soil types and the risk of P pollution from agricultural land.

1.3   Impact of phosphorus losses to the environment

The main environmental risk of excessive P accumulation in agricultural land is the risk of P losses from the land to surface waters which impacts surface water quality and can reduce the functioning and biodiversity of the aquatic ecosystem (Scheffer, 1998; Smith et al., 1999). Eutrophication is the over-enrichment of surface waters with mineral nutrients, which stimulates the growth of algae and cyanobacteria. High productivity of bacterial populations leads to high respiration rates, which causes low oxygen concentrations (hypoxia) or total depletion of oxygen (anoxia) in poorly mixed water bodies, or at night in surface waters during calm and warm conditions. Low dissolved oxygen causes the loss of aquatic fauna and flora and the release of many compounds that are normally bound to sediments, including various forms of P. This release of P further reinforces the eutrophication process (Correll, 1998). Harmful algal blooms associated with eutrophication produce toxic algal substances that kill fish (Carpenter et al., 1969; Jaworski, 1981) and cause disease in animals (Kotak et al., 1994; Main et al., 1977) and humans (Falconer, 1989; Lawrence et al., 1994).

Since the mid-20th century, nutrient losses to the aquatic ecosystems have been declining throughout Europe, mainly because of targeted measures, such as decreasing the number of houses not connected to a sewage system, introducing the denitrification of N and precipitation of P in sewage water treatment plants, purifying industrial wastewater and banning P in detergents. Yet despite these trends in reducing the nutrient losses from identified and targeted point sources and the implementation of EU directives to reduce nutrient loads (EEC, 1991a; EEC, 1991b; EEC, 1996; EEC, 2000), the water quality in many rivers, lakes and estuaries is still poor (Figure 2), largely due to diffuse pollution from land entering surface water systems (EEA, 2012b). In many European countries and also in regions in the USA, P losses from agricultural land have become the main cause of ongoing eutrophication of freshwater lakes, reservoirs and streams (Correll, 1998; Sharpley et al., 2000; Tunney et al., 1997b). By contrast, in marine systems, N has often been identified as the growth-limiting nutrient, especially in summer (Anderson and Glibert, 2002 ; Ärtebjerg and Carstensen, 2001).
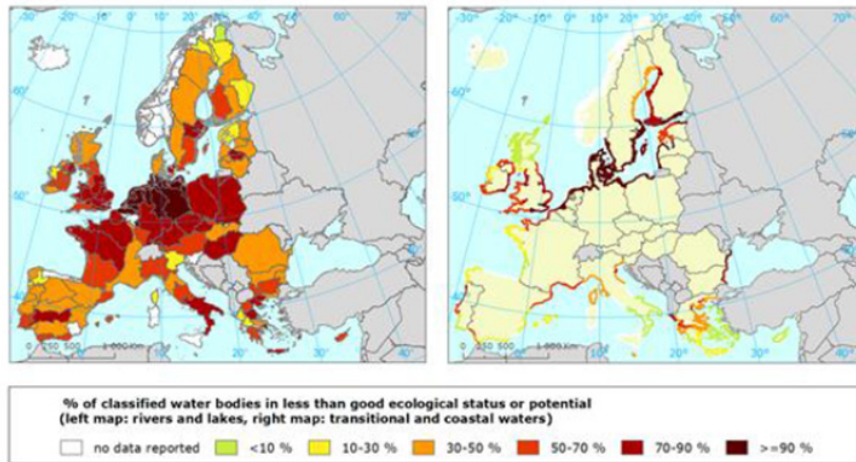
Figure 2. *Ecological water quality status in EU Member States (EEC, 2012).*

1.4   Sources and pathways of phosphorus losses to the environment

The main sources of P pollution from land to surface water are the amounts of P accumulated in the soil and the presence of P on the soil surface (e.g. cow patches, fertiliser granules). Both sources affect the P concentration in soil solution and runoff water. In mineral fertilisers and in manure, P is mainly present in easily soluble mineral forms (inorganic P). Nutrient losses from agricultural soils enter water systems as a result of transport by runoff and leaching. One of the most important pathways of P loss in hilly and mountainous areas occurs when rainfall and surface runoff detach soil particles during overland flow (Panagos et al., 2014; Toy et al., 2002). In flat or less hilly areas, the main pathways of P losses to surface waters are subsurface runoff and leaching through the soil and/or bypasses via artificial drainage systems (Chapman et al., 2005; Chardon and Schoumans, 2007; Grant et al., 1996; Heathwaite et al., 2005; Kronvang et al., 1997; Nelson et al., 2005; Ulén and Mattsson, 2003).

Quantifying diffuse losses from a field to surface water in flat areas is complex, since, for example, the contribution of subsurface losses to the surface water cannot be measured directly. In addition, variations in groundwater levels during the year affect which part of the soil contributes to the P losses from the field to surface water. Nevertheless, information on the sources and pathways of P losses is needed in order to identify the areas that cause the P losses (the 'critical source areas') and to select effective mitigation measures. The amount of P bound to a soil and its chemical properties determine the ortho-P concentration in the liquid fraction of soil layers. The

risk of P losses to the surface water needs to take those interactions into account, in combination with the hydrological conditions that determine the pathways.

1.5   Research questions

The reaction mechanisms between soil particles and mineral P (ortho-P) in soil solution are complex and more attention is needed to assess the risk of P losses from different soil types. Much information is available for soils where Al- and Fe-(hydr)oxides dominate the sorption and desorption characteristics of P, as in non-calcareous sandy soils (Borggaard et al., 1990; Kato and Owa, 1989; Van der Zee and Van Riemsdijk, 1986). However, the behaviour of mineral P in peaty clay soils and in calcareous sandy soils is neither well understood nor quantified, and it is known that in areas in the Netherlands with those soil types, high P concentrations are measured in surface water (De Klijne et al., 2007; Groenenberg et al., 2013; Klein et al., 2012b; Portielje et al., 2002). The impression is that also peaty clay soils and calcareous soils are vulnerable to inorganic P losses. Although a risk indicator has been developed to assess the potential P loss to groundwater from acid sandy soils and a critical value has been defined for the degree of P saturation, so far this approach has never been developed for peaty clay soils and non-calcareous sandy soils. Furthermore, approaches are needed to assess the actual P loss from land to surface waters rather than the potential P loss. Finally, measures and management strategies are needed to reduce agricultural P losses from land to surface waters and for a better closure of the P balance, to prevent a further deterioration of our environment in the long term.

With the above in mind, the following research questions were formulated:
-   Are Dutch peaty clay soils and calcareous sandy soils vulnerable to P losses?
-   Can we develop an indicator of the actual P risk of P losses based on information of soil characteristics, P sorption kinetics and hydrological conditions?
-   Which options are available for reducing P losses to surface water and for a better closure of the P balance?

1.6   Objectives

The main objectives of the research described in this thesis were:
-   To quantify the capacity of peaty clay soils and calcareous sandy soils to bind and release mineral P, the main P form in manure and in mineral P fertilisers;
-   To estimate the area of phosphate-saturated soils in the Netherlands as an indicator of the potential risk of P leaching;

- To develop new methods for quantifying the actual risk of P pollution;
- To give an overview of mitigation measures to reduce P pollution from land to surface waters and strategies for a better closure of the P balance.

1.7   Outline

In chapters 2 and 3 the phosphate sorption kinetics in peaty clay and calcareous soils are described, based on batch experiments in the laboratory. In chapter 4 this information is used to derive critical phosphate saturation values for these soil types, as a risk indicator of potential P loss. Furthermore the area of phosphate-saturated soils is quantified based on the defined critical phosphate saturation degrees and information from a stratified sampling of the soils in the Netherlands.

In chapter 5 the modelling of soil P status and P leaching is described and in chapters 6 to 8 the focus is on different approaches for modelling actual P losses from agricultural land. In chapter 9 an overview is given of options to reduce P losses from land to surface water and in chapter 10 the options to close the P balance are described. Finally, in chapter 11 I reflect on the research questions and objectives of this thesis.

CHAPTER 2

Description of the phosphorus sorption and desorption processes in lowland peaty clay soils

Abstract

To determine phosphorus (P) losses from agricultural land to surface water information is needed about the behavior of P in soils. In this study the sorption and desorption characteristics of lowland peaty clay soils are described based on experimental laboratory studies. The maximum P sorption capacity (PSC_{max}) is comparable with acid sandy soils if based on the amount of oxalate extractable aluminum (Al_{ox}) and iron (Fe_{ox}). A fraction of the maximum amount of sorbed P is bound reversibly (Q), which can be measured with an iron impregnated paper. The fraction of the maximum reversibly sorbed P depends on the amount of oxalate extractable aluminum (Al_{ox}) and iron (Fe_{ox}). In the top soil the maximum of the fraction of reversibly bound P (Q_m) is about one third of PSC_{max}, and in the subsoil about two third. All sorption and desorption parameters are related to soil characteristics of peat samples.

Keywords: phosphate, sorption, desorption, lowland peaty clay soils.

Introduction

In many Western European agricultural areas with intensive livestock, high P surpluses occur (EEA, 2005a; Oenema et al., 2007) and the contribution of agriculture to the P losses to surface water is significant (EEA, 2005b; Kronvang et al., 2007). The biogeochemistry of P is important as P is the limiting nutrient for algae blooming in aquatic environments (Edwards and Chambers, 2002; Gibson, 1997; Sharpley and Rekolainen, 1997). Research is mostly focused on areas with the highest surplus of P. However, also in areas with lower livestock densities, like lowland peaty clay soils, high P losses have been found (Blankenburg, 1983; Cogger and Duxbury, 1984; Gelbrecht et al., 2005; Reddy, 1983; Van Beek et al., 2004), but the description of P sorption and desorption has got much less attention. Lowland peaty clay soils mostly consist of organic matter and clay minerals, and the organic matter content often increases with increasing depth (up to more than 70%; Eutric Histosols). The behavior of P in peat soils is complex and not well understood, since many soil components can contribute to P sorption. The main phosphate reactive soil components in this peat soils are: (a) micro-crystalline Al- and Fe-(hydr)oxides, (b) $AlOH_x^{(3-x)+}$ and $FeOH_y^{(3-y)+}$ bound to organic material, (c) positive charged edges of clay minerals and (d) $AlOH_x^{(3-x)+}$ and $FeOH_y^{(3-y)+}$ bound to the surface of clay minerals. Furthermore, in more alkaline peat soils, P can also precipitate in Ca-HCO_3-P phases because of occurrence of gypsum and calcite (Litaor et al., 2004; Litaor et al., 2003; Litaor et al., 2005). Because peat soils are often located in lowlands attention should be given to oxidation and reductions processes (Brand-Klibanski et al., 2007; Khalid et al., 1977; Pant and Reddy, 2001; Patrick and Khalid, 1974; Sah and Mikkelsen, 1986; Torrent, 1997). Especially when rewetting measures are implemented to restore degraded fens (Meissner et al., 2008; Renger et al., 2002; Shenker et al., 2005). In our study the focus is on P sorption on samples from the top 1 m of lowland peat soils in agricultural polders in the Western part of The Netherlands, which are located about 4 - 6 m below sea level. These peat areas are still being drained in order to facilitate agriculture, but as a result additional P loss occur due to peat mineralization (Chardon and Schoumans, 2007; Van Beek et al., 2004).

Based on the complex interaction between P and soil components it is important to gain a clear understanding of the reaction kinetics (sorption and desorption) and the binding capacity of peat soils in lowland areas, in order to determine the risks of P leaching to groundwater and surface waters on the short and long term. Furthermore, information is needed about in influence of soil characteristics on the sorption and desorption processes. This study gives the results of sorption and desorption experiments with different soil samples of peaty clay soils and the influence of soil characteristics on the sorption and desorption parameters.

Materials and methods

The soil samples were collected from representative soil horizons of peaty clay soils (Terric Histosols; FAO classification) in a peat area in the west of The Netherlands (province South Holland; peat area approx. 800 km^2). A total of 11 representative profiles were sampled and only non-(heavily)-disturbed layers were included. Five different depths were sampled which will be referred to as V1 - V5. At one soil profile two layers were sampled within the layer of V3 (so n=12) and in some profiles the top soil was heavily disturbed and not included (so n < 11). Soil samples were freeze-dried and stored at room temperature. Of each sample the oxalate extractable Al, Fe and P content was determined (Schwertmann, 1964) and the organic matter content (NEN5754, 2005). The main characteristics of the soil samples are given in Table 1. The organic matter content of the top layers varies from 24 to 55% (V1 – V2) while in the subsoil (V3 – V5) it varies from 59 to 92%.

Table 1. *Characteristics of soil samples studied (min – max values are shown).*

Layer	Depth (m)	Samples	Soil material [†]	OM [‡] (%)	pH	Clay[¶] (%)	P_{ox} (mmol kg^{-1})	$(Al+Fe)_{ox}$ (mmol kg^{-1})
V1	0.0 – 0.2	9	clay + peat	24 - 47	3.9 - 5.7	36 - 66	21 - 84	319 - 666
V2	0.2 – 0.4	7	clay + peat	20 - 55	4.4 - 5.6	46 - 75	11 - 29	287 - 531
V3	0.4 – 0.6	12	peat (+clay)	59 - 69	3.8 - 5.8	49 - 77	1 - 16	100 - 540
V4	0.6 – 0.8	11	peat (+clay)	79 - 91	4.1 -5.8	46 - 74	1 - 10	26 - 333
V5	>0.8	11	peat (+clay)	80 - 92	4.2 - 5.7	43 - 77	1 - 10	16 - 172

† soil survey

‡ Organic matter content

¶ lutum (percentage of mineral fraction)

The influence of the reaction time on the P sorption was determined for all soil samples. P sorption isotherms and the P desorption was studied on three profiles. Since large desorption fractions were measured in layer V5, additional samples were selected. Phosphate sorption experiments were carried out at a pH of 5 (± 0.2) which is within the range of the pH of the soil (Table 1).

a) Influence of the reaction time

The amount of P sorbed was determined after 1, 2, 7, 14, and 28 d at an initial ortho-P concentration of 50 mg P L^{-1} as KH_2PO_4 in 0.02 *M* KCl (reference P concentration; c_r). A soil sample of 0.5 ± 0.05 gram air dry 2 mm sieved soil was slowly shaken with 200 mL solution. For each reaction time a separate soil sample was used. After the reaction a few drops of 0.1% Sedipur® flocculants (type CF; combination of polyacrylamide, copolymers of acrylamide, acrylic acid and acrylic esters, and polyethylenimine) was added to stimulate deposition of the soil material. Thereafter, the samples were filtered over a Whatman 589(3) blue filter (Schleicher and Schuell) and a few mL of 80% alcohol was used to wash the soil sample in order to remove P rich solution. Finally, the soil

sample and filter were placed in a 200 mL polyethylene bottle and 50 mL of oxalate solution (Schwertmann, 1964) was added and shaken for 2 h. In the oxalate extract, the amount of sorbed P was determined on an inductively coupled plasma atomic emission spectrometer and the total amount of sorbed P was corrected for the initial amount of sorbed P (P_{ox}) in order to determine the additional amount of P sorbed (F_t^a).

Data on the influence of the reaction time on P sorption were fitted on the Elovich equation (Aharoni and Tompkins, 1970), which has been extended and used to describe the decrease in rate of the chemical sorption of phosphorus with soils due to an increase of phosphate coverage (Chien and Clayton, 1980; Torrent, 1987; Van Riemsdijk, 1979):

$$\frac{dF}{dt} = k_1 \, e^{-k_2 F} \tag{1}$$

Integration of Eq. 1 (t=0; F=0 to t=t; F=F) results in:

$$F = \frac{1}{k_2} \ln(k_1 \, k_2) + \frac{1}{k_2} \ln\left(t + \frac{1}{k_1 \, k_2}\right) \tag{2}$$

If t >> $\dfrac{1}{k_1 \, k_2}$ Eq, 2 becomes

$$F = \frac{1}{k_2} \ln(k_1 \, k_2) + \frac{1}{k_2} \ln(t) \tag{3}$$

To determine the slow sorption rate, the sorption was related to the sorption after one day (t=1 d) because it was assumed that the fast (ad)sorption reaction has taken place completely. The sorption after one day is described by (Eq. 3 inserting t=1 d):

$$F_{1d} = \frac{1}{k_2} \ln(k_1 \, k_2) \tag{4}$$

Substitution in Eq. 3 results into:

$$F = F_{1d} \left(1 + \frac{1}{\ln(k_1 \, k_2)} \ln(t)\right) \tag{5}$$

This equation can be simplified as:

$$F_t^a = F_{1d}^a (1 + a \, \ln \, t) \tag{6}$$

where F_t^a (mmol kg^{-1}) is the extra amount of P sorbed after reaction time t (d), and a is the sorption rate constant of the slow reaction (d^{-1}) compared to the amount of sorbed P after 1 d (F_{1d}).

b) Influence of the P concentration (sorption isotherm)

The P sorption isotherm was determined at initial ortho-P concentrations of 0.15, 0.5, 1, 2, 3, 6, 10, 25, 50, 90, and 150 mg P L^{-1} (as KH_2PO_4) at a reaction time of 2 months (reference reaction time; t_r). The same procedure was used as described above to determine the amount of sorbed P. A period of two months was used to ensure sufficient P sorption. Also the final concentration of the P solution used for sorption experiments was measured. The Freundlich equation was used to describe the P sorption isotherm at t=2 months:

$$F = k\,c^n \tag{7}$$

where F is the amount of ortho-P sorbed (mmol kg^{-1}), k is the sorption constant (mmol kg^{-1} L^n mol^{-n}), c is the concentration of ortho-P in solution (mol L^{-1}), and n is the Freundlich coefficient (-).

Each soil sample has its own specific parameters k and n. The parameter k can be eliminated by relating the sorption to the sorption at a certain reference concentration (c_r). In this study a reference concentration of 50 mg P L^{-1} was used as a standard in Dutch studies (Schoumans et al., 1986).

$$F_{c_r} = k\,c_r^n \tag{8}$$

Which results in:

$$F_c = F_{c_r}\left(\frac{c}{c_r}\right)^n \tag{9}$$

Because some soil samples already had a relative high initial P content, the P sorption curve becomes automatically concave. Therefore, the isotherm is related to the additional amount of sorbed P (F^a).

$$F_c^a = F_{c_r}^a\left(\frac{c}{c_r}\right)^n \tag{10}$$

The 'n' value is determined via linear regression analysis of the logarithmic transferred data and for practical reasons both c and c_r were expressed as mg L^{-1} P, which has no influence on the derived n value.

c) Maximum amount of reversibly sorbed P and the desorption rate

In practice only a part of the amount of sorbed P is reversibly bound, and can be considered as a fast adsorption-desorption reaction (Van der Zee and Van Riemsdijk, 1986). In order to determine the maximum amount of reversibly bound P and the desorption rate, the soil samples were first loaded with P to saturate all adsorption sites of the samples. A sample of 0.5 ± 0.05 g air dry 2 mm sieved soil was slowly shaken during 7 d with 200 mL of a 150 mg P L^{-1} solution in 0.02 *M* KCl, just to be sure that all adsorption sites were occupied. After the reaction, a few drops of 0.1% Sedipur solution was added to stimulate deposition of the soil material. Thereafter, the samples were filtered over a 589(3) blue filter (Schleicher and Schuell) and a few mL of

80% alcohol was used to wash the soil sample. Finally, the soil sample and the filter were placed in a 200 mL poly-ethylene bottle, and 150 mL 0.01 M KCl was added plus an iron-hydroxide paper with a high affinity for P as described as the P_i method (Menon et al., 1989b). The P desorbed from the soil sample into solution will react directly with the iron-paper, maintaining the P concentration in solution at almost zero; the iron-paper was replaced every 2 h. The amount of P on each iron-paper was determined separately. In non-calcareous soils, the Al- en Fe-hydroxides dominate the P sorption reaction and the fast adsorption – desorption reaction is often described by the Langmuir equation ((Van der Zee and Van Riemsdijk, 1986)). As a result, the cumulative amount of P adsorbed on the papers, which equals the cumulative amount of desorbed P from the soil, can be described by assuming Langmuir adsorption – desorption kinetics at c=0 (using the iron-paper as infinite sink) (Van der Zee et al., 1987):

$$Q_{\text{Fe-pap,t}} = Q_m \left(1 - e^{-k_d t} \right)$$

(11)

where $Q_{\text{Fe-pap,t}}$ is the cumulative amount of ortho-P sorbed by the iron-papers (mmol kg^{-1}), Q_m is the maximum amount of P that can be desorbed (mmol kg^{-1}), k_d is the desorption rate constant, and t is the desorption time (d).

Q_m and k_d were determined by fitting Eq. 11 using non-linear regression statistics (GENSTAT). Because the maximum desorption capacity depends on the reactive soil components, the ratio between Q_m and $(Al+Fe)_{ox}$ was also determined (both expressed as mmol kg^{-1}). After desorption the residual amount of P in the soil sample was determined using an oxalate extraction. The total amount of sorbed P in the sample after loading with P for one week (F_{1w}) is calculated by means of the sum of desorbed P and extracted residual amount of P_{ox}.

d) Al and Fe speciation

Separate extractions were used to determine different fractions of Al and Fe as described by Zevenbergen and De Vries (1985). Free exchangeable Al and Fe were determined with 0.01 M silver-thiourea (AgTu; (Pleysier and Juo, 1980)); exchangeable Al and organic bound Al with lanthanum chloride (LaCl$_3$; (Bascomb, 1968; Bloom et al., 1979; Oates and Kamprath, 1983)); exchangeable Fe and organic bound Fe by means of 0.1 M sodium pyrophosphate and partly also amorphous hydroxides (Na$_4$P$_2$O$_7$; (McKeague, 1967)); exchangeable Al/Fe, organic bound Al/Fe and Al/Fe polymers and amorphous hydroxides by means of oxalate extraction (Schwertmann, 1964). Although the LaCl$_3$ method is more specific for organic bound Al and sodium pyrophosphate for organic bound Fe, in both extractions Al as well as Fe were determined.

e) Determination of the sorption capacity.

Since the influence of the reaction time (*a*) and concentration (*n*) on the amount of sorbed P are independent (Schoumans et al., 1987; Schoumans and Groenendijk, 2000; Schoumans et al., 1989; Van der Zee and Van Riemsdijk, 1986; Van der Zee and Van Riemsdijk, 1988; Van Riemsdijk et al., 1984; Van Riemsdijk and De Haan, 1981b), the P sorption capacity (PSC) for each soil sample can be calculated by the initial amount of P (P_{ox}) plus the extra amount of P sorbed at a reaction time t (d) and a concentration c (mg L^{-1} P) by combining equations (6) and (10):

$$PSC = P_{ox} + F_{1d,\ 50\ ppm\ P}^{a} \left(\frac{c}{50} \right)^{n} (1 + a\ \ln(t)\ ) \tag{12}$$

The maximum total P sorption capacity (PSC_{max}) of the soil samples was estimated by means of the soil sample specific n-value and a-value for a reaction time of 5 year at a concentration of 90 mg P L^{-1}, but in fact also other concentrations and reaction times can be used. A period of 5 year (=1825 d) was used because after this reaction time further P sorption is assumed to be negligible and the total sorption can be considered as a "pseudo sorption maximum". The P concentration of 90 mg L^{-1} was used because this concentration was measured in the soil solution of P saturated layers in non-calacerous sandy soils (De Haan and Van Riemsdijk, 1986). The calculated maximum total P sorption capacity of the samples was related to the oxalate extractable Al and Fe content of the soil samples in order to derive a direct relationship between the maximum total sorption capacity of the soil layer and the total reactive available Al and Fe content as important soil characteristics.

Results and discussion

Influence of the reaction time on P sorption

In Figure 1 the time dependent phosphate sorption is shown, scaled to the amount of P sorbed after 1 day (F_{1d}^{a}) which can be described by Eq. 6. The layers V1 and V2 are combined, because similar results of the slow sorption rate ('a'-value) are obtained (Table 2). The mean value and standard deviation of the slow sorption rate constant 'a-value' of the five layers (V1-V5) are given in Table 2.
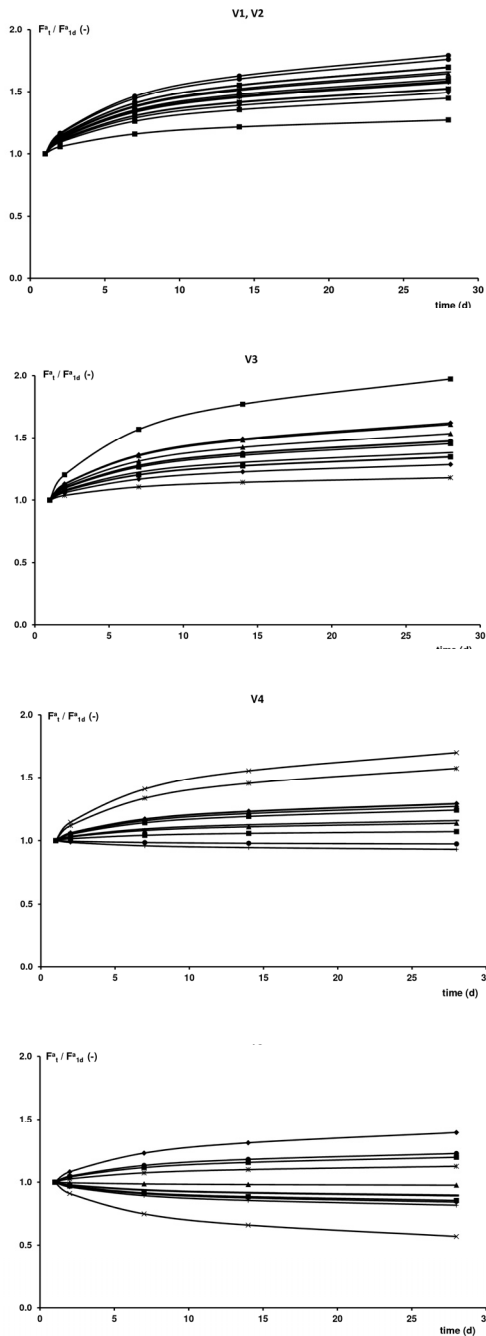
Figure 1. *The available amount of sorbed P after a reaction time t days* (F_t^a) *scaled to the available amount of sorbed P after 1 day* (F_{1d}^a).

Table 2. *Mean rate constant (a) and standard deviation (between brackets) of the slow P sorption reaction of the soil samples for the five soil layers*

Layer	Depth	Samples	$a^{1)}$	$R^{2\dagger}$
	(m)		(d^{-1})	(-)
V1	0.0 – 0.2	9	0.18 (± 0.04)	0.845 (± 0.138)
V2	0.2 – 0.4	7	0.18 (± 0.04)	0.869 (± 0.091)
V3	0.4 – 0.6	12	0.14 (± 0.06)	0.847 (± 0.147)
V4	0.6 – 0.8	11	0.05 (± 0.05)	0.417 (± 0.363)
V5	>0.8	11	-0.01 (± 0.07)	0.269 (± 0.253)

$^{1)}$ As defined by Eq. 6: $F_t^a = F_{1d}^a (1 + a \ln(t))$

$\dagger$ Mean coefficient of determination and standard deviation (between brackets) of the fit of Eq. 6

The R^2 is high for the top layers V1-V3 but low at greater depth in layers V4-V5.The results for the top layers (peat and clay material; V1-V3) are in line with the reaction of P in mineral soils. In the top layers (V1-V3), which contain clay particles, organic matter and relative high amounts of (micro)crystalline Al- and Fe-(hydro)oxides, a time dependent slow sorption is observed. The value for a (0.18 ± 0.04; Table 2; Figure 1), is slightly higher than the value found for acid sandy soils (0.12 ± 0.03; (Schoumans et al., 1989)).There are two possible explanation for this: (1) the affinity and permeability of the (polymers of) sesquioxides located at the surface of the clay plates to sorb P is higher than for the amorphous Al/Fe-(hydr)oxides, which are the main reactive components for P in acid sandy soils, or (2) due to the relative high content of organic (carboxylate) bound Al in the V1-V3 samples, which has a high affinity to sorb phosphate (Bloom, 1981; Bloom et al., 1978; Oates and E.J., 1983).

The relative amount of P sorbed after 1 day (Figure 1) decreases with depth (Figure 1) and the organic matter content increases with depth (Table 1). Consequently, the 'a'-value decreases with depth (Table 2). In the deepest soil layer V5 the average 'a'-value is almost zero, implying the absence of a slow reaction or at least a slow reaction that is often difficult to determine (see the relative low values of R^2). Since the deepest layer (V5) has a high organic matter content, it can be concluded that the P sorption kinetics to the organic-sesquioxides-complexes is fast (within 1 d). The negligible value of 'a' (average of -0.01; Table 2) shows that after a reaction time of 1 d, often no additional sorption is measured.

Influence of the P concentration (sorption isotherms)
Figure 2 shows the P sorption isotherms after the two months reaction time. Within the studied P concentration range no maximum was found for the amount of sorbed P. In Table 3 the mean values of the parameter n are presented for the samples from the different soil layers.
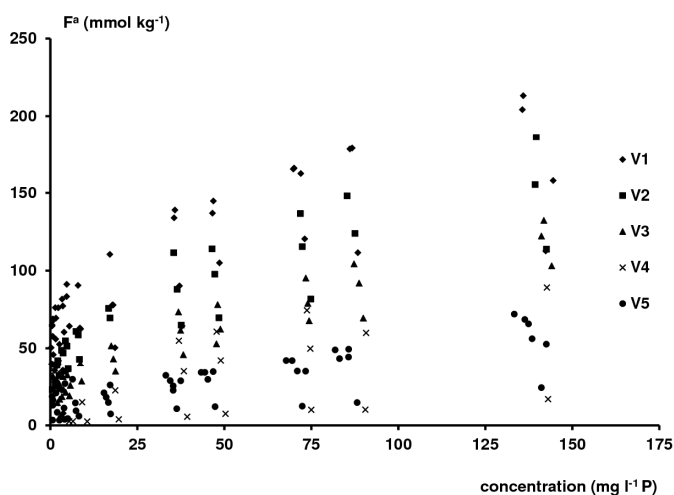
Figure 2. *The P sorption isotherm after 2 months reaction time.*

Table 3. *Mean exponent coefficient (n) and standard deviation (between brackets) of the modified Freundlich equation for the five soil layers.*

Layer	Depth (m)	Samples	$n^{1)}$ (-)	$R^{2 \dagger}$ (-)
V1	0.0 – 0.2	3	0.45 (± 0.03)	0.961 (± 0.018)
V2	0.2 – 0.4	3	0.46 (± 0.03)	0.987 (± 0.004)
V3	0.4 – 0.6	3	0.61 (± 0.05)	0.970 (± 0.025)
V4	0.6 – 0.8	3	0.70 (± 0.19)	0.971 (± 0.022)
V5	>0.8	4	0.62 (± 0.22)	0.956 (± 0.046)

[1] As defined by Eq. 10: $F_c^a = F_{c_r}^a \left(c/c_r\right)^n$

† Mean coefficient of determination and standard deviation (between brackets) of the fit of Eq. 10

The R^2 is high in all soil layers (Table 3), which implies that the Freundlich equation describes the sorption data well. In the top layers (V1 and V2) the value of 'n' is lower (n=0.46 ± 0.03) than in the layers V3-V5 (0.64 ± 0.16) which contain higher amounts of organic matter. In the literature both a positive and a negative influence of organic matter have been reported on P sorption. Since phosphate can react with Al- and Fe-hydroxide cations (e.g. $Al(OH)^{2+}$ and $Al(OH)_2^+$) associated with organic complexing agents (Appelt et al., 1975; Schnitzer and Kahn, 1972; Schnitzer and Kahn, 1978; Van Dijk, 1971a; Van Dijk, 1971b), a positive influence can be expected. Several studies showed the importance of Al/Fe-sequioxides-organo-complexes for P sorption onto organic material (Anderson, 1974; Appelt et al., 1975; Bloom, 1981; Bloom et al., 1978; Dormaar, 1963; Oates and E.J., 1983; Williams, 1960). This explains why in peat soils often positive correlations between P sorption and the Al and Fe content or the organic matter content are found (Cuttle, 1983; Daughty, 1930; Kaila, 1959; Mandel and Islam, 1979; Saunders, 1965; Schalscha et al., 1972; Schoumans et al., 1989). A negative

influence has been ascribed to competing effects with poly-anions of organic matter complexes, e.g. in mineral soils (Borggaard, 1990; Borggaard et al., 1990; De Haan, 1965; Parfitt, 1979; Sibanda and Young, 1986). Based on the results presented in Table 3 it is concluded that the P sorption isotherm in the peaty clay soils becomes more linear (higher n-value) with increasing organic matter content, suggesting an overall positive influence of organic matter on P sorption, due to the high amounts of sesquioxides associated with the organic material.

Estimation of the total P sorption capacity
For each soil sample the maximum total sorption capacity (PSC_{max}) was estimated for a long term reaction time of 5 years at a P concentration of 90 mg L^{-1}. The calculated maximum sorption capacity is related to the sum of oxalate extractable Al and Fe of the samples (Fig. 3; 0.49 $(Al+Fe)_{ox}$; R^2=0.94). The average value of the ratio PSC_{max} and (Al_{ox} + Fe_{ox}) is: 0.48 (± 0.07). The values of 0.49 (via regression) and 0.48 (average) determined for these peaty clay soils is comparable with the results found for acid sandy soils (average value 0.5 ± 0.1) (Breeuwsma and Silva, 1992; Van der Zee and Van Riemsdijk, 1988). Although the sorption rate constant (a-value; table 2) and exponent (n-value; table 3) differ, the maximum total sorption capacity could be assessed by the available amount of oxalate extractable Al and Fe, which seems to be important soil characteristics.
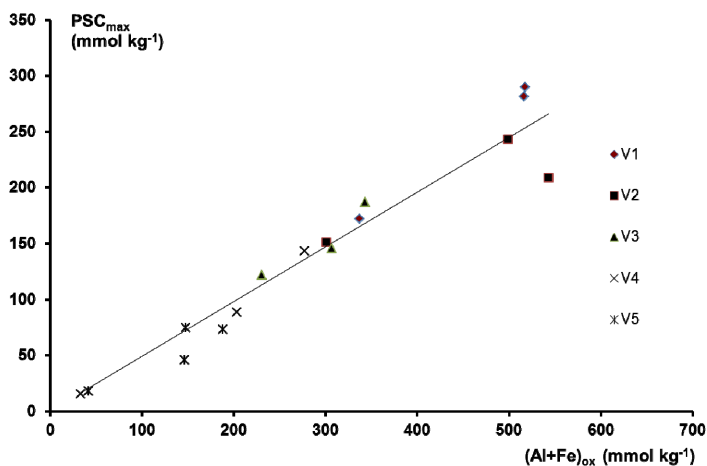

Figure 3. *Prediction of the maximum P Sorption Capacity (PSC_{max}) as a function of the sum of oxalate extractable Al and Fe.*

Desorption characteristics
Figure 4 shows the amount of desorbed P over time extracted in the presence of a sink of iron-paper (P_i) as a percentage of the total amount of P sorbed before desorption

started ($F_{1w, \text{ 150 ppm}}$). The amount of reversibly sorbed P increases with depth from top layer V1 to subsoil layer V5. The desorption rate seems to increase with depth. The desorption maximum is reached within 10 hours in layer V5, while more time is needed in the layers V1-V4. The sorption rate and the maximum amount or reversibly sorbed P (Q_m) were determined by fitting Eq. 11.
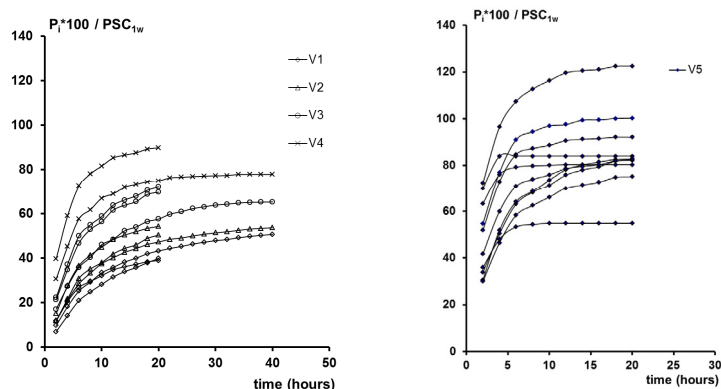

Figure 4. *Percentage desorbed P with iron-paper (as infinite sink) as a function of desorption time (100%=total amount of P sorbed before desorption started; PSC_{1w}).*

In Table 4 the average values of the maximum amount of desorbed P (Q_m) and the desorption rate constant (k_d) (Eq. 11) are shown. Q_m is also presented as a percentage of the amount of sorbed P determined after one week loading the samples with P (Q_m * 100/PSC_{1w}) and as a function of the oxalate extractable Al and Fe content ($Q_m/(Al+Fe)_{ox}$).

Table 4. *Desorption rate constant (k_d), maximum amount of reversibly sorbed P (Q_m) and Q_m related to amount of P sorbed after 1 week (PSC_{1w}) and the amount of oxalate extractable Al and Fe in peat soils.*

Layer	Depth	N	k_d	Q_m	Q_m *100/ PSC_{1w}	Q_m / $(Al+Fe)_{ox}$	R^2
	(m)		(h^{-1})	(mmol kg^{-1})	(%)	(-)	(-)
V1	0.0 – 0.2	3	0.126 (0.046)	51.3 (38.8)	45.4 (5.3)	0.152 (0.028)	0.997 (0.002)
V2	0.2 – 0.4	3	0.141 (0.025)	66.4 (19.3)	53.9 (1.6)	0.144 (0.015)	0.996 (0.002)
V3	0.4 – 0.6	3	0.158 (0.031)	62.1 (14.7)	69.4 (4.1)	0.211 (0,015)	0.993 (0.003)
V4	0.6 – 0.8	3	0.459 (0.368)	35.8 (20.7)	88.3 (11.3)	0.314 (0.126)	0.990 (0.005)
V5	> 0.8	11	0.434 (0.224)	28.2 (15.1)	84.8 (16.1)	0.318 (0.130)	0.990 (0.010)

The R^2 varies from 0.993 to 0.997. This means that the results fit to Eq. 11 and as a result the P desorption can be described by assuming Langmuir adsorption – desorption kinetics at c=0 (using the iron-paper as infinite sink) (Van der Zee et al.,

1987). Furthermore, both the relative amount of reversibly bound P ($Q_m * 100 / PSC_{1w}$) and the desorption rate constant (k_d) increase with depth. In the subsoil layers (V4 and V5) more than 80% of the amount of sorbed P (after loading the soil sample with P for 1 week at 150 ppm P; F_{1w}) is reversibly bound. In the top soil (V1 and V2) lower percentages are measured (e.g. 45-54% of F_{1w}). The mean desorption rate constant (k_d) of the top soil (V1 and V2) is relative low (0.13 ± 0.03 h^{-1}) compared to the mean values measured in sandy soils ($k_d = 0.2 \pm 0.08$; (Van der Zee et al., 1987; Van der Zee et al., 1988). In the subsoil (V5), which contains mainly peat material, k_d had a significantly higher, but had a more uncertain value (0.434 ± 0.224).

These results are in line with the results of the sorption reaction, because in the subsoil almost no slow reaction was observed (a= -0.01; Table 2) indicating a fast reversible sorption reaction, while in the top soil (V1, V2) a significant slow reaction was determined (a=0.18; Table 2) and in those layers a smaller fraction of the sorbed P is easily desorbable. Furthermore, the maximum amount of reversibly sorbed P is related to the $(Al+Fe)_{ox}$ content (Table 4) and in the subsoil V5 the amount of reversibly sorbed P is 32% of the $(Al+Fe)_{ox}$ content. This means that 65% of the *maximum* total P sorption capacity ($PSC_{max}=0.5$ $(Al+Fe)_{ox}$; Fig. 3) can be considered as readily desorbable P and about one third is relatively strongly sorbed. In sandy soils the opposite has been found; two third strongly sorbed and one third reversibly sorbed P (Van der Zee et al., 1988; Van der Zee and Van Riemsdijk, 1986). The results of the top soils of these peaty clay soils are in line with the results of experiments with sandy soils.

Al and Fe speciation
In Tables 5 and 6 the results of the determination of Al and Fe speciation are presented as percentage of resp. the amount of oxalate extractable Al and Fe (Al_{ox} and Fe_{ox}).

Table 5. *Average values of Al speciation in soil samples.*

Layer	Samples	Al_{ox}	AgTu	LaCl$_3$ (cumulative)				Na-pyro-phosphate
				1	2	3	4	
		(mmol kg^{-1})	(%)	(%)				(%)
V1	8	168.3	2.8	19.0	25.7	29.0	31.6	40.9
V2	7	164.5	1.1	12.8	18.2	20.9	23.1	37.8
V3	6	149.4	1.3	22.5	31.7	36.4	39.5	75.1
V4	7	76.3	7.4	30.9	40.0	43.9	45.5	92.4
V5	11	49.2	4.7	24.1	32.6	37.4	40.2	88.9

Table 6. *Average values of Fe speciation in soil samples.*

Layer	Samples	Feox	AgTu	LaCl$_3$ (cumulative)				Na-pyro-phosphate
				1	2	3	4	
		(mmol kg-1)	(%)	(%)				(%)
V1	8	272.3	0.2	2.3	3.1	3.6	4.1	71.7
V2	7	268.6	0.1	1.7	2.3	2.7	3.0	50.3
V3	6	206.7	0.2	5.2	7.2	8.2	9.0	72.6
V4	7	120.1	3.4	5.9	20.2	22.0	25.0	64.2
V5	11	51.2	6.5	25.1	31.1	33.6	37.3	59.1

The free exchangeable Al and Fe, extracted with AgTu, was only a small percentage of Al$_{ox}$ and Fe$_{ox}$ and LaCl$_3$ extracts were 13 to 31% of Al$_{ox}$ and 2 to 25% of Fe$_{ox}$. Even after a fourfold sequential extraction with LaCl$_3$ the percentage increased only up to 23 to 46% of Al$_{ox}$ and 3 to 37% of Fe$_{ox}$. Higher values were expected, at least in the subsoil, since LaCl$_3$ is assumed to be specific in extracting Al and Fe bound to organic matter (Bascomb, 1968; Bloom et al., 1979; Oates and Kamprath, 1983). These results suggest that also large amounts of Al/Fe polymers and/or amorphous Al/Fe are present in the subsoil. However, no slow sorption reaction was found in samples from layer V5 (Table 2), and this layer has also a very high desorption rate constant (k_d, Table 4). Both results suggest a highly reversible P sorption/desorption process in the subsoil. If this is indeed caused by complete organic bound Al en Fe, LaCl$_3$ seems to be not specific enough to represent this overall effect. With pyrophosphate 86% of Al$_{ox}$ is extracted in samples with a high organic matter content (V3, V4, V5), and 64% of Fe$_{ox}$. The large fraction for Fe-pyrophosphate was expected, because pyrophosphate extracts organic bound Fe preferentially. Furthermore, it is noticed that the percentage of Fe$_{ox}$ extracted with pyrophosphate does not vary much with depth (50-73%; 63 ± 9 %), while for Al the percentage pyrophosphate extractable Al increased with depth.

Influence soil characteristics on the process parameters
The relation between the P sorption-desorption parameters (Q_m, k_d, *a and n*) and soil characteristics was analyzed with multiple regression analyses. Only the relationships with a significant correlation between the parameter and soil characteristics are presented in Table 7. Both the regression coefficients and the t-test values are given. Figure 5 and 6 show the regression lines of the single linear relationships of the parameters a and n (as presented in Table 7), and figure 7 and 8 show resp. the fit of the multiple regression of the parameters Q_m and k_d.

Table 7. *Coefficient of determination (R^2), regression coefficients and t-test values (between brackets) of (multiple) regression analysis to predict the sorption and desorption parameters by the organic matter content and / or the extracted amounts of Al and/or Fe.*

Para-meter	unit	R^2	Intercept	Organic matter	Al-LaCl$_3$	Fe-Oxalate	(Al+Fe) LaCl$_3$	Oxalate
		(-)	(-)	(%)	(mmol kg^{-1})		(mmol kg^{-1})	
a	-	0.877	0.162 (2.4)	-0.002219 (-3.3)	-	-	-	0.000273(2.8)
a	-	0.801	0.332 (10.0)	-0.003709 (-7.5)	-	-	-	-
n	-	0.654	0.443 (5.2)	0.004216 (3.9)	-	-	-0.00375 (-2.9)	-
n	-	0.419	0.303 (3.4)	0.004238 (3.2)	-	-	-	-
Q$_m$	mmol.kg^{-1}	0.985	-	0.2220 (5.4)	-	-	-	0.141 (17.5)
k$_d$	h^{-1}	0.762	0.575 (9.7)	-	-0.003836 (-2.5)	-0.001284 (-5.0)	-	

The value of the slow sorption rate (*a)* is slightly correlated with the sum of Al$_{ox}$ and Fe$_{ox}$ (relative low t-test; 2.8). If this content is omitted, the significance of organic matter increases (t-test value increases from -3.3 to -7.5) and the R^2 reduces slightly from 0.88 to 0.80. Obviously, an increase of the organic matter content reduces the slow P sorption rate. The exponent of the sorption isotherm (*n*) increases with increasing organic matter content, but the relationship is poor ($R^2 = 0.42$ and the t-test value of 3.2 is relative low). A slightly better result is obtained if the sum of Al and Fe extracted by LaCl$_3$ is included ($R^2 = 0.65$), but the t-test value is still low (t=-2.9). The maximum amount of reversibly bound P (Q$_m$) is strongly determined by the amount of the sum of oxalate extractable Al and Fe (t=17.5) and the organic matter content (t=5.4). The desorption rate (k$_d$) decreases if the oxalate extractable Fe (t=-5.0) and LaCl$_3$ extractable Al (t=-2.5) increases. Obviously, the affinity to sorb P is higher in case more oxalate or LaCl$_3$ extractable Al is present, which is in line with the results of (Bloom, 1981; Bloom et al., 1978; Oates and E.J., 1983) who showed that carboxylate bound Al has a high affinity to sorb P.
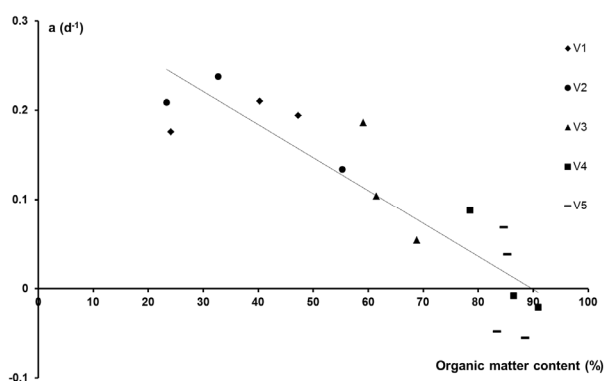
Figure 5. *The relation between the slow sorption rate of the modified Elovich equation (a-value; Table 2) and the organic matter content.*
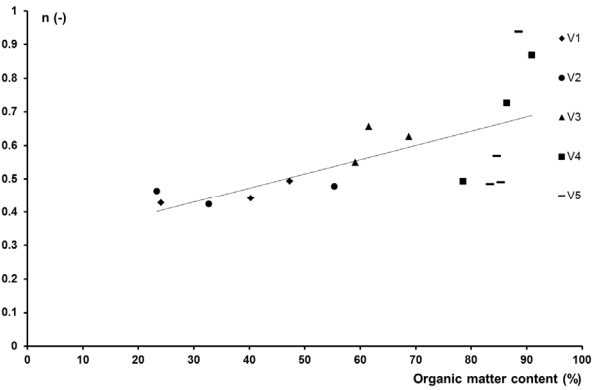
Figure 6. *The relation between the exponent of the modified Freundlich equation (n-value; Table 3) and the organic matter content.*
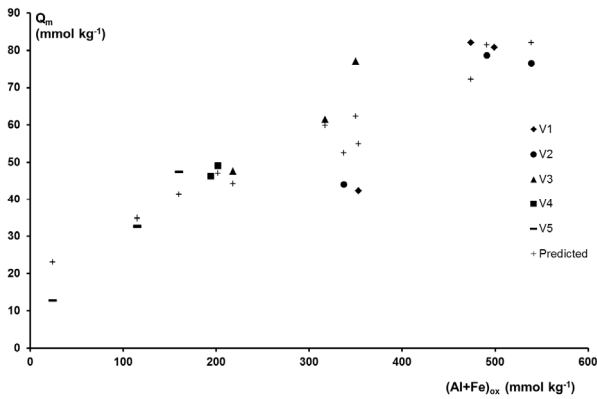

Figure 7. *Measured and predicted maximum amount of reversible sorbed P (Q_m) based on the sum of oxalate extractable Al and Fe (x-axis) and the organic matter content.*
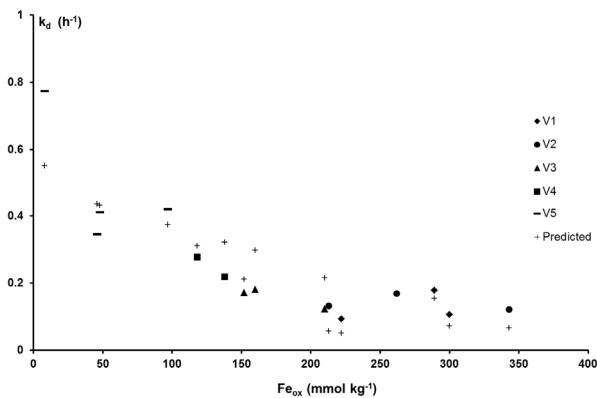

Figure 8. *Measured desorption rate (k_d) and the values predicted based on the amount of oxalate extractable Fe (x-axis).*

Environmental implications

Peaty clay soils have the ability to react with P and the maximum P sorption capacity is related to the sum of the amount of oxalate extractable Al and Fe $(Al+Fe)_{ox}$. In the soil profiles we observed that the $(Al+Fe)_{ox}$ content decreases with depth. In the top layers the amount of Al- and Fe-hydroxides is high due to the high clay content from river sediments, but also a substantial amount of organic matter is present (25-50%) from the origin peat profile. The affinity to sorb P ('a'-value) is higher in peaty clay soils compared to sandy soils which contain a considerable lower amount of organic matter (< 10 %). However, the maximum P sorption capacity seems to be comparable. The deeper layers of the profiles (> 80 cm) consist of almost pure peat and the dominant sorption reaction is a fast reaction which is complete within 1 day. In the subsoil most of the sorbed P is reversibly bound and the desorption rate constant (k_d) is higher than in non-calcareous mineral soils. As a consequence P will leach more easily in the subsoil than in the top soil. Therefore, P accumulation in the soil, e.g. as a result of agricultural practices, should be prevented, because P losses to surface waters will increase in situations of P accumulation in deeper layers. Implementation of the process description of P sorption and desorption kinetics in soil-water modelling, together with the derived parameters, will help to understand the impact of manure and fertilizer applications on P losses on this soil type.

Conclusions

We studied P sorption and desorption in peaty clay soils because relative large P losses have been reported on this soil type. The P sorption and desorption could be described similar to mineral soils, and the maximum P sorption capacity is also well related to the oxalate extractable Al and Fe content. However, the rate constants of sorption and desorption differ and the influence of the organic matter content on P sorption and desorption is important. In the subsoil of peat soils, with a high organic matter content, mainly a fast sorption reaction is observed and about two third of the maximum total P sorption capacity is reversibly sorbed, while in the top soil only one third is reversibly sorbed and a slow sorption reaction is observed. The P sorption and desorption parameters are related to soil characteristics. The P sorption isotherms are less concave (higher n-value) compared to mineral soils, and the slow sorption rate constant 'a' decreases at higher organic matter content. The desorption maximum (Q_m) depends strongly on the amount of oxalate extractable Al and Fe and the organic matter content has an additional positive effect. The desorption rate constant (k_d) decreases if the oxalate extractable Fe increases and/or the $LaCL_3$ extractable Al increases. Since the sorption and desorption parameters are related to soil characteristics, these pedotransfer functions can be used to estimate the P sorption and desorption parameters in other peaty clay soils. Based on our results it is concluded that, due to the

strong reversibility of P sorption in the subsoil, P accumulation in peaty clay soils should be prevented.

Parameters used

a	= Elovich sorption rate constant	(d^{-1})
Al_{ox}	= oxalate extractable aluminum	$(mmol\ kg^{-1})$
c	= phosphorus concentration	$(mg\ L^{-1})$
c_r	= reference phosphorus concentration	$(mg\ L^{-1})$
F	= amount of sorbed P	$(mmol\ kg^{-1})$
F_t^a	= extra amount of sorbed P after t days	$(mmol\ kg^{-1})$
Fe_{ox}	= oxalate extractable Fe	$(mmol\ kg^{-1})$
K	= Langmuir adsorption coefficient	$(m^3\ mol^{-1})$
k	= Freundlich coefficient	$(mmol\ kg^{-1}\ L^n\ mol^{-n})$
k_1	= rate constant at constant c	$(mmol\ kg^{-1}\ d^{-1})$
k_2	= constant at constant c	$(kg\ mmol^{-1})$
k_a	= Langmuir adsorption rate constant	$(m^3\ mol^{-1}\ kg^{-1})$
k_d	= Langmuir desorption rate constant	(h^{-1})
n	= Freundlich exponent	$(-)$
P_i	= amount of P extracted in the presence of an infinite sink source	$(mmol\ kg^{-1})$
P_{ox}	= oxalate extractable P	$(mmol\ kg^{-1})$
PSC_{max}	= maximum P sorption capacity = (F_m)	$(mmol\ kg^{-1})$
Q	= amount of adsorbed P	$(mmol\ kg^{-1})$
Q_m	= maximum of amount of P adsorbed	$(mmol\ kg^{-1})$
t	= time	(d)
t_o	= reference reaction time	(d)

CHAPTER 3

Description of the phosphorus sorption and desorption processes in coarse calcareous sandy soils

O.F. Schoumans

Abstract

In order to understand and predict the behaviour of P in calcareous sandy soils, sorption and desorption studies were carried out. Two main processes were distinguished: a fast, reversible phosphate reaction (within 1 day), which can be described by the Langmuir equation, and a precipitation reaction that can be described by a time-dependent Freundlich equation. The maximum phosphate sorption capacity (PSC_m) in the top 50 cm of the soil ranged from 3–6 t P_2O_5 ha^{-1}. About 85–95% of the maximum amount of P bound was poorly soluble; the remaining portion of bound P determines the ortho-P concentration in soil solution under desorption conditions. The breakthrough curves of the two column experiments were described reasonably well by the proposed process description and the associated parameters which were derived from batch experiments.

Keywords: phosphorus, phosphate, kinetics, sorption, desorption, precipitation, calcite, calcareous soils, phosphate sorption capacity

Introduction

In the Netherlands, much research has been carried out on the effect of high P application rates on P losses to groundwater and surface waters in areas with high livestock densities (Breeuwsma et al., 1995; Oenema et al., 2004; Schoumans, 1997; Schoumans and Chardon, 2015). Most of the intensive livestock farms in the Netherlands are located on the non-calcareous (acid) sandy soils in the east of the country. However, elsewhere in the Netherlands (e.g. in the bulb-growing areas with calcareous soils in the west) the P concentrations in surface waters can also be above the environmental targets (De Klijne et al., 2007; Groenenberg et al., 2013; Klein et al., 2012a; Portielje et al., 2002). The risk of P losses from bulb cultivation is high because high phosphate application rates in the past have resulted in substantial P accumulation in soils (Van Aartrijk et al., 1995). In many P sorption studies with calcareous material as adsorbent, the focus was on pure calcite or calcareous soil types with a high silt and/or clay content which often also have a high content of active Fe and Al forms (Bertrand et al., 2003; Carreira et al., 2006; Harrell and Wang, 2006; Jalali, 2006; Shariatmadari et al., 2006; Zhou and Li, 2001). Even though the behaviour of P in coarse calcareous sandy soils with low clay, Al and Fe contents is poorly understood, no parameters of sorption and desorption kinetics have been published. Consequently, it is difficult to predict the P accumulation in these soils and the risk of P losses due to fertilisation. Here I describe a study in which coarse calcareous sandy soils were used to derive the parameters of P sorption and desorption kinetics and the consequences of P loading of the soil on the P concentrations and P losses via leaching.

Reaction mechanisms

In coarse sandy calcareous soils the Ca/Mg carbonates dominate the behaviour of P, because in these soils the Al and Fe contents are much lower than in calcareous silty or clay soils. The pH, Ca and P concentrations influence the P sorption kinetics, as will be discussed in more detail below.

The pH determines the dominance of the inorganic phosphate anions in soil solution (Lindsay, 1979). At pH between 2.15 and 7.1 $H_2PO_4^-$ dominates, and between 7.2 and 12.3 HPO_4^{2-} becomes dominant. At pH < 6 calcium phosphates are fairly soluble and Al and Fe oxides and hydroxides are the main adsorbents for P, and form stable soil components. In Fig. 1 the relationship between the P concentration and pH is shown, based on the solubility constants of Al, Fe and Ca phosphate precipitates. For calcareous systems, the precipitation/solubility lines of the most soluble calcium phosphates (brushite or Dicalcium Phosphate Dihydrate: DCPD) and insoluble calcium phosphate (hydroxyapatite) are presented.
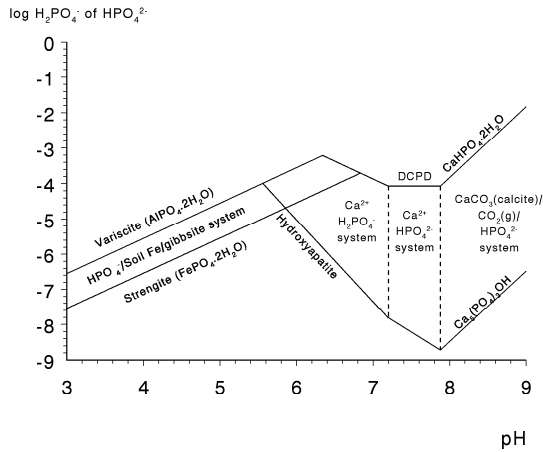
Figure 1. *Effect of the pH on the solubility of Al, Fe and Ca phosphate precipitates (after Lindsay, 1979).*

Previous researchers (Cole et al., 1953; Freeman and Rowell, 1981; Griffin and Jurinak, 1973; Griffin and Jurinak, 1974; Kuo and Lotse, 1972) concluded that in the presence of calcite and at P concentrations below about 5 mg L^{-1} P, first of all a fast surface reaction (< 1 day) occurs; they reported total amounts of adsorbed P on calcite with a specific surface area between 1.5–1.8 m^2 g^{-1} ranging between 25 and 100 µg P g^{-1} calcite. In the calcite crystal each Ca^{2+} ion is associated with six oxygen atoms from six different CO_3^{2-} groups. At the edge of the crystal, associations can be found between Ca^{2+} ions, oxygen atoms and H_2O molecules, bicarbonate or hydroxyl ions. (Kuo and Lotse, 1972) concluded that bicarbonate and hydroxyl anions at the surface of calcite probably exchange with phosphate (phosphate adsorption reaction). As a result of strong weathering conditions in soils, the specific surface areas of calcium carbonate components in soils can be up to 500 m^2 g^{-1} (Holford and Mattingly, 1975c); the authors found an inverse hyperbolic relationship between the specific surface area and the $CaCO_3$ content. However, Del Campillo et al. (1992) reported specific surface areas of $CaCO_3$ ranging from 1.5 to 22 m^2 g^{-1} and argued that the values published by Holford and Mattingly (1975a) are probably an artefact of the used methodology.

It is evident that the surface adsorption reaction and the subsequent precipitation reaction are major mechanisms of P immobilisation in calcite-rich alkaline soils (Avnimelech, 1980; Freeman and Rowell, 1981; Holford and Mattingly, 1975a; Holford and Mattingly, 1975b; Holford and Mattingly, 1975c; House and Donaldson, 1986; Sø et al., 2011; Stumm and Leckie, 1970). The first process to occur is the formation of calcium phosphate on the surface of calcite ('nuclei growth'), which can be considered

as a fast precipitation reaction (< 1 day). (Sø et al., 2011) studied phosphate sorption and desorption kinetics at low P concentrations (< 50 µM ≈ 1.5 ppm P) in different calcite-equilibrated solutions that varied in pH, P_{CO2}, ionic strength and Ca concentration. The fast reaction was completed in 2–3 h, and desorption / dissolution equilibrium was reached in less than 0.5 h. At these low P concentrations, complete reversibility of bound P was observed. The time-dependent process of phosphate sorption in calcite-rich systems is associated with the calcium phosphate cores clumping into crystals, followed by the growth of nuclei (Freeman and Rowell, 1981; Wang et al., 2012). Different forms of precipitation nuclei have been calculated, using the composition of the final solution e.g. dicalcium phosphate (DCP), Octacalcium phosphate (OCP) and hydroxyapatite (HA). It appears that the formation of these products is influenced by the initial P concentration and the ratio of H^+ to Ca (Avnimelech, 1980; Clark and Peech, 1955; Cole et al., 1953; Wang et al., 2008). Using atomic force microscopy (AFM) (Wang et al., 2012) showed in detail that the mineral surface-induced formation of Ca~P phases is initiated by the aggregation of clusters on calcite, which leads to the nucleation and subsequent growth of Ca~P phases on calcite.

Process description

Three reaction mechanisms are observed for the sorption of P in calcareous systems: (1) a fast reversible surface adsorption reaction, (2) a fast reversible precipitation reaction on the surface of calcite, and (3) a time-dependent precipitation reaction of calcium phosphate cores clumping into crystals (Cole et al., 1953; Freeman and Rowell, 1981; Holford and Mattingly, 1975a; Holford and Mattingly, 1975b; Holford and Mattingly, 1975c; Kuo and Lotse, 1972; Sø et al., 2011; Stumm and Leckie, 1970). Hereafter, the process description of these reaction mechanisms, as used in my study, are described in more detail.

Fast reversible surface reaction

At pH 8 and a phosphate concentration below the Ca~P solubility product, the main reaction is specific adsorption on the surface of calcite. This reaction is described as an exchange of hydroxyl groups with phosphate at the edges of calcium carbonate (Freeman and Rowell, 1981; Kuo and Lotse, 1972):

$$Ca \sim\sim OH + P^- \underset{\longleftarrow}{\longrightarrow} Ca \sim\sim P + OH^- \tag{1}$$

which can be described by the Langmuir equation:

$$Q = \frac{K\,C\,Q_m}{1 + K\,C} \tag{2}$$

Q = amount of adsorbed P   (mol kg^{-1})

C	= concentration of the P during the experiment	(mol m^{-3})
Q_m	= P adsorption maximum	(mol kg^{-1})
K	= Langmuir adsorption affinity coefficient	(m^3 mol^{-1})

The fast reversible precipitation reaction on the surface of calcite caused by the formation of calcium phosphate ('nuclei growth') is difficult to separate from the fast reversible adsorption reaction. Therefore, in our study the two processes combined were described with the Langmuir equation (Eq. 2). (Cole et al., 1953; Holford and Mattingly, 1975a; Kuo and Lotse, 1972) showed that the Langmuir equation adequately describes the description of the fast reversible phosphate reaction in calcareous soils or on calcite.

Precipitation

At P concentrations higher than about 5 mg L^{-1} P a slow precipitation reaction also occurs, initiated by the adsorption of phosphate and the Ca~P nuclei on the surface of calcite. Easily soluble dicalcium phosphate dihydrate (DCPD; brushite) is probably formed (Griffin and Jurinak, 1974). At P concentrations >100 mg L^{-1} calcium phosphate forms directly (Freeman and Rowell, 1981); this process is strongly influenced by the pH of the system (Lindsay, 1979).

(Enfield et al., 1981a; Freeman and Rowell, 1981) assume that the precipitation rate is the result of the super saturation of several calcium phosphate precipitation products (parallel precipitation processes), and that this can be described by:

$$XP_j = \sum_{j=1}^{n} \left(\int_{t=0}^{t} k_{pj} \left[C(t) - CE_{pj} \right] dt \right) \tag{3}$$

XP_j	= amount of precipitated calcium phosphate j	(mol kg^{-1} P)
$C(t)$	= P concentration during the precipitation process	(mol m^{-3})
CE_{pj}	= equilibrium concentration of calcium phosphate precipitate j	
	(depends on Ca^{2+} concentration and pH)	(mol m^{-3})
k_{pj}	= precipitation rate constant of precipitate j	(mol P kg^{-1} m^3 mol^{-1} h^{-1})
t	= reaction time	(h)

This process description is comparable with the one derived by Van der Zee and Van Riemsdijk (1986, 1988, 1991) to describe the diffusion / precipitation reaction with Fe and Al oxides and hydroxides.

For 14 calcareous sandy soils (Enfield et al., 1981b) showed that the overall P sorption could be described by an adsorption reaction in combination with the formation of two precipitation products (DCPD and HA). The precipitation reaction depended on the pH of the samples, but even at the same pH the precipitation rate varied by a factor of 10. Similar results were obtained by (Shaviv and Shachar, 1989) for the precipitation reaction, using Eq. 3. Phelan and Mattigod (1987) described the precipitation process by means of a power function version of Eq. 3:

$$XP = \int_{t=0}^{t=t} k_S \ s \ (C(t) - CE_p)^{n_{prec}} \ dt \tag{4}$$

XP = amount of precipitated calcium phosphate   (mol kg^{-1} P)
$C(t)$ = concentration of P during the experiment   (mol m^{-3})
CE_p = equilibrium concentration of a calcium phosphate precipitate   (mol m^{-3})
s = specific surface area of the material   (m^2 kg^{-1})
k_s = specific surface area precipitation rate   (mol P kg^{-1} m^{-2} (mol m^{-3})$^{-n}$ h^{-1})
n_{prec} = exponent of the precipitation reaction   (-)

(Enfield et al., 1981a; Freeman and Rowell, 1981; Phelan and Mattigod, 1987) presented the description of the precipitation process (Eqs 3 and 4) as empirical functions. However, in Appendix A I show that a general equation of the precipitation kinetics can be described, which results in:

$$\frac{dXP}{dt} = k_2 \left(K_p \ (Ca)^a \ (C(t))^b - XP \right) \tag{5}$$

where

$$K_p = \frac{1}{K_{sol}}$$

In fact, Eq. 5 is also known as the rate-dependent Freundlich equation, because at constant buffered Ca concentration Eq. 5 becomes:

$$\frac{dXP}{dt} = k_2 \left(K_F \ C^b - XP \right) \tag{6}$$

K_F = Freundlich constant   (mol kg^{-1} (mol m^{-3})$^{-b}$)
C = Phosphorus concentration   (mol m^{-3})

In practice, several forms of calcium phosphate are produced and for each precipitate Eq. 6 is valid if no interactions are assumed. Therefore, the time-dependent precipitation reaction of the formation of calcium phosphate products in soils is used (Eq. 6) to describe this overall precipitation reaction. The amount of total bound P (F^t) is equal to the sum of Eq. 2 and Eq. 6. From Eq. 6 it can be concluded that the precipitation rate decreases over time until the maximum amount of precipitate is formed ($\delta XP/\delta t$=0 Based on the precipitation kinetics it becomes clear that the K_p and CE values (Eqs 5 and 4) are not constants, since they are determined by the Ca concentration. In situations where the Ca concentration is buffered by calcite, these values become constant if the pH and CO_2 pressure of the system are constant. (Enfield et al., 1981b) showed that the k_s value (Eq. 4) depends on the pH.

Materials

Seven soil samples were collected from representative soil horizons of calcareous fine dune and coastal sandy soils (Haplic Arenosols and Eutric Fluvisols; FAO classification) in the west of the Netherlands. A total of four representative profiles with a low P content were sampled, and only layers that had been disturbed slightly or not at all were included. All soil samples were air-dried and sieved according to Dutch standard instruction (NEN5751, 1989). The following were determined for each sample: pH (NEN5750, 1989), organic matter content (NEN5754, 2005), carbonate content (NEN5752, 1995), oxalate-extractable Al, Fe and P contents (NEN5776, 2006; Schwertmann, 1964) and total P (NEN6961, 2001; NEN15681-1, 2005; NEN15681-2, 2005). The results are presented in Table 1.

Table 1. Characteristics of the calcareous sandy soil samples.

Profile Code	FAO Soil[1]	Layer depth (cm)	pH-H_2O (-)	pH-$CaCl_2$ (-)	Organic Matter (g/100g)	$CaCO_3$ (g/100g)	P_{ox} (mmol kg^{-1})	Al_{ox}	Fe_{ox}	P_{tot}
DK1	EF	0-25	8.4	7.8	0.3	2.0	0.5	1.0	8.9	1.7
DK1	EF	26-39	8.5	7.6	0.2	1.0	1.5	0.7	5.0	2.2
DK2	EF	64-94	7.4	7.1	0.3	1.1	2.9	1.7	1.9	4.1
DK4	HA	88-110	8.3	7.9	0.3	4.9	0.3	0.9	1.8	3.4
DK5	HA	12-52	6.8	6.7	1.1	0.3	2.2	5.7	12.3	5.4
DK5	HA	53-72	7.5	8.4	2.7	0.2	0.6	2.2	3.3	3.2
DK5	HA	73-84	8.0	8.5	2.5	0.3	0.6	1.8	1.8	3.2

[1] EF = Eutric Fluvisol and HA = Haplic Arenosol

The pH-H_2O of the samples ranged from 6.8 to 8.4, and the pH-$CaCl_2$ from 6.7 to 8.4. The organic matter content (OM) was low (< 2.7%) because most of the soil samples were from the subsoil, and also because in calcareous sandy soils with high pH values the organic matter decomposes rapidly. The clay content in the coarse calcareous soil samples is negligible. The lowest carbonate contents (0.2–0.3%) were measured in profile DK5. The particle size distribution and specific surface areas of calcite in the soil samples was not determined. The oxalate-extractable Al and Fe contents were lower in the calcareous sandy soils than in the non-calcareous sandy soils where amorphous Al and Fe (hydr)oxides occur as typical weathering product under acidic conditions and also organically complexed Al and Fe can be formed (Chadwick and Chorover, 2001). The low Al and Fe content might also have been caused by the high calcium concentrations in the ammonium oxalate extract which induces calcium oxalate precipitates and makes the oxalate extraction less effective to extract Al and Fe (Del Campillo and Torrent, 1992; Loeppert and Inskeep, 1996). The total P content ranged between 1.7 and 5.4 mmol kg^{-1}.

Methods

Phosphate sorption experiments

From each soil sample, 8 subsamples of 120 g were taken. Each subsample was placed in a 250 ml polyethylene bottle and 240 ml phosphorus solution in a background of 0.02 M KCl was added. Eight initial P concentrations were tested: 0, 2.5, 5, 10, 25, 50, 75 and 90 mg L^{-1}. After the P solution had been added, the pH was adjusted to 8. In order to reduce algal growth, a few drops of chloroform were added to the solution and the bottles were kept in a dark place and slowly shaken at 30 rpm. Over a period of 56 days the pH, Ca concentration and P concentration were measured, starting on day 1 and then at 10 points in time: days 2, 4, 8, 14, 21, 28, 35, 42, 47 and 56. If necessary, the pH was adjusted. The additional amount of P bound (F^a) was calculated by means of the reduction in P concentration. After 56 days the solutions were filtered over a 0.45 µm filter (using a vacuum pump) and a few millilitres of 80% alcohol were used to wash the soil sample to remove P-rich solution. To derive the sorption parameters the actual time- dependent pH and Ca and P concentrations were used. At the end of the sorption experiments, the P enriched soil samples were subsequently used for the desorption experiments.

Phosphate equilibrium concentration resulting from desorption of adsorbed P and/or dissolution of soluble calcium phosphates.

About 10 g of P-enriched soil (air-dried) was mixed with 20 ml 0.02 M KCl solution (pH 8). Twice a day the samples were shaken manually end-over-end. After 8 days the pH was measured and the samples were filtered (0.45 µm filter). The P and Ca concentrations in the supernatant were measured on an inductively coupled plasma atomic emission spectroscopy.

Total amount of reversibly bound P

The P_i method (Menon et al., 1989b) was used to measure the total amount of soluble and reversibly bound P. About 30 g air-dried P-enriched soil was mixed with 150 ml 0.02 M KCl solution (pH 8). After 24 hours of shaking the iron-impregnated paper was changed; this was repeated three times, and then the three Fe-impregnated papers of each soil sample were combined. At the end, the pH and calcium concentration were measured. The total amount of P desorbed from the soil accumulated on the three Fe papers was measured in 150 ml 0.2 M H_2SO_4 solution after 4 hours' shaking. The P concentration in the H_2SO_4 was measured on an inductively coupled plasma atomic emission spectroscopy.

Poorly soluble P

After removing the last iron-impregnated paper the soil–KCl solution was shaken for 7 days. The samples were then filtered over a 0.45 µm filter, and the pH of the

supernatant was measured with a pH electrode and the Ca and P concentrations were measured on an inductively coupled plasma atomic emission spectroscopy.

Column experiment

To assess the validity of the parameter values derived by the sorption and desorption batch experiments, column experiments were carried out for the samples DK1 0-25 and DK5 52-72. About 150 g of the original soil sample was used in this column experiment. The diameter of the column was 3.5 cm (A= 9.62 cm^2), the length 10.5 cm, the volume 101 cm^3 and porosity 30.7% (Vo = 31.0 cm^3). A tap at the base of the column allowed effluent samples to be taken; the top of the column was closed with a cap to reduce evaporation. After being filled with soil, the sand column was saturated with a solution of 0.02 M KCl for 5 days and thereafter percolated with 0.02 M KCl until a constant calcium concentration was reached in the effluent. At that time the column had been refreshed with about 200 ml and the equilibrium Ca concentration was approximately 40 mg L^{-1}. For a further 41 days, 5 ml of 50 mg L^{-1} P (in 0.02 M KCl) was added to the column every day all at once (sorption experiment; flux 5.2 mm d^{-1}). Thereafter, the column was percolated with a P-free 0.02 M KCl solution, again at 5 ml per day all at once, to validate the desorption/dissolution process.

Results

Phosphate sorption experiments

For all soil samples, the reduction of the P concentration of the solution was greatest during the first 4 to 7 days (Fig. 2); thereafter the P concentration decreased more slowly. Within the first 4 days the greatest reduction in Ca concentration occurred (data not shown). At the end of the experiment the lowest Ca concentrations were determined in the systems with the highest initial P concentration (reductions up to about 60%: Fig. 3). Throughout the experiment the pH was stable (8.0 ± 0.1). Obviously, Ca was removed from the solution while calcium phosphate was precipitating. The dissolution rate of the CaCO$_3$ in the soil samples was lower than the precipitation rate of calcium phosphate because the calcium concentration did not increase to the initial Ca concentration during the batch experiment (Fig. 3). Although the soil samples had a similar initial pH and initial Ca and P concentrations, the final P concentration differed. Apparently, the reduction of the P concentration did not depend mainly on the initial Ca concentration of the soil sample but also depended on the affinity of soil material to react with P.
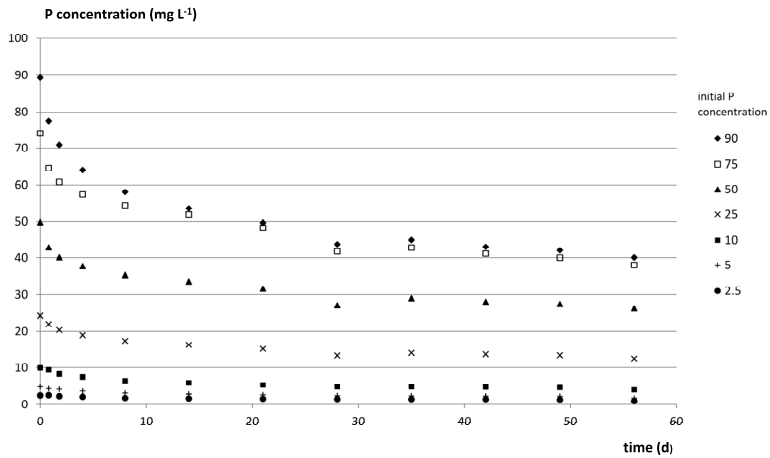
Figure 2. Influence of time on the P concentration, averaged for all soil samples, during the P sorption experiment.
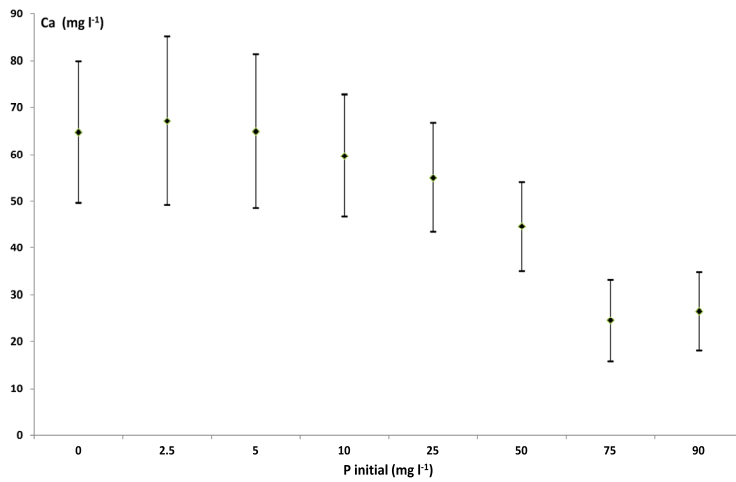
Figure 3. The final calcium concentrations (average and standard deviation of all soil samples) as a function of the initial P concentration.
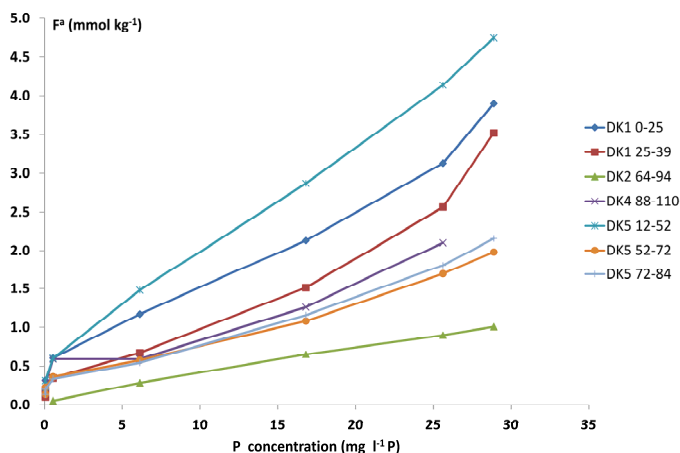
Figure 4. *Additional amount of P bound (F^a) after 56 days as a function of the final P concentration.*

Fig. 4 shows the additional amount of P bound (F^a) to the soil material after 56 days (at pH 8) as a function of the final P concentration. The soil sample with the highest initial P content (DK5 12-52) had the highest P accumulation during the sorption experiments; this sample also had the highest oxalate-extractable Al and Fe contents. It seems that Al_{ox} and Fe_{ox} influence the total amount of sorbed P even at high pH. This is in accordance with results of (Borrero et al., 1988; Pena and Torrent, 1990) who showed the importance of Fe for phosphate sorption in calcareous soils.

The total amount of bound P (F^t) after 56 days reaction at the highest initial P concentration of 90 mg P l^{-1} is presented in Table 2 and it was calculated as the sum of the initial P content (P_{tot}; Table 1) and the amount of P bound during the experiment (F^a). No correlation was found between the total amount of P bound after two months and the total $CaCO_3$ content of the soil sample ($R^2 = 0.04$). The coefficient of determination did not increase significantly if also the oxalate extractable Al- and Fe content was taken into account ($R^2 = 0.05$).

Table 2. *Calculated amount of P bound (F^t) after 56 days at an initial P concentration of 90 mg L^{-1} P.*

Soil sample	CaCO$_3$ (g/100g)	P_{tot}	F^t
		----- (mmol kg^{-1}) ----	
DK1 0 - 25	2.0	1.7	5.2
DK1 25 - 39	1.0	2.2	5.3
DK2 64 - 94	1.1	4.1	8.0
DK4 88 - 110	4.9	3.4	7.9
DK5 12 - 52	0.3	5.4	9.7
DK5 52 - 72	0.2	3.2	5.0
DK5 72 - 84	0.3	3.2	5.2

Phosphate desorption / solubility

The P equilibrium concentration due to desorption / dissolution (C_{des}) was lower than the final P concentration measured after sorption (data not shown). This is in accordance with the well-known hysteresis effect of P sorption, since a part of the P bound is not easily soluble. The desorption equilibrium P concentrations were often less than 10 mg L^{-1}. In addition to the P equilibrium concentration, the maximum amount of reversibly bound P was also determined according to the P_i method. About 10–25% of the total amount of P bound after 56 days was easily soluble or reversibly bound P. Consequently, most of the P bound was not readily available or soluble. These poorly soluble P forms resulted from precipitation of non-soluble calcium phosphates or were formed by soluble P forms becoming poorly soluble P forms or being bound on internal sorption sites in aggregates during the 2-month sorption experiment. As most of the bound P is not readily available or soluble, it is assumed that the phosphate equilibrium concentration is not determined by the total amount of P bound but by the amount of fast adsorbed or precipitated P (Q; Eq. 2). For all the soil samples there was a good relationship between the phosphate equilibrium desorption/dissolution concentration (C_{des}) and the amount of reversibly bound P (P_i): see Fig. 5. All samples follow the same curve, except for sample DK5 12-52. This sample has the highest Al_{ox} and Fe_{ox} contents and the lowest pH (Table 1), and seems to have the greatest affinity for P adsorption and therefore has the lowest desorption concentrations.
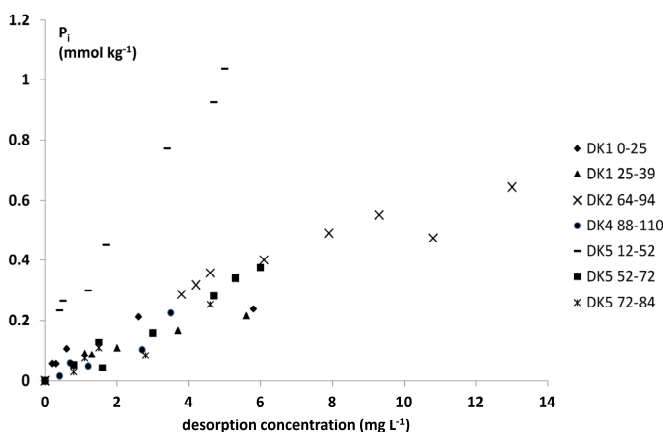
Figure 5. *Relation between P_i and C_{des} (desorption isotherm).*

Poorly soluble calcium phosphate

After measuring P_i, the equilibrium concentration of the bound P remaining in the soil was determined (CE_{ns}). The calcium concentration was about 15 mg L^{-1}, which is similar to the calcium concentration during the determination of the phosphate equilibrium concentration directly after sorption (C_{des}). The P concentration of the poorly soluble calcium phosphates ranged from 0.1 and 0.7 mg L^{-1}; on average it was 0.15 ± 0.15 mg L^{-1}.

Parameterisation

In order to determine the process parameters a distinction was made between:

a) a fast reversible adsorption / precipitation reaction on the surface of calcite

b) a poorly soluble precipitation reaction (crystals)

a) Fast reversible surface reaction

The Langmuir equation (Eq. 2) was used to describe the fast surface reaction mechanism of reversible amount of bound phosphate. We assumed that the total amount of reversibly bound P (Q as measured with the P_i method) is in equilibrium with the measured desorption concentration. In order to derive the parameters of the Langmuir equations the measured Pi was corrected for the amount of P which came into solution due to desorption/dissolution. This corrected amount equals the total amount of reversibly bound P in equilibrium with the measured concentrations. Table 3 shows the parameters of the fitted Langmuir equation of each sample and Figure 6 shows the fitted lines for each sample. The coefficients of determination (R^2) of the fitted Langmuir equations are good: they range between 83% and 97%.

If the sample with the high Al and Fe contents (DK5 12–52) is excluded, an overall Langmuir isotherm can be fitted with an R^2 of 0.864 (figure 6). The overall phosphate adsorption capacity (Q_m) is 0.96 mmol kg^{-1}, while the affinity to adsorb phosphate (K) is 0.101 L mg^{-1}.
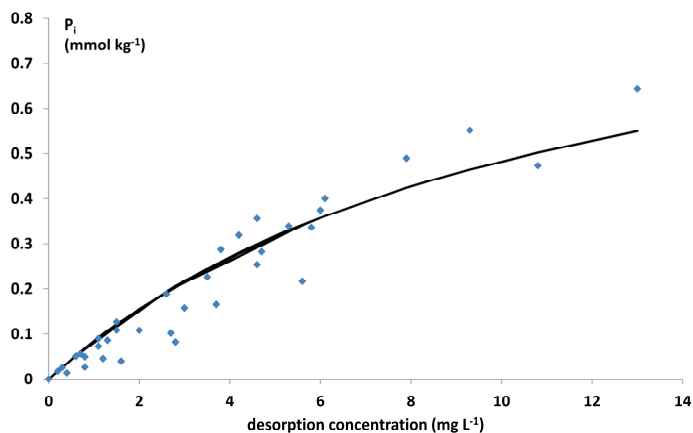
Figure 6. *Overall Langmuir isotherms of the calcareous sandy soil samples (excluding sample DK5 12-52 with high Al and Fe contents).*

Table 3. Fitted parameters of the Langmuir equation.

Sample	K	Q_m	R^2
	(L mg^{-1})	(mmol kg^{-1})	(-)
DK1 0 – 25	0.0994	0.919	0.890
DK1 25 – 39	0.0877	0.768	0.935
DK2 64 – 94	0.0797	1.230	0.923
DK4 88 – 110	0.1021	0.582	0.882
DK5 12 – 52	0.2542	1.643	0.969
DK5 52 – 72	0.1391	0.471	0.828
DK5 72 – 84	0.1234	0.691	0.966
All[1]	0.101	0.96	0.864

[1] Excluding sample DK5 12-52 with high Al and Fe contents

b) Poorly soluble precipitation reaction

The precipitation reaction is described by Eq. 5. During the sorption experiment, P and Ca concentrations were measured over time. The amount of poorly soluble P (XP) over time can be calculated as the total amount of P bound during the experiment minus the calculated amount of reversibly bound P (Q) at each moment in time. Consequently, the unknown parameters k_2, K_P, a and b were fitted, using the measured concentrations over time (Table 4). The coefficient of determination (R^2) was high except for one sample: DK2 64-94.

Table 4. *Parameter values of the precipitation reaction (Eq. 5).*

Sample	$K_P (*10^{12})$	b	k_2	a	R^2
DK1 0 – 25	1.6904	1.322	0.02372	0.6215	0.779
DK1 25 – 39	0.0498	1.069	0.06275	0.6491	0.750
DK2 64 – 94	0.2154	1.390	0.001689	0.4386	0.218
DK4 88 – 110	1.7564	1.139	0.01647	0.8186	0.919
DK5 12 – 52	0.0364	0.558	0.02349	1.049	0.953
DK5 52 – 72	0.2445	0.7786	0.03205	1.045	0.893
DK5 72 – 84	0.1832	0.9833	0.01504	0.8192	0.943
All[1]	0.1114	1.024	0.02529	0.732	0.895

[1] Excluding sample DK2 64-94

For each soil sample the maximum Phosphate Sorption Capacity ($PSC_{max} = F_{max} = Q_{max} + XP_{max}$) was calculated, using a time span of 5 years to assess the sorption maximum. Since the total amount of P bound (precipitated) depends on the calcium concentration, an observed maximum Ca concentration of 80 mg L^{-1} (Fig. 3) was used as initial calcium concentration. Figure 7 shows the extrapolated phosphate sorption capacity (t = 5 years) as a function of the initial P concentration.
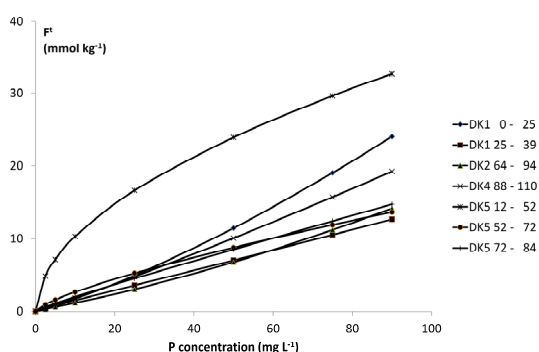
Figure 7. *Total amount of P bound (t = 5 years) as a function of the P concentration (at pH=8 and a Ca concentration of 80 mg L^{-1}).*

Sample DK5 12-52 has the highest PSC_{max}. This is also the sample with the lowest pH and highest Al and Fe contents. In this soil sample reactive Al and Fe forms could also be responsible for P binding. If this sample is omitted, the average precipitation reaction derived has a high coefficient of determination (R^2 = 0.895: Table 4). The (long-term) maximum phosphate sorption capacity of the calcareous soil samples at a P concentration of 50 mg L^{-1} ranges between 6–11 mmol kg^{-1}.

Column experiment

Figures 8 and 9 show the breakthrough curves of the column experiment. The simulated values were based on the flow rate of the ingoing solution and the soil sample's specific sorption and desorption parameters. During the column experiment, the pH was constant (pH: 8.2 ± 0.1 for DK1 0-25 and 8.1 ± 0.1 for DK5 52-72). Because of the precipitation reaction, the calcium concentration decreases from approx. 40 mg L^{-1} to 15 mg L^{-1}.
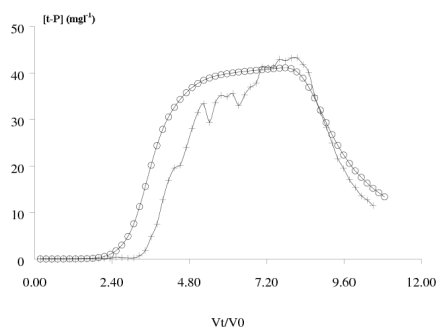
Figure 8. *Breakthrough curve of DK1 0-25.*
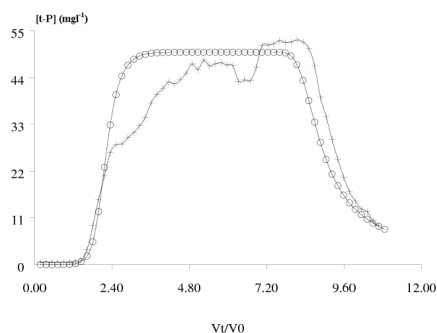
Figure 9. *Breakthrough curve of DK5 52-72.*

The shapes of measured and simulated phosphate breakthrough curve of sample DK1 0-25 are very similar, but the starting point of the increase of P concentrations differs slightly. This means that the total phosphate sorption capacity (Q_m and/or XP_{max}) is slightly higher compared to the fitted parameters of the sorption batch experiments (probably K_F, since the shape is correct). The simulated starting point of P increase of sample DK5 52-72 is correct, but after a certain point the simulated values diverge from the measured values. In this case, the precipitation rate (k_2) in the column seems to be slightly less than what was predicted on the basis of the sorption batch experiments. With respect to the leaching part of the column experiment, it is concluded that the desorption isotherm can describe the decrease in P concentration quite well, which means that the fitted parameters of the Langmuir equation (easily reversible bound P) can describe the inorganic P concentration in the soil and the soil solution.

Discussion

It is known that in calcareous soils three reaction mechanisms are important (a) a fast reversible surface adsorption reaction, (b) a fast precipitation reaction of easily soluble calcium phosphates on the surface of calcite caused by the formation of calcium phosphate ('nuclei growth'), and (c) a time-dependent precipitation of a poorly soluble calcium phosphate caused by calcium phosphates cores clumping into crystals. Since the first two reactions are difficult to separate, the two processes combined were described with the Langmuir equation. The coefficient of determination (R^2) of the fitted Langmuir equations of the coarse calcareous sandy soils in this study ranges from 0.83–0.97. The overall phosphate adsorption capacity (Q_m) of these calcareous sandy soils with low oxalate-extractable Al and Fe contents is 0.96 mmol kg^{-1}, while the average affinity to adsorb phosphate (K) is 0.101 L mg^{-1}. This is almost twice as high as the Langmuir adsorption constant (K) measured by (Kolahchi and Jalali, 2013) in sandy soils in the Middle East, which ranged from 0.053 to 0.049 L mg^{-1}, but is similar to the K values Harrell and Wang (2006) reported for calcareous sandy loam in Louisiana, which were 0.125–0.167 L mg^{-1} .

The phosphate adsorption maximum on $CaCO_3$ ranges between 25–100 µg/g at a specific surface area of 1.5–1.8 m^2 g^{-1} calcite (Holford and Mattingly, 1975b; Kuo and Lotse, 1972), which is equal to 0.8–3.3 mmol per kg $CaCO_3$. The $CaCO_3$ content of our calcareous sandy soil samples is less than 5%, so a maximum phosphate adsorption capacity of 0.165 mmol kg^{-1} soil is expected. However, weathering increases the surface area of carbonate components (Holford and Mattingly, 1975c), which would explain why the maximum phosphate adsorption capacity (Q_m) measured was higher than the expected phosphate adsorption capacity based on the $CaCO_3$ content. In our

study the Q_m value ranges between 0.5 and 1.6 (Table 3), which is in the range Sø et al. (2011) found as adsorption maxima in calcite-dominating systems: 0.121–4.14 mmol P kg^{-1}.

The precipitation reaction of the poorly soluble calcium phosphate was described by the time dependent Freundlich equation. The R^2 of this equation for our soil samples ranged from 0.750 to 0.953. This time-dependent precipitation reaction fitted all samples but one. The exception was sample DK2 64-94, which had a phosphate precipitation rate that was about one-tenth of that of the other samples (Table 4) .

The maximum total phosphate sorption capacity at a buffer concentration of 50 mg L^{-1} P ranges from 6 to 11 mmol P kg^{-1}, which is approximately equivalent to 2700–5100 kg P_2O_5 ha^{-1} (first 0.5 m of the soil profile). Only a small part (5%–15%) of the maximum total phosphate sorption capacity is reversibly bound P (0.5 to 1.2 mmol kg^{-1} P; 230–550 kg P_2O_5 ha^{-1} in the top 0.5 m of soil). In acid sandy soils a larger part of the maximum bound P is reversibly bound (about 33%; (Van der Zee and Van Riemsdijk, 1988)) and also the total phosphate sorption capacity is higher: 15 to 50 mmol P kg^{-1} (Schoumans et al., 1987; Schoumans and Chardon, 2015; Van der Zee et al., 1990a; Van der Zee et al., 1990b). Consequently, calcareous sandy soils are vulnerable for P leaching if the P content in the soil increases. Under leaching conditions, the amount of reversibly bound P will determine the P concentration in soil solution. Based on the Langmuir parameters, at high P accumulation the P concentration in soil solution will vary between 3 and 8 mg L^{-1}. At a net precipitation surplus of 400 mm y^{-1} the root zone P losses will vary from 12 to 24 kg P ha^{-1} y^{-1}. In the long term high P concentrations will be found in groundwater and drainage water. This largely explains why the P concentrations measured in the calcareous sandy soils in the west of the Netherlands are high (De Klijne et al., 2007; Klein et al., 2012a; Portielje et al., 2002). Most of the total amount of bound P is 'poorly' soluble. However, the inorganic P concentration after mining the amount of readily available P is expected to vary between 0.1 and 0.4 mg L^{-1} P (0.15 ± 0.15 mg L^{-1} P), which is still appreciable from an environmental point of view.

The column experiments demonstrated that the desorption / dissolution of P could be reasonably well described, although the precipitation rate in the experiments sometimes differed slightly from the rate found in sorption batch experiments. This suggests that using the Langmuir equation and the modified Freundlich equation to describe the kinetics of phosphate sorption and desorption / dissolution processes in coarse calcareous sandy soils captures the interaction between inorganic soil P accumulation and inorganic P concentrations in soil solution.

Finally, it has to be mentioned that the number of soil samples was limited and restricted to coarse calcareous sandy soils. Nevertheless, these results indicates that coarse calcareous sandy soils are very vulnerable in terms of phosphate leaching. The process description and parameters described in this laboratory study will be helpful in relation to agri-environmental studies.

Conclusions

In coarse calcareous sandy soils, the kinetics of P sorption and desorption can be described by a combination of the Langmuir equation and a time-dependent Freundlich equation. The coefficients of determination (R^2) of the fitted equations are between 0.8–0.98. The total phosphate sorption capacity measured varies between 6 to 11 mmol P kg^{-1}, which is lower than that measured in non-calcareous sandy soils, where Al and Fe oxides and hydroxides determine the phosphate sorption capacity. Only a small part (5%–15%) of the P is reversibly bound, but relatively high P concentrations are measured in solution. Coarse calcareous sandy soils are vulnerable for P leaching losses from the root zone.

Abbreviations

Q	=	amount of adsorbed P	(mmol kg^{-1})
Q_m	=	maximum amount of adsorbed P = P adsorption maximum	(mmol kg^{-1})
K	=	Langmuir adsorption affinity coefficient	(m^3 mol^{-1})
$[X]$	=	concentration of X (X=OH$^-$, P$^-$, Ca~P and Ca~OH)	(mol m^{-3})
$[X_e]$	=	equilibrium concentration of X (X=OH$^-$, P$^-$, CA~P and Ca~OH)	(mol m^{-3})
$C(t)$	=	P concentration during the precipitation process	(mol m^{-3})
CE_{pj}	=	P equilibrium concentration of calcium phosphate precipitate j	(mol m^{-3})
CE_p	=	equilibrium concentration of a calcium phosphate precipitate	(mol m^{-3})
k_{pj}	=	precipitation rate of calcium phosphate precipitate j	(m^3 mol^{-1} kg^{-1} h^{-1})
t	=	reaction time	(h)
XP_j	=	amount of precipitated calcium phosphate j	(mol P kg^{-1})
s	=	specific surface area of the material	(m^2 kg^{-1})
k_s	=	specific surface area precipitation rate	(mmol m^{-2} (mol m^{-3})$^{-n}$ h^{-1})
n_{prec}	=	exponent of the precipitation reaction	(-)
k_1	=	precipitation rate of calcium phosphate precipitate	(mmol kg^{-1} (m^3 mol^{-1})$^{a+b}$ h^{-1})
k_2	=	dissolution rate of calcium phosphate precipitate	(h^{-1})
K_{sol}	=	solubility product	((mol m^{-3})$^{a+b}$)
K_p	=	reciprocal of the solubility product	((mol m^{-3})$^{-a-b}$)
a	=	exponent of Ca concentration	(-)
b	=	exponents of P concentration	(-)
K_F	=	Freundlich constant	(mol kg^{-1} (mol m^{-3})$^{-b}$)
F^t	=	total amount of P bound	(mmol kg^{-1})

APPENDIX A

$$a\ CaOH + b\ P \underset{k_2}{\overset{k_1}{\rightleftarrows}} Ca_a P_b\ (= XP) \tag{A.1}$$

Where XP refers to the calcium phosphate formed. At constant pH the calcium phosphate precipitation rate becomes:

$$\frac{dXP}{dt} = k_1\ (Ca)^a\ (P)^b - k_2\ XP \tag{A.2}$$

k1	= precipitation rate of calcium phosphate precipitate	(mmol kg^{-1} (m^3 mol^{-1})$^{a+b}$ h^{-1})
k2	= dissolution rate of calcium phosphate precipitate	(h^{-1})
(Ca)	= Ca concentration	(mol m^{-3})
(P)	= P concentration	(mol m^{-3})
a	= exponent of Ca concentration	(-)
b	= exponents of P concentration	(-)

At equilibrium $\dfrac{dXP}{dt} = 0$ Eq. A.2 becomes

$$\frac{k_2}{k_1} = \frac{(Ca_e)^a (P_e)^b}{XP} = K_{sol} \tag{A.3}$$

K$_{sol}$	= solubility product	((mol m^{-3})$^{a+b}$)
(Ca$_e$)	= Ca equilibrium concentration	(mol m^{-3})
(P$_e$)	= P equilibrium concentration	(mol m^{-3})

Rewriting Eq. A.2 leads to:

$$\frac{dXP}{dt} = k_1\ (Ca)^a \left((P)^b - \frac{k_2}{k_1 (Ca)^a}\ XP \right) \tag{A.4}$$

and substitution of Eq. A.3 in Eq. A.4 results in:

$$\frac{dXP}{dt} = k_1\ (Ca)^a \left((P)^b - \left(\frac{(Ca_e)}{(Ca)} \right)^a (P_e)^b \right) \tag{A.5}$$

Which can be simplified to

$$\frac{dXP}{dt} = k_p \left((P)^b - (CE)^b \right) \tag{A.6}$$

$$k_p = k_1\ (Ca)^a \tag{A.7}$$

$$CE = \left(\frac{(Ca_e)}{(Ca)} \right)^{a/b} (P_e) \tag{A.8}$$

With respect to the precipitation of DCPD (= CaHPO$_4$; a=1 and b=1) Eq. A.6 becomes equal to the one used by Enfield et al. (1981a). However, the n-power function (Eq. 4) used by (Phelan and Mattigod, 1987) cannot be derived from Eq. A. and does indeed seem to be an empirical function.

CHAPTER 4

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

Abstract

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

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

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

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

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

Keywords: phosphate, phosphate accumulation, phosphate sorption capacity, phosphate saturation degree, phosphate saturated area, sand, peat and clay

Introduction

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

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

In the early 1990s, a straightforward approach for non-calcareous sandy soils was developed to determine a critical value for the degree of phosphate saturation (known as phosphate saturation degree, abbreviated as PSD) in the Netherlands (Van der Zee et al., 1990a; Van der Zee et al., 1990b). The criteria required, namely the acceptable P concentration and reference soil depth that should be protected, were defined by a technical committee (TCB, 1990). As acceptable P concentration the natural background concentration was chosen (0.1 mg L^{-1} ortho-P) and as reference depth, the mean highest water level (MHW). In lowland countries like The Netherlands the groundwater is shallow and fluctuates during the year. In the summer period the lowest groundwater levels and during the winter period (autumn-spring) the highest groundwater levels are reached. In The Netherlands the mean highest and lowest groundwater level (MHW and MLW respectively) are defined as resp. the average of the three highest or lowest groundwater levels during a period of 8 successive years. In the wet areas the MHW varies between 0 and 0.4 m and the MLW between 0.6 and 1.4 m. During the year the groundwater levels can be above or below this level for a short period (< 2 months). Using these criteria and the phosphate kinetics of non-calcareous sandy soils, a critical PSD of 25% was calculated, which means that the actual phosphate accumulation in the soil should be less than 25% of the total phosphate sorption capacity of the soil between the soil surface and the MHW. When this critical value for non-calcareous

sandy soils was used in a modelling application it was found that about 70% of the agricultural land in non-calcareous sandy soils in areas with intensive husbandry in the Netherlands exceeded the defined critical PSD (Breeuwsma and Silva, 1992). At that stage it was not possible to define a critical value for the other soils in the Netherlands because no information was available on the phosphate sorption and desorption parameters and, moreover, the reference criteria had not been defined. Since then, the sorption and desorption processes in other Dutch soil types have been studied (Schoumans, 2013; Schoumans, 2014; Van Beek et al., 2003) and the phosphate accumulation has been determined by measurements (Finke et al., 2001). The main aim of this paper is to derive indicative critical values of phosphate saturation for different soil types and estimate the phosphate-saturated area and phosphate accumulation in The Netherlands.

Materials and methods

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

Table 1 gives the number of locations sampled (n) and the area represented for combinations of soil type and land use. The average density is approximately one sampled location per 2000 ha agricultural land. Although the sample density is not high, it is the only statistical database available for the entire country that includes the parameters needed to determine the PSD. For each stratum the PSD of each location was calculated in order to produce a map of the average degree of phosphate saturation for all strata. The phosphate-saturated area (abbreviated as PSA) of each stratum was determined by the number of locations where the PSD of the profile exceeded the critical PSD of the soil type, taking into account the total number of locations sampled within the stratum and the area of the stratum. The determination of the PSD and critical PSD is described hereafter.

scale 1 : 1,500,000

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

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

Soil type		Land use				
		Maize	Arable	Grass	Nature[§]	Total
Non-calcareous sandy soils[*]	n	64	82	312	218	676
	Area (ha)	168540	185774	748136	441866	1544316
Non-calcareous clay soils[**]	n	5	21	156	17	199
	Area (ha)	10073	63480	325693	24785	424032
Calcareous clay soils[***]	n	8	113	98	15	234
	Area (ha)	27230	355066	227116	10493	619904
Peat soils[****]	n		9	175	16	200
	Area (ha)		17151	230383	12479	260013
Calcareous sandy soils[*****]	n	1	22	13	23	59
	Area (ha)	1362	39800	22821	27203	91186
Total locations		78	247	754	289	1368
Total area (ha)		207205	661271	1554149	516826	2939451

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

63

Methodology: Definition of the critical Phosphate Saturation Degree (PSD$_{crit}$)

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

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

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

where

$\overline{\rho_{0-L_s}}$ = average dry bulk density of layer 0-L_s (kg m^{-3})

$\overline{\rho_{L_s-L_{ref}}}$ = average dry bulk density of layer L_s–L_{ref} (kg m^{-3})

L_s = maximum phosphate penetration depth   (m)

L_{ref} = reference depth where the critical P concentration (C_p) should not be exceeded   (m)

$\overline{Q_{m,0-L_s}}$ = average maximum amount of reversible bound P in layer 0-L_s (mmol kg^{-1} P)

$\overline{Q_{C_p,0-L_s}}$ = average amount of reversible bound P in layer 0-L_s (mmol kg^{-1} P)

$\overline{F_{C_p,L_s-L_{ref}}}$ = average phosphate sorption capacity at concentration C_p of layer L_s–L_{ref} (mmol kg^{-1} P)

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

In Appendix A the chemical methods are mentioned and the critical Phosphate Saturation Degree (PSD$_{crit}$) is derived, based on the conditions mentioned in Eq. 1, giving:

$$PSD_{crit} = \frac{\gamma\,K\,C_p}{1+\gamma\,K\,C_p}*100\ \ (\%) \qquad \text{(see Appendix, Eq. 13)}$$

PSD_{crit} = critical Phosphate Saturation Degree of a soil type   (%)

K = soil type specific Langmuir adsorption coefficient   (m^{-3} mol^{-1})

C_p = maximum ortho-P concentration for a soil type at reference depth L_{ref} (mol m^{-3})

γ = soil type specific coefficient   (-)

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

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

PSD	= Phosphate Saturation Degree of the soil to depth L_{ref}	(%)
$P_{act,\,0-L_{ref}}$	= actual amount of phosphate accumulation in the soil in layer 0-L_{ref}	(kg P_2O_5 ha^{-1})
$PSC_{m,\,0-L_{ref}}$	= maximum phosphate sorption capacity of the soil in layer 0-L_{ref}	(kg P_2O_5 ha^{-1})

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

Results

(a) Reference conditions of the soil types

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

The maximum acceptable P concentration (C_p) for non-calcareous sandy soils has been defined as the natural background concentration of inorganic P, which was determined at an average ortho-P value of 0.1 mg l^{-1} P (TCB, 1990). The background concentration of phosphorus varies across the Netherlands, especially in areas with marine sediments and in peat areas. The maps of the phosphorus background concentrations in the deep groundwater (> 13 m) are based on the database that supplies model input data for the national evaluations of the Dutch manure policy (Wolf et al., 2003).The most recent mapped information is used (Griffioen et al., 2006; Groenendijk et al., 2013a). It is assumed that inorganic P concentrations at those depths are not influenced by agricultural practices due to the high phosphate sorption capacity of the overlying soil. We used this dataset to calculate the background P concentration for five main soil types in the Netherlands. Figure 2 shows that the highest ortho-P concentrations are measured in the areas with marine sediments (coastal area). These sediments consist of calcareous material (sand or clay) containing Ca/Mg-P precipitates. Due to chemical and physical weathering and precipitation of secondary (amorphous) minerals, relatively

high P concentrations can occur. The average concentration of ortho-P of all soil types in this database is 0.36 mg P L^{-1} and the median concentration is 0.13 mg P L^{-1}, which is higher than the concentrations used for non-calcareous sandy soils (TCB, 1990). With respect to the definition of a phosphate-saturated soil, it is important that the natural background concentrations (C_p) that contribute to the diffuse losses to surface waters (trenches, ditches, brooks and rivers) at higher groundwater levels are accurately determined, because they directly affect the value of the critical PSD.

ortho-P concentration
- < 0.1
- 0.1 - 0.2
- 0.2 - 0.35
- 0.35 - 1.0
- > 1.0
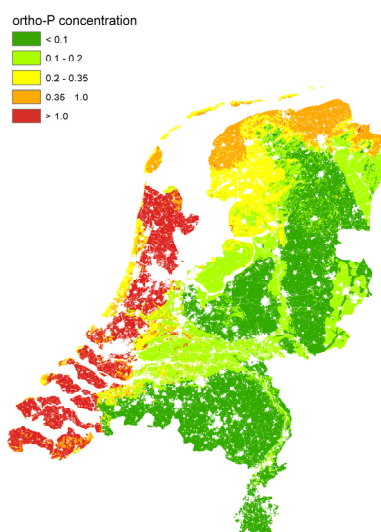
Figure 2. *Inorganic P concentrations (mg L^{-1} P) in deep groundwater in The Netherlands.*

(b) Soil chemical P characteristics of the different soil types

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

In non-calcareous sandy soils and peaty clay soils, the maximum sorption capacity can be determined by Eq. 15, with a value of 0.5 for α (Schoumans, 2004; Schoumans, 2013; Van der Zee et al., 1990a; Van der Zee et al., 1990b). In clay soils different clay minerals can occur like kaolinite, illite, and montmorillonite. Under weathering conditions the primary clay minerals are dissolved and mixtures of Al- and Fe-sesqui(hydr)oxides (e.g. gibbsite $Al_2O_3 \cdot 3H_2O$; goethite $Fe_2O_3 \cdot 3H_2O$; $Al(OH)_x^{(3-x)+}$ and $Fe(OH)_y^{(3-y)+}$). These sesqui(hydr)oxides can be partly associated with the electric negative charged clay plates or organic complexes (Bolt and Bruggenwert, 1978; Rowell, 1994). It is well known that phosphate can be sorbed to the clay minerals and micro-crystalline Al- and Fe-sesqui(hydr)oxides beyond the adsorption maximum of the primary clay minerals due to phosphate adsorption and a diffusion precipitation

reaction with micro-crystalline Al- and Fe-sesqui(hydr)oxides (Celi et al., 2000; Ler and Stanforth, 2003; Martin et al., 1988; Torrent et al., 1990; Van Riemsdijk and Lyklema, 1980). The micro-crystalline Al- and Fe (hydr)oxides (free, associated with the clay plates and/or organic complexes) which influences the phosphate sorption capacity, can be extracted with oxalate (Schwertmann, 1964). The amount of oxalate extractable Al and Fe is much higher in clay soils than in sandy soils (Finke et al., 2001), but the reaction mechanisms (fast adsorption reaction and slow diffusion / precipitation reaction) are similar, due to the role of micro-crystalline Al- en Fe-sesqui(hydr)oxides. When the phosphate sorption capacity of Dutch calcareous clay soils (3-12% $CaCO_3$; pH 7-8) was compared with non-calcareous clay soils (<3% $CaCO_3$; pH 5-7), no positive or negative influence was found of the $CaCO_3$ content on the P sorption capacity (unpublished data Schoumans), therefore, we decided to use Eq. 15 with a value of 0.5 for α. In calcareous sandy soils the amount of oxalate extractable Al and Fe (resp. Al_{ox} and Fe_{ox}) is low and the measured total sorption capacity was also found to be unrelated to the $CaCO_3$ content and/or to the contents of Al_{ox} and Fe_{ox} (Schoumans, 2014). The lack of effect of $CaCO_3$ on P sorption has been shown by Frossard et al. (1992) and Holford and Mattingly (1975c) and in the second paper it was shown that the specific area of $CaCO_3$ is a more important parameter in relation to the P sorption kinetics than the $CaCO_3$ content. In order to determine the critical PSD of calcareous sandy soils (Eq. 13), the ratio of F_m and Q_m was used (Eq. 3; see appendix) to calculate the value of γ.

The phosphate desorption parameters were derived from the Langmuir equation (see Appendix Eq. 2) which was applied on desorption experiments. For non-calcareous sandy soils we used the parameters given in the protocol for non-calcareous sandy soils (Van der Zee et al., 1990a; Van der Zee et al., 1990b). Indicative parameters for calcareous sandy soils were based on experiments described in Schoumans (2014). The parameters for peat soils in the Netherlands were derived from experiments described in Schoumans (2013) and Van Beek et al. (2003). For this soil type the values of β and K differ between the soil horizons. As a result, the general equation for the critical PSD will not be constant but will depend on the characteristics of the soil horizons above the reference depth (L_{ref} = MHW). However, in low-lying peat soils the MHW always reaches the topsoil (< 0.4 m below ground level) and in this part of the soil the parameters do not differ significantly.

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

Table 2. *Parameters used to calculate critical phosphate saturation degree (PSD$_{crit}$).*

Soil type	Parameters					Remarks and references
- Al/Fe dominated soils	α	β	K	$C_p{}^a$	$PSD_{crit}{}^b$	
	(-)	(-)	$(m^3 mol^{-1})$	$(mg\ L^{-1})$	(%)	
Non-calcareous sandy soils	0.5	0.167	35	0.09 (0.03-0.31)	25	Van der Zee et al. (1990a,b)
Non-calcareous clay soils	0.5	0.167[c]	35[c]	0.13 (0.09-0.34)	31 (23-54)	Unpubl. data
Calcareous clay soils	0.5	0.167[c]	35[c]	1.06 (0.31-1.78)	78 (51–86)	Unpubl. data
Peat soils	0.5	0.10-0.15	1–2	0.25 (0.09-1.78)	5 (1–36)	Van Beek et al., 2003 Schoumans, 2013
- Carbonate dominated soils	γ (=F_m/Q_m)		K	$C_p{}^a$	PSD_{crit}	
	(-)		$(mol\ m^{-3})$	$(mgLl^{-1})$	(%)	
Calcareous sandy soils	6.3-11.5		3.1	0.34 (0.34 -0.52)	23 (18-37)	Schoumans (2014)

a) Median *ortho-P concentrations (C$_p$) based on the data of Figure 2. Between brackets the 5 and 95 percentile values are mentioned.*

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

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

The PSD$_{crit}$ of peat soils is low when compared to the other soil types due to the low affinity to bind P (low K-value; Table 2), which means that phosphorus is relative mobile in peat soils. The range in P concentrations (5 and 95 percentile) mainly determines the range in critical phosphate saturation degree. Especially in the Western part of the Netherlands the range in P concentrations in deep groundwater is large (Table 2). The highest P concentrations are measured in geological formations containing marine sediments. It is questionable whether these highest measured P concentrations in deep groundwater may be applied to the defined reference depth MHW, since it is unclear if these concentrations always represent the background concentration at this shallow depth. It is well known that phosphate in nutrient rich groundwater will be immobilized during aeration by co-precipitation with CaCO$_3$ or Fe(III) oxides, even in calcareous clay soils (Griffioen, 2006). In peat areas also high P concentrations can be measured in deep groundwater, but the median value is much lower than in calcareous clay soils. In shallow groundwater in peat areas total-P concentrations were measured between 0.17 and 0.57 mg L^{-1} P (Zwart et al., 2010), but also relative high ortho-P concentrations up to 1 mg L^{-1} P in soil solution (< 4 m) were measured at a nutrient rich peat location (Van Beek et al., 2004).

(d) Distribution of the phosphate saturation degree (PSD)
The PSD of each sampled location was calculated by Eq. 14 and for each stratum the average PSD was calculated based on the soil profile data. Figure 3 shows the

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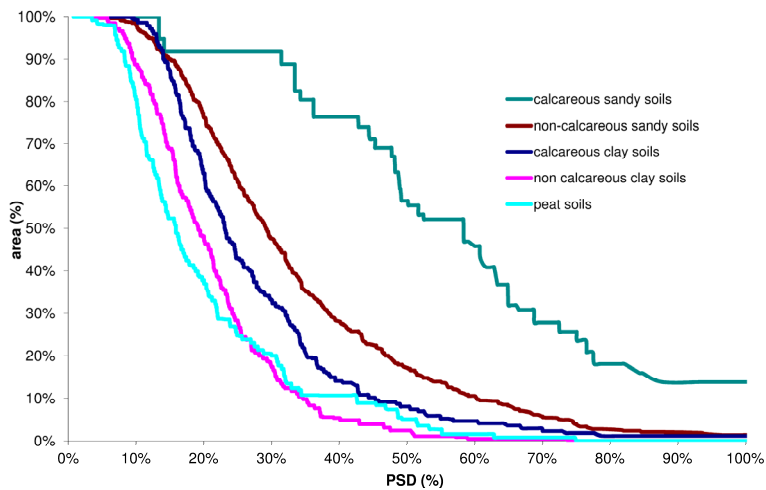
Figure 3. *Cumulative percentage distribution of the area agricultural land of the main soil types in the Netherlands in which a given PSD is exceeded.*
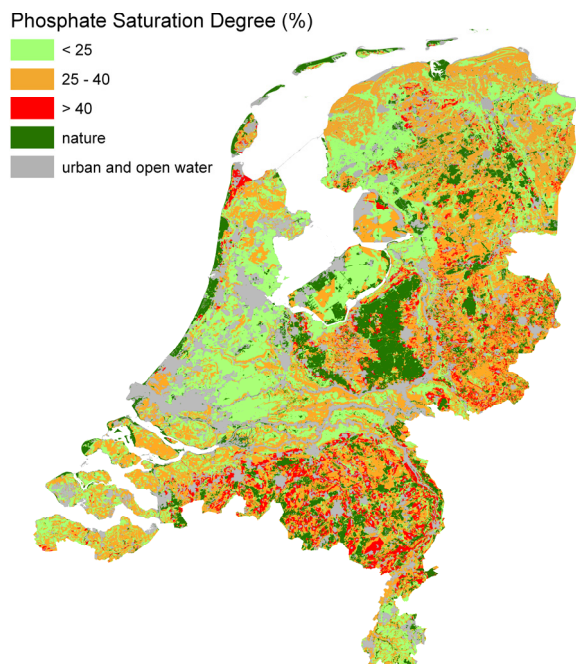
Figure 4. *Average PSD of the 95 sampled strata.*

(d) Distribution of the phosphate-saturated (PSA)

For each stratum the phosphate saturated area (PSA) is calculated by means of the percentage of profiles exceeding the critical phosphate saturation degree. In Figure 5 the PSA of agricultural land of each stratum is shown for two criteria: a PSD_{crit} of 25% and the PSD_{crit} specific to the soil type (Table 2). The critical PSD value of 25% represents the situation if the critical PSD value for non-calcareous soils (Van der Zee et al., 1990a) is applied to all soil types; consequently, differences in process parameters and background concentrations of the different soil types are not taken into account. If a PSD_{crit} of 25% is used, about 48% of the agricultural land is deemed to be phosphate-saturated. If the soil-specific PSD_{crit} is used, this percentage is lower (43%). If this PSD_{crit} is used the area of phosphate saturated clay soils is lower due to the higher reference concentration (C_p; table 2); many of the yellow areas (figure 5 left side) become green (figure 5 right side). On the other hand peat areas in the Western and North-western parts of the Netherlands become red, and seem to be vulnerable for P leaching to groundwater and subsequently to surface water.
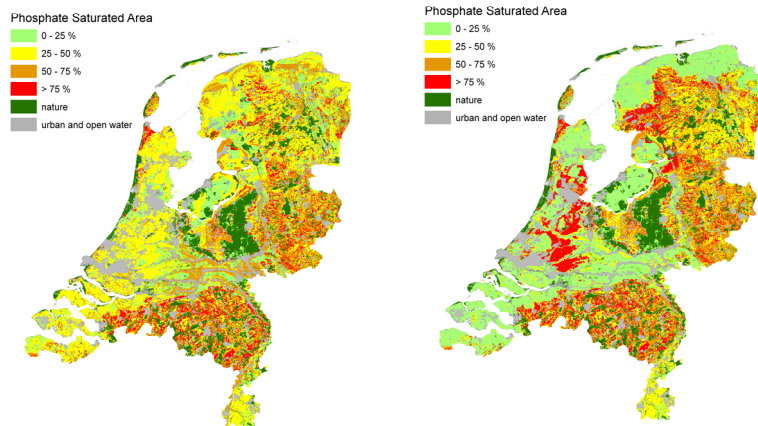
Figure 5. *Percentage of the area classified as phosphate-saturated soil for agricultural soil use: left-hand map, based on PSD_crit of 25%; right-hand map, based on the PSD_crit specific to the soil type (see Table 2).*

(e) Distribution of the P accumulation in soils

In addition to yielding information on the PSD and the PSA it is also possible to obtain an impression of the P accumulation of the main land uses (maize, grass, and other arable crops), because information on land use was collected during the sampling. In accordance with other measurements on P accumulation in soils (Lexmond et al., 1982), we found that maize land has the highest P accumulation (Figure 6). The main reason for this high P content is that maize can tolerate high manure application rates, so more P has been applied on maize and thus more P has accumulated in these soils. Furthermore, in the past the legislation of the P application rates for maize weas high in The Netherlands (about 350 kg P_2O_5 per ha; (Neeteson et al., 2001)). The measured average amount of P in agricultural soils in the Netherlands in the top layer (0.5 m) is about 2050 kg P ha^{-1} (4700 kg P_2O_5 ha^{-1}) and the 5‰ and 95‰ are approximately 850 and 4500 kg P ha^{-1} which equals to about 2000 and 10 000 kg P_2O_5 ha^{-1} (Figure 6).
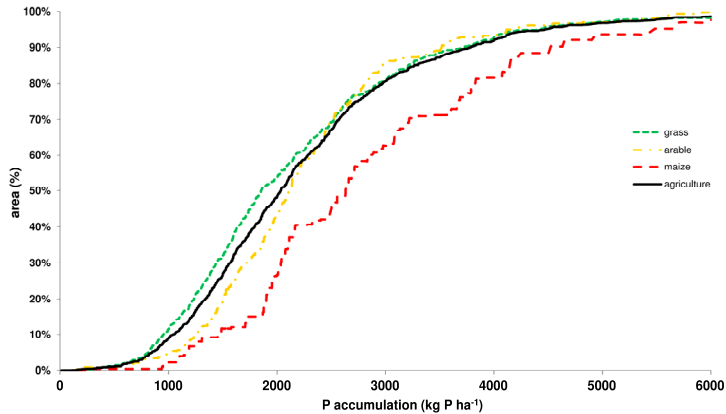
Figure 6. *Cumulative frequency distribution for the measured P accumulation in the topsoil (0 – 0.5 m) of various agricultural land uses.*

Discussion

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

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

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

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

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

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

The PSD is an indicator for the potential risk of P losses to surface water. However, soils that are phosphate-saturated are not always the soils with the greatest P losses to surface waters. The actual risk of P leaching depends on the location and on the hydrological situation, e.g. the elevation of the field in relation to ditches, brooks and rivers, and drainage conditions. In addition, for many regions there is insufficient data on the contribution of background losses to total P losses at catchment scale. Furthermore, in practice the relationship between PSD and the actual P loss is not one to one because during excessive use of P fertilizers and manure, a major part of the P accumulation becomes strongly sorbed and the reversibility is poor (Koopmans et al., 2004a; Koopmans et al., 2004b). When a P-rich sandy soil was depleted in the laboratory using a membrane filled with FeO, ortho-P measured in a 1:2 (w:v) water extract decreased much faster than the PSD and it was found that the relationship between P-1:2 and PSD for undepleted soil samples was not valid for the depleted soil samples (Koopmans et al., 2001). The consequence is that the soil PSD will remain high, whereas the P concentration in the soil solution decreases relatively fast (Koopmans et al., 2004b). This implies that at a certain PSD different P concentrations

in soil solution can be observed which is visualized in figure 7 as example. The curve can be different for different soil types, but the principle is valid for all soil types. This is known as the hysteresis effect of P sorption and P desorption in soils (Barrow, 1983). These findings also imply that a relationship between soil test P and P loss via leaching or surface runoff that has been developed for field sites where P is accumulating may not be valid in situations where prolonged depletion of soil P has taken place; this hampers the interpretation of the PSD in relation to the actual risk of P losses. It is important that these aspects are taken into account with respect to the Water Framework Directive (EEC, 2000), because the areas and fields that contribute most to P losses to surface water should be identified. Nevertheless, despite these notices the PSD is a simple method to assess the potential risk of P loss to groundwater, and subsequently to surface water. Strategies and additional measures are needed for fields with a high PSD and shallow groundwater levels in order to reduce the P losses from agricultural land to surface waters within a catchment.
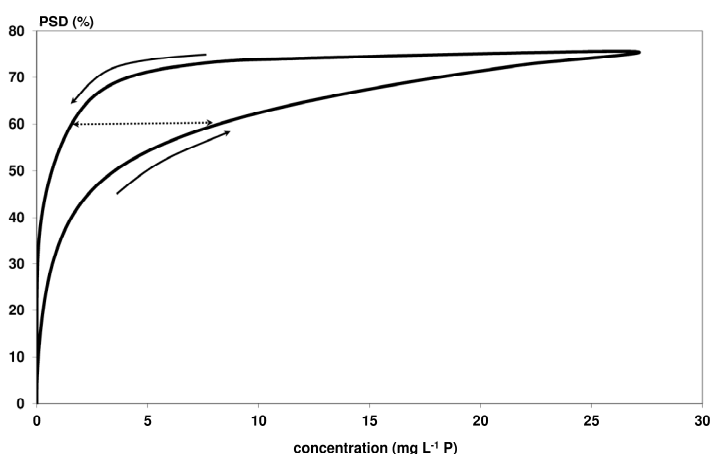
Figure 7. *Relation between the PSD and the ortho-P concentration in soil solution during loading of the soil with phosphate (upward line) and mining of the soil (backward line).*

Alternative ways of calculating PSD

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

Uusitalo and Tuhkanen (2000) found that oxalate extracted the same amounts as those found in inorganic fractions subjected to the Chang & Jackson procedure (NH_4F, NaOH and H_2SO_4), and stated that "oxalate extraction estimates total inorganic P rather than the pool relevant in environmental risk assessment". In order to measure a pool of P that is assumed to be more relevant, Beauchemin and Simard (1999) used colorimetry

instead of ICP for measuring P in the oxalate extract, to avoid including organic forms of P. Sharpley (1996) used FeO strips for measuring the amount of reversibly sorbed P. Since oxalate may dissolve hardly mobile apatitic P, Turtola and Yli-Halla (1999) used the sum of NH_4F + NaOH extractable P instead of P_{ox}, in combination with $Fe_{ox}+Al_{ox}$. The presence of Ca-P compounds in manured soils has been demonstrated by various researchers (Beauchemin et al., 2002; De Haan and Van Riemsdijk, 1986; Sharpley et al., 2004).

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

sorbed P, extractant	sorption maximum	ref. *
oxalate	a_m * (Al + Fe)-oxalate	see text
oxalate	(Al + Fe)-oxalate (a_m =1)	[1]
oxalate (MRP)	(Al + Fe)-oxalate	[2]
FeO-strip P	(Al + Fe)-oxalate	[3]
NH_4F (Al-P)	Al-oxalate	[4,20]
NaOH (Fe-P)	Fe-oxalate	[4]
NH_4F + NaOH	(Al + Fe)-oxalate	[5]
Mehlich I	(Al + Fe)-oxalate	[6]
Mehlich I	(Al + Fe)-Mehlich (molar)	[6,19]
Mehlich III	(Al + Fe)-Mehlich (molar)	[7,19]
Mehlich III	Al - Mehlich (molar)	[17]
FeO-strip P	sorption max adsorption isotherm	[8]
oxalate	sorption max + P-oxalate	[9,10]
Mehlich III	sorption max	[11]
Mehlich III	sorption max + Mehlich III	[12]
Mehlich I	sorption index + Mehlich I	[10]
Mehlich III	sorption index	[13]
water	sorption index	[13]
0.1 N NaOH	sorption index	[14]
used for predicting plant-P		
isotopic exchange	sorption max	[15]
NaOAc or $NaHCO_3$	sorption max	[16]
NH_4OAc + NH_4F	Al - NH_4Oac	[18]

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

As mentioned above, in the Netherlands the long-term P sorption maximum of non-calcareous soils is estimated as α_{m*} ($Fe_{ox}+Al_{ox}$) with α_m = 0.5. However, Beauchemin and Simard (1999) stated that "the factor 0.5 is empiric, and was obtained from a given set of soils and experimental conditions". For this reason, some authors have simply used α_m = 1 (see Table 4), whereas others have determined α_m themselves. Pautler and Sims (2000) calculated α_m by multiplying the sum of P_{ox} and Q_{max} of soils by 1.8, and found an average value of 0.61. By contrast, Van der Zee and Van Riemsdijk (1988) calculated α_m by $F_m = P_{ox} + 1.8 F_r$, where F_r is the amount of P sorbed after 40 h.

In many countries, soil laboratories do not routinely apply the oxalate extraction as it is

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

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

Conclusions

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

However, the PSD is still only an indicator that gives information about the potential risk of P losses from land to groundwater, since e.g. prolonged anaerobic conditions and preferential transport in cracked soils are not taken into account. In order to predict the

actual risk, more information is needed about the local conditions of a field, particularly about the hydrological conditions, like groundwater fluctuation during the year and amount of water discharges via different pathways (surface runoff, subsurface runoff, tile drains, deep groundwater flows) to adjacent surfaces waters. Nevertheless, the PSD, as defined in the protocol phosphate saturated soils, is a simple indicator to assess the potential risk of P loss to groundwater, and subsequently to surface water.

Parameters

Q	= amount of adsorbed phosphate	(mmol kg^{-1} P)
Q_m	= maximum phosphate adsorption capacity	(mmol kg^{-1} P)
F	= amount of sorbed phosphate	(mmol kg^{-1} P)
F_m	= maximum phosphate sorption capacity	(mmol kg^{-1})
ρ	= dry bulk density	(kg m^{-3})
L	= depth	(m)
L_s	= maximum phosphate penetration depth	(m)
L_{ref}	= reference depth	(m)
K	= k_a / k_d = Langmuir adsorption coefficient	(m^3 mol^{-1})
M	= molar mass of P (=31)	(g mol^{-1})
c	= ortho-P concentration	(mol m^{-3})
C_p	= maximum ortho-P concentration at reference depth (L_{ref})	(mol m^{-3})
$\alpha, \beta, \gamma, \epsilon, \lambda, \tau$	= defined coefficients	(-)
P_{ox}, Al_{ox}, Fe_{ox}	= oxalate-extractable P, Al and Fe	(mmol kg^{-1})
Z	= phosphate saturation fraction to depth L_{ref}	(-)
PSD_{crit}	= critical phosphate saturation degree to depth L_{ref}	(%)
PSD	= phosphate saturation degree of the soil to depth L	(%)
P_{act}	= actual amount of phosphate accumulation in the soil to depth L	(kg P$_2$O$_5$ ha^{-1})
PSC	= phosphate sorption capacity of the soil to depth L	(kg P$_2$O$_5$ ha^{-1})
PSC_m	= maximum phosphate sorption capacity of the soil to depth L	(kg P$_2$O$_5$ ha^{-1})

Annex A Phosphate Saturation Degree (PSD)

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

$$Q = \frac{K \, c \, Q_m}{1 + K \, c} \tag{2}$$

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

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

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

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

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

Further we define:

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

PSD = phosphate saturation degree of the soil (%)

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

In the Dutch protocol on phosphate saturation soils, the soil-specific values have been

set for non-calcareous sandy soils (Van der Zee et al., 1990a; Van der Zee et al., 1990b) and the reference ortho-P concentration was set by a technical committee (TCB, 1990). The used parameters are described hereafter.

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

$$F_m = \alpha \, (Al_{ox} + Fe_{ox}) \tag{15}$$

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

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

$$Q_m = \beta \, (Al_{ox} + Fe_{ox}) \tag{16}$$

β	= maximum phosphate adsorption coefficient	(-)

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

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

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

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

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

CHAPTER 5

Modeling soil phosphorus levels and phosphorus leaching from agricultural land in the Netherlands

O.F. Schoumans & P. Groenendijk

Abstract

The contribution of non-point pollution of P leaching and P runoff from agricultural soils is very important, especially in those areas with intensive livestock production systems. Prediction of the impacts of fertilization reduction measures on P loads from agricultural soils to surface water requires a sound description of the accumulation of P. In this article an overview is given of the Dutch approach. The presented methodology has been developed for non-calcareous sandy soils in flat areas where P loss by subsurface runoff is the dominating pathway. Based on the kinetics of P sorption and desorption of these soil types, P accumulation in soils, and inorganic P concentrations in soil solution can be modeled. Furthermore, methods have been deduced to translate the description of soil chemical P processes into commonly used soil P tests. As a result of this interaction, soil P tests can be used as an initial approach to estimate the potential risk of P leaching and runoff from agricultural soils in non-calcareous sandy areas. The description of the kinetics of inorganic P reactions and the modeling of soil P tests have been implemented in the ANIMO model in addition to an organic P cycle that is related to organic C and N dynamics. With this model, the fixation and immobilization of P by soil components can also be assessed. As a result of annual losses by fixation, immobilization, and subsurface runoff/leaching, changes in soil P test values with time can be estimated.

Introduction

Intensive livestock systems and their associated large rates of manure production in many European countries (Lee, 1992) has caused enhanced soil P levels (Hanotiaux and Vanoverstraeten, 1990; Oenema and Van Dijk, 1994; Steen, 1997; Wadman et al., 1987). A similar problem is found in the USA where in many states high soil P test values have been recorded for more than half of all samples analyzed (Sims, 1993). As a result of continuous rise in soil P levels, agriculture increasingly contributes to the eutrophication of surface water by surface runoff (Pote et al., 1996) and leaching (subsurface runoff) (Breeuwsma et al., 1995; Schoumans et al., 1991). As is generally considered to be the key element that controls or limits productivity of fresh waters, the potential impacts of agricultural loads one eutrophication has become a major concern in many countries (Lee, 1973). To predict the environmental impact of P applications to agricultural soils, the influence of soil chemical and hydrological processes should be well understood. This must include relationships between P accumulation and soil P levels as determined by soil P tests. Since policy makers are mainly interested in the long-term effects of manure strategies (Van der Molen et al., 1997), model-based approach has to be developed to predict the impact of changes in soil P levels on P loss. In this article an overview is given of such an approach that has been developed by order of the Dutch Ministry of Agriculture, Nature Management and Fisheries for non-calcareous sandy soils.

Phosphorus dynamics modeling phosphorus accumulation

Most (70-90%) of the P in pig (Sus scrofa) and liquid manure is present as inorganic P (Fordham and Schwertmann, 1977; Gerritse and Vriesema, 1984; Gerritse and Zugec, 1977). In animal manure the major mineral that determines the inorganic P concentration in the liquid phase is struvite (Bril and Salomons, 1990). The reaction of inorganic P in soil is characterized by a fast reversible process and a slow, almost irreversible process that causes the hysteresis effect of phosphate sorption and desorption (Barrow, 1983). The fast reaction is generally attributed to P adsorption on surface sites (Van der Zee, 1988). The slow reaction is mostly viewed as diffusion or nucleation controlled precipitation reaction. For example, diffusion of P into particles of microcrystalline Al and Fe oxides (Barrow, 1983; Van Riemsdijk et al., 1984) or slow nucleation and growth of a Ca-P-precipitate at the surface of calcium carbonate (Enfield et al., 1981a; Freeman and Rowell, 1981). For non-calcareous sandy soils, Van der Zee (1988) showed that the fast reversible P reaction could be described by the kinetic Langmuir equation:

$$\frac{\partial Q}{\partial t} = k_a \, c \, (Q_m - Q) - k_d \, Q \tag{1}$$

where Q = amount of adsorbed P (mmol kg^{-1} P); k_a adsorption rate constant (m^3 mol^{-1} h^{-1}); k_d = desorption rate constant (h^{-1}); c = ortho P concentration (mol m^{-3}); Q_m= maximum amount of P that can be adsorbed (mmol kg^{-1} P).

At equilibrium Eq. [2] is valid:

$$Q = \frac{K \, c \, Q_m}{1 + K \, c} \tag{2}$$

where K = k_a/k_d = adsorption constant (m^3 mol^{-1}). The amount of adsorbed P (Q) can be determined by the Fe oxide-impregnated paper method (P$_i$; Menon et al. (1989b)) with desorption times up to 48 h.

The maximum amount of adsorbed P (Q$_m$) is determined after increasing the P content of the soil. This is achieved by shaking the soil sample during 1 week with a P solution (KH$_2$PO$_4$) of 3 mol^{-3} at a 1:50 soil/solution ratio (m/v) (Van der Zee, 1988). For non-calcareous sandy soils, varies between 10 and 100 m^3 mol^{-1} and Q$_m$ was related to the amount of oxalate-extractable Al and Fe (Schoumans, 1995; Van der Zee, 1988):

$$Q_m = \beta \, (Al + Fe)_{ox} \approx \frac{1}{6} \, (Al + Fe)_{ox} \tag{3}$$

where (A1 + Fe)$_{ox}$ = sum of the amount of oxalate extractable Al and Fe (mmol kg^{-1}).

The slow practically irreversible P sorption reaction (S) can be derived by calculating the difference between the amount of total sorbed P (F) and the amount reversible adsorbed P (Q). In situations in which the slow reaction is assumed fully irreversible, the reaction can be described with functions of the exposure integral (Van der Zee, 1988). However, Lookman (1995) showed that, with long-term Fe oxide-impregnated paper desorption experiments (up to 1600 h), most of the irreversible sorbed P will be released. Based on the mean overall sorption characteristics of non-calcareous sandy soils and the mean desorption characteristics of similar non-calcareous sandy soil samples, Schoumans (1995) showed that description of the slow sorption process could be described by:

$$\frac{\partial S}{\partial t} = \sum_{i=1}^{3} a_i \, (K_F \, C^N - S_i) \tag{4}$$

where S = amount of P sorbed by the slow reaction (diffusion/precipitation) (mmol kg^{-1} P); K$_F$= Freundlich sorption coefficient [(m^3 mol^{-1})$^{1/N}$ mmol kg^{-1}]; N =Freundlich exponent (-); a$_i$ = diffusion or precipitation rate constant (h^{-1}); C = ortho P concentration (mol m^{-3}).

From Eq. [4] the maximum amount of P diffused into soil particles can be calculated (assuming t = ∞):

$$S_m = \sum_{i=1}^{3} K_F \, C^N \tag{5}$$

For acid sandy soils the amount of S_m was related to the amount of oxalate-extractable Al and Fe in the soil samples (Schoumans, 1995; Van der Zee, 1988). In situations with large manure/fertilizer applications and high P concentrations (up to 3 mol m^{-3}) S_m becomes:

$$S_m = \varepsilon \, (Al + Fe)_{ox} \approx \frac{1}{3} \, (Al + Fe)_{ox} \tag{6}$$

where S_m = maximum amount of diffused or precipitated P (mmol kg^{-1} P).

The maximum or total P sorption capacity (PSC$_{max}$ or F_m) can be estimated by the sum of the amount of adsorbed (Q_m) and diffused (S_m) P. For non-calcareous sandy soils, the total P sorption capacity becomes:

$$F_m = PSC_{max} = \alpha \, (Al + Fe)_{ox} \approx 0.5 \, (Al + Fe)_{ox} \tag{7}$$

where F_m or PSC$_{max}$ = total P sorption capacity (mmol kg^{-1} P).

The extent to which the P sorption capacity of the soil has been saturated is expressed by the degree of P saturation:

$$DPS = \frac{P_{ox}}{F_m} \, 100 \, \% \tag{8}$$

where DPS = degree of P saturation (%) and P_{ox} amount of sorbed P (extractable by oxalate) (mmol kg^{-1}).

To reduce the risk of contamination of ground water, a critical degree of P saturation has been defined in the Netherlands. The definition of a *phosphate saturated* soil is still restricted to non-calcareous soils because high manure application rates are only common in these particular areas. The general idea behind the definition is that the concentration of ortho P should not exceed 0.10 mg L-1 at the mean highest water table (MHW) (Breeuwsma and Silva, 1992). Based on the P sorption and desorption kinetics, (Van der Zee, 1988) proved that the P saturation degree of a layer is related to the maximum P concentration leaching out of that layer at the long term. The derived equation does not depend on thickness of the layer. The inverse of this equation is described by:

$$c = \frac{\beta}{\alpha \, K} \frac{DPS}{100 - DPS} \tag{9}$$

The experimentally determined mean values for α, β, and K of non-calcareous sandy soils are 0.5 (-), 0.167(-), and 35 m^3 mo1^{-1}, respectively. At a critical value of DPS of 25% (of the topsoil above MHW) the maximum acceptable ortho P concentration of 3.2×10^{-3} mol m^{-3} (approx. 0.10 mg L^{-1} P) is leaching out of that layer at the long term. Figure 1 shows the relation between the degree of P saturation and the ortho P equilibrium concentration after complete redistribution of the amount of reversibly bound P within the observed layer.
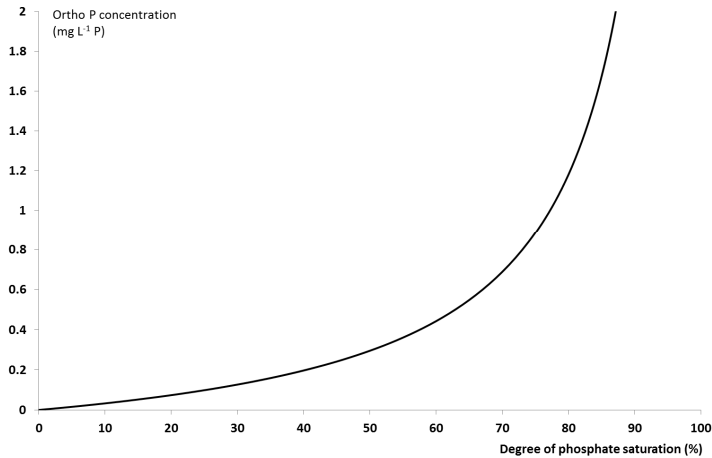
Figure 1. *Relation between ortho P equilibrium concentration in soil solution and degree of phosphate saturation (DPS).*

Modeling soil phosphorus tests values

The Pw (water-soluble P) value is used in the Netherlands as a soil test for arable land. The Pw value is determined at a 1:60 soil/solution ratio (v/v). About 1.2 mL soil is incubated together with 2 mL water for 20 h. After incubation, 70 mL water is added and the soil suspension is shaken for 1 h. After filtration, the P concentration is measured in the filtrate according to Murphy and Riley (1962). The Pw value is expressed in mg P kg^{-1} (substituting mg P$_2$O$_5$ L^{-1} soil as the standard agricultural unit; Sissingh (1971)). If the slow reaction is indeed practically irreversible, the amount of water-soluble P as measured by the Pw method can be derived from Eq. [1]. In situations where the amount of adsorbed P at the soil surface (Q) does not change significantly during the water extraction, a simple formula was obtained (Schoumans, 1997):

$$Pw\ value = \frac{Q}{K(Q_m - Q)}\ \lambda_{corr} \cdot 2.4163 \cdot 10^3 \tag{10}$$

$$\lambda_{corr} = 1 - 0.9722\ e^{-21.67 \cdot 10^{-3}\ K\ k_d\ (Q_m - Q)} \tag{11}$$

where 2.4163×10^3 is the conversion factor (from mol m^{-3} P to mg kg^{-1} P).

If the change in Q cannot be ignored, the formula becomes more complex (Schoumans, 1997):

$$Pw\ value = \frac{(a_1 - \sqrt{D}) - (a_1 + \sqrt{D})}{2\ a_2\ (\tau - 1)}\ 2.4163 \cdot 10^3 \tag{12}$$

Where $a_2 = -k_a s$; $a_1 = -k_a(Q_m - Q_o) - k_d s$; $a_0 = k_d\ Q_o$; $s = 1/y$; $y = V_{soil}\ \rho_d / (V_{H2O} \times 10^3)$; $V_{soil} =$ incubated volume of soil sample (m^3); $V_{H2O} =$ volume of the extractant (m^3); $\rho_d =$ dry bulk density $(kg\ m^{-3})$; $10^3 =$ conversion factor $(mmol\ mol^{-1})$; $\tau = p\ e^{yt\sqrt{D}}$; $p = (2\ a_2\ c_1 + a_1 - \sqrt{D})/$ $(2\ a_2\ c_1 + a_1 + \sqrt{D})$; $D = a_1^2 - 4\ a_2\ a_o$; $c_1 = Q_o/(36\ K\ (Q_m - Q_o))$; $Q_0 =$ initial amount of adsorbed P $(mmol\ kg^{-1})$; $36 =$ dilution factor after incubation $(-)$; $t =$ shaking time after dilution $(1\ h)$ (h).

Figure 2 shows the measured(Schoumans, 1995) and predicted Pw values as a function of the measured P concentration in the soil solution (C_e). The predicted values are calculated with Eq. [12]. The parameters used are: $K = 33\ m^3\ mol^{-1}$, $\beta = 0.1645$, and $k_d = 0.2\ h^{-1}$. These values are in agreement with data of Van der Zee (1988) for acid sandy soils $(K = 35\ mol^{-1}$, $\beta = 0.167$, and $k_d = 0.2\ h^{-1})$. The Pw values were also predicted (Fig. 3) as a function of measured adsorbed (Q) using another data set (Schoumans et al., 1991). Figure 3 shows that predicted and measured values are in agreement with the 45° line. As a result of this good relationship, the water-soluble soil P test is a powerful tool from an environmental point of view, because the soil fertility level can be directly translated to an equilibrium soil P concentration (ortho P) in the tillage layer. Furthermore, the effect of P surplus/deficiency on changes in soil P test values, P concentrations (ortho P), and P content $(Q_o$ and $P_{ox})$ can be predicted for these non-calcareous sandy soils.
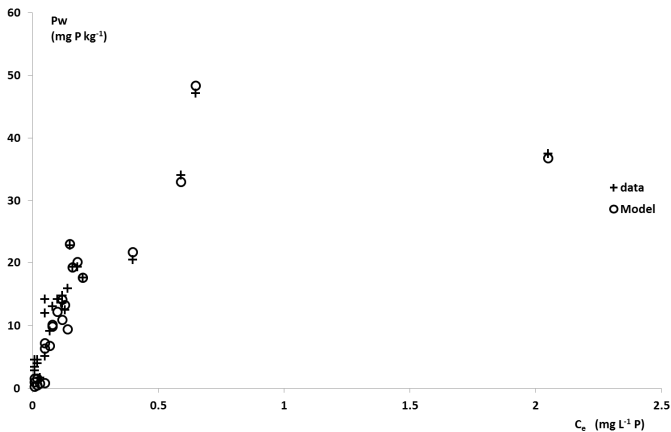
Figure 2. *Relation between predicted (modeled) and measured Pw value as a function of the ortho P equilibrium concentration in soil solution.*
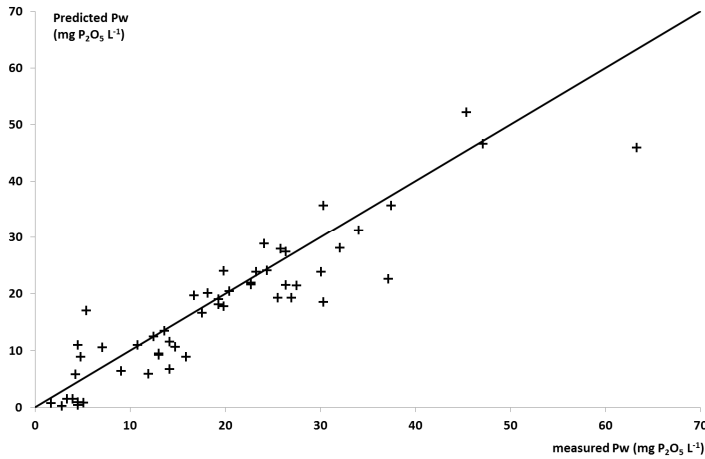
Figure 3. *Relation between predicted and measured Pw values.*

In many countries soil P tests are based on extractions with acid or alkali reagents rather than water (e.g., P-Olsen, P-CAL, PAL, P-Morgan). Nonetheless, a semi- deterministic approach can also be used with these extractants. This will be illustrated for the PAL value, which is used in the Netherlands as a soil P test for grassland. The PAL value is determined at a 1:20 soil/ solution ratio (w/v). About2.5 g of soil is shaken with 50 mL ammoniumlactate-acetic acid solution (pH 3.75) for a period of 4 h (Egnér et al., 1960). The PAL value is expressed in mg P kg^{-1} soil (substituting for mg P_2O_5 100 g^{-1} soil as the standard agricultural unit). This ammoniumlactate-acetic acid solution will extract part or all of the amount of reversible sorbed P (Q) and a part of the initial amount of diffused P (S):

$$PAL = M_p \left(\varepsilon_o \, Q_o + \varepsilon_1 \, S_o \right) \tag{13}$$

where M_p = mol mass of P = 31 (mg mmol^{-1}), and ε_0, ε_1 = factors between 0 and 1 (proportions) (-).

The ability of an extractant to release P from the pools Q and S will depend on the characteristics of the soil sample (e.g., amount of oxalate-extractable Al and Fe, pH, organic matter content). The data set of Schoumans et al. (1991) was used to determine the influence of these factors on the amount of P extracted with the PAL method. For non-calcareous sandy soils, the values of ε_0 and ε_1 depended mainly of the amount of oxalate-extractable Al and Fe, and the following linear functions were derived:

$$\varepsilon_o = 1.704 - \frac{23.28}{(Al + Fe)_{ox}} \tag{14}$$

$$\varepsilon_1 = \frac{15.268}{(Al + Fe)_{ox}} \tag{15}$$

If both functions (Eq. [14] and [15]) are substituted in Eq. [13], the semi deterministic model predicts the PAL value with a percentage of variance accounted for of 96.5%. Figure 4 shows the relationship between predicted and measured values.
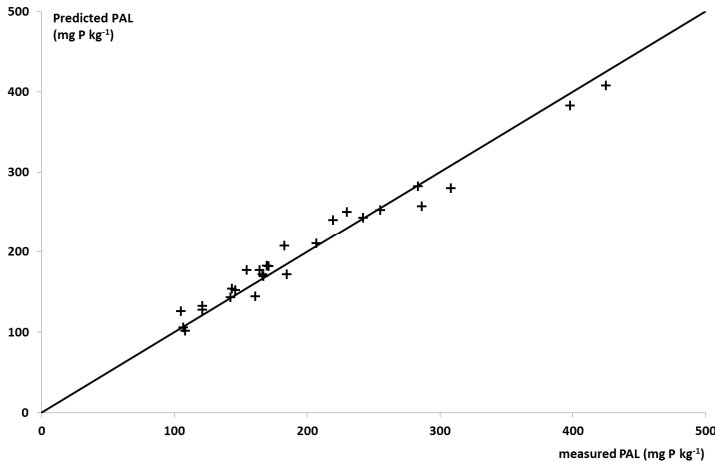
Figure 4. *Relation between predicted and measured PAL values.*

Use of soil phosphorus tests for environmental purposes

If Eq. [2] is substituted in Eq. [12] a relation is derived between the Pw value of a soil layer and the P equilibrium concentration in soil solution of the observed layer (e.g., topsoil layer: 0-0.20 m; Fig. 5). In Figure 5 the parameter values of non-calcareous soil samples are used. In this case the P equilibrium concentration of the soil solution depends on the amount of oxalate-extractable Al and Fe of the layer. The range of Al_{ox} + Fe_{ox} content in tillage layers of non-calcareous acid sandy soils varies from about 50 to 110 mmol kg^{-1}; accordingly this range has been used to calculate the P equilibrium concentration. Sibbesen and Sharpley (1997) illustrated concave relationships between amount of dissolved P relative to P test values of Olsen P and resin P for seven Danish soils. Soil P desorption to water was determined at a water/soil ratio of 50 L kg^{-1} after a reaction time of 3 h. The soils, ranging in texture from coarse sands to fine sandy loams, had a varying P status within each soil. For each of the seven Danish soils different concave curves were determined. The results indicate that the potential for release of dissolved P from soil increases disproportionately with increasing soil-P status. The concave relationships of the seven soils were closer to each other when related to resin

P than to Olsen P. As a result of the different concave relationships between the seven Danish soils, differences in soil chemical characteristics of the soils (such as Al_{ox} and Fe_{ox}) and their effect on P loss from the topsoil (leaching and runoff) are probably also relevant under these circumstances.
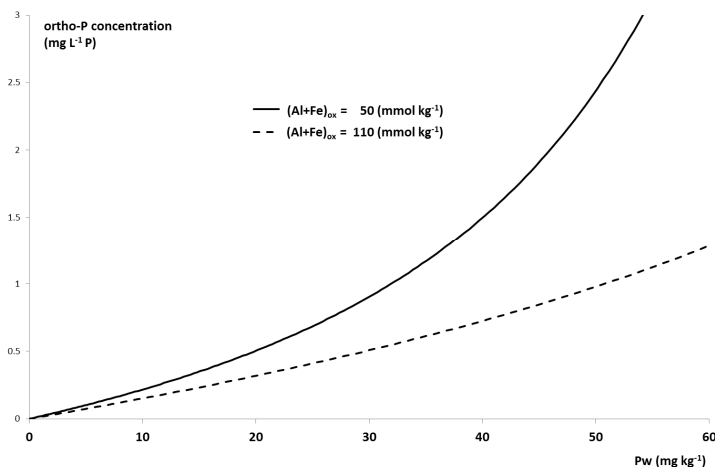
Figure 5. *Ortho P equilibrium concentration in soil solution as a function of the Pw value (upper and lower boundary calculated at $Al_{ox} +Fe_{ox}$, value of 50 and 110 mmol kg^{-1}, respectively).*

These results show that critical soil P test values, as an indicator for environmental impact such as P leaching, can only be derived if besides hydrological characteristics (e.g., net precipitation surplus); also, the relevant soil chemical characteristics are taken into account (e.g., in non-calcareous sandy soil the content of Al_{ox} and Fe_{ox}). In the definition of a P-saturated soil, the value of 0.1 mg L^{-1} P should not be exceeded at the highest ground water level. If leachate concentrations from the topsoil (e.g., 0-0.20 m) are continuously more than 0.1 mg L^{-1} P as a result of high soil P test values, the P concentrations in the subsoil will also increase to this value in the long term. In flat areas with shallow ground water, P leaching is one of the major reasons for the contribution of agriculture to enrichment of ground water and surface water. When the P concentration of the leachate of the topsoil (0-0.20 m) has to be reduced a mean concentration of 0.10 mg L^{-1} P, the Pw values must be reduced to 5 to 7 mg kg^{-1}. However, from an agronomic point of view these Pw values are classified as low soil P fertility. More destructive chemical soil P tests such as P-CAL, P-Mehlich, P-Joret-Hebert, and P-Morgan can probably be described by a function similar to Eq. [13], because these chemicals will extract a part of the amount of adsorbed and diffused P fractions. In this case, a critical soil P test value can be estimated if, not only information on the amount of oxalate-extractable A1and Fe is available, but on the amount of oxalate-extractable P

as well. From an environmental perspective, this soil P test (PAL) provide little additional information about pollution risk from agricultural land. Nonetheless, estimations can be made about reductions in soil P fertility levels of tilled land, which should be necessary to reduce soil P losses to an acceptable level.

Influence of phosphorus leaching on soil phosphorus levels

Annual leaching rates in Dutch agricultural non-calcareous soils has been calculated as a function of soil P levels by assuming a constant soil concentration and an excess rainfall of 0.3 m yr^{-1} (Schoumans, 1997). Oxalate-extractable A1 and Fe varies from 50 to 110 mmol kg^{-1}, which is quite common in the tillage layer of sandy soils. Losses of P by leaching vary from 1 to 2 kg ha^{-1} yr^{-1} P at medium Pw (17-23 mg kg^{-1}) to 3 to 10 kg ha^{-1} yr^{-1} P at high Pw values (43-57 mg kg^{-1}). However, it should be noted that the data have to be considered as a first approximation because daily variations in soil concentration and rainfall have not been included. Nevertheless, calculations by Van der Salm and Breeuwsma (1996) using the ANIMO model daily basis (Groenendijk and Kroes, 2000) yield similar results. It should be mentioned that in soils with very high P levels (Pw values > 85 mg P kg^{-1}), leaching rates from the topsoil increase significantly up to 4 to 18 kg ha^{-1} yr^{-1}, depending on the degree of saturation and P surplus (Groenenberg et al., 1996; Schoumans and Breeuwsma, 1997).

Losses of P by leaching or runoff lead to a decrease in the amount of reversibly adsorbed P (Q), which will influence soil P test values, although annual decreases in soil P test values are likely to be small. However, soil P test values may drop rapidly if losses by fixation (part of sorbed P is irreversibly bound P) and/or net immobilization (over a long time period) also occurs. Tunney et al. (1997b) summarized P losses by fixation and net immobilization in the topsoil at, respectively, 0 to 11 and 0 to 9 kg ha^{-1} yr^{-1} P (at optimum soil P level). In the ANIMO model (Groenendijk and Kroes, 2000), which was originally set up to simulate organic matter and N-related processes in agricultural soils, the P cycle has been included to describe the fate of P excess on agricultural land. Phosphate sorption is modeled by assuming an adsorption (Eq. [2]) and diffusion (Eq. [4]; fixation) process. Furthermore, immobilization of inorganic P (and mineralization of organic P) is related to organic matter dynamics in the soil. According to this model, four organic substances are distinguished: (i) fresh organic matter; (ii) root exudates; (iii) dissolved organic matter; and (iv) humus(dead soil organic matter and living biomass). The transformation of fresh organic material leads to the formation of a humus/biomass pool (assimilation). Depending on P availability, assimilation efficiency, and C/P ratio of the humus/biomass pool, organic matter transformations processes can result in a net production or net consumption of mineral P. In a study by Van der Salm and Breeuwsma (1996), results of the ANIMO model were validated on long-term field experiments at two sites [maize (Zea mays L.) and pasture]. In this study, net immobilization of P varied

from 0 to 9 kg ha^{-1} yr^{-1}. Habekotté et al. (1998) examined changes in soil fertility over the period 1989 to 1997 as a function of P balance (positive as well as negative) in 51 field plots. The sizes of all plots are about 1 ha. In field plots with a rotation of maize and grassland, losses by fixation and net immobilization were estimated to vary from 2 to 8 kg ha^{-1} yr^{-1} P, at Pw values of 14 and 57 mg kg^{-1} respectively (linear relationship; (Schoumans, 1998)). The influence of Pw values on these P losses by fixation and net immobilization is probably caused by differences in P concentration. At high soil P test values (Pw), the concentration will be higher and therefore, the diffusion of P into soil aggregates (fixation) will be greater than P diffusion at lower soil P test values. If environmental losses by leaching and losses by fixation and net immobilization are combined, the decrease of the soil P values can be predicted in time. Figure 6 shows the effect of a P surplus (P application - P in harvest) of 0.45 kg ha^{-1} yr^{-1} P on soil P values of the topsoil. A mean value of 80 mmol kg^{-1} is assumed for the amount of oxalate-extractable Al_{ox} + Fe_{ox} of the topsoil. A P excess of 0.45 kg ha^{-1} yr^{-1} is assumed because the maximum acceptable environmental P loss has been set to this value in the Netherlands. This environmental P loss has been calculated at a precipitation surplus of 0.3 m yr^{-1} and a maximum acceptable total P concentration of 0.15 mg P L^{-1} (approx. 0.10 mg L^{-1} ortho P). From an agronomic point of view, Pw values below 11 mg kg^{-1} are classified as low and Pw values above 34 mg kg^{-1} as high. From Fig. 6 it is concluded that in sites with moderate Pw values (14 mg kg^{-1}) the Pw value will decrease to the required lower soil fertility class within a period of 10 yr. However, most soils in the Netherlands have relatively high soil P levels (particularly in areas with intensive husbandry) and P leaching is a serious problem. In those areas it will take many decades before Pw values have been reduced to levels that are acceptable from an environmental point of view.
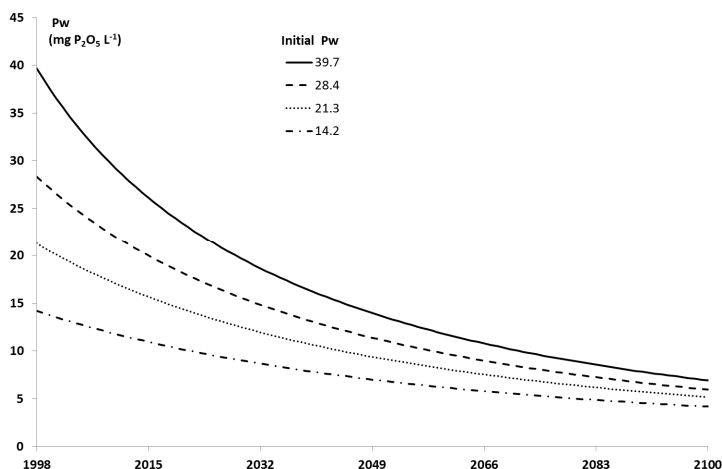
Figure 6. The impact of agricultural and environmental P losses on the decrease of the soil test P value Pw starting with different initial values.

Conclusions

In flat areas where P leaching and subsurface runoff is the major source of P losses from agricultural land to surface waters, the contribution of agricultural soils to the P losses of the surface waters is strongly influenced by P sorption and desorption kinetics of the soil. For non-calcareous sandy soils in the Netherlands it has been proved that the use of soil test P values as an indicator of pollution risk is possible, if the values are related to soil chemical P characteristics. For less destructive chemical soil P test methods, such as Pw and P_i an analytical equation can derived between soil test P values, P desorption parameters and equilibrium P concentrations in the soil solution. For more destructive chemical soil P test methods, such as PAL, additional information about the total amount of sorbed P is necessary. The use of soil test P as an environmental risk indicator has significant practical advantages because soil test data are widely available and their agronomic interpretation is well established. In addition to estimating actual P losses from agriculture, the impact of nutrient management strategies on the reduction of the P losses and soil P test values can also be predicted and evaluated. Simple model calculations showed that it will take many decades before high soil P levels in non-calcareous sandy soils have been reduced to levels that are acceptable from an environmental point of view.

CHAPTER 6

Description of nine nutrient loss models: capabilities and suitability based on their characteristics

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Abstract

In EUROHARP, an EC Framework V project, which started in 2002 with 21 partners in 17 countries across Europe, a detailed intercomparison of contemporary catchment-scale modelling approaches was undertaken to characterise the relative importance of point and diffuse pollution of nutrients in surface freshwater systems. The study was focused on the scientific evaluation of different modelling approaches, which were validated on three core catchments (the Yorkshire Ouse, United Kingdom; the Vansjo-Hobøl, Norway; and the Enza, Italy), and the application of each tool to three additional, randomly chosen catchments across Europe. The tools involved differ profoundly in their complexity, level of process representation and data requirements. The tools include simple loading models, statistical, conceptual and empirical model approaches, and physics-based (mechanistic) models. The results of a scientific intercomparison of the characteristics of these different model approaches are described. This includes an analysis of potential strengths and weaknesses of the nutrient models.

Keywords: diffuse pollution, nutrient losses, simulation models, catchments.

Introduction

The pollution of fresh water systems with nutrients is acknowledged as a major problem in many European countries because of the eutrophication of the surface waters. In order to implement the Water Framework Directive (2000/60/EC) many countries are concerned about this problem which is mainly caused by high P losses to the fresh water environment. Eutrophication also presents problems to the marine environment. Within the OSPAR (Oslo-Paris Commission for the protection of the northeast Atlantic) framework, a commitment was made in 1988 to achieve a 50% target reduction in nutrient pollution to the marine environment. To monitor performance against this target, between 1996 and 2000 OSPAR developed a series of nine "HARP" guidelines (Borgvang and Selvik, 2000) to assess the contribution of nutrient pollution of river basins from different sources. However, the contribution of diffuse nutrient losses caused by agricultural activities is not well understood compared to the contribution of other sources to the total nutrient losses. No single method for estimating diffuse losses from agricultural land to surface waters could be agreed upon, because of fundamental differences in the methodologies which have been developed in individual countries. One of the main criticisms in recent years concerns the lack of transparency and comparability in different model approaches that were used for policy support purposes. The EUROHARP project was developed to compare these different approaches across test catchments covering a range of different soils, land uses, hydrology and climates. EUROHARP is also of direct relevance to other policy drivers, including the Nitrates Directive (91/676/EEC) and Water Framework Directive (2000/60/EC), which require the identification and assessment of agricultural contributions to surface water quality, usually achieved through a combination of targeted monitoring and/or modelling studies.

Objectives

One of the major aims of the EU-project EUROHARP was to determine the performance and potential capability of different type of models. A scientific evaluation and a 'practical' test were set up to compare the effects of the models on the measured data of three core catchments. The major aim of this study is to describe, compare and evaluate, in a comprehensive scientific way, the models which are used within the EUROHARP project in order to provide end-users with objective information on the quality and applicability of the models. This paper provides an a priori overview (pre evaluation) of the main model elements as documented, and an intercomparison of the approaches used in relation to their potential suitability for modelling different catchment typologies for the implementation and evaluation of catchment management policies. The final scientific evaluation of the actual performance of each model is also published (Kronvang et al., 2009a; Schoumans et al., 2009b; Silgram et al., 2009a; Silgram et al., 2009b; Vagstad et al., 2009).

Methodologies

Several different types of models for nutrient losses to river basins have been developed during the last decade in European countries. Their approaches were established for different climatic regions and for different tasks (e.g. coarse "screening" tool for identifying high risk areas or detailed scenario tools for exploring management options), and they vary in their complexity, their resolution in time and space, and their input data requirements (Figure 1). In this article the term "model" usually covers a combination of specific models, (*e.g.* a hydrological model, a nutrient process model and a hydraulic model). The models used within EUROHARP (Table 1) range from spatially lumped static models to fully distributed process orientated dynamic models.
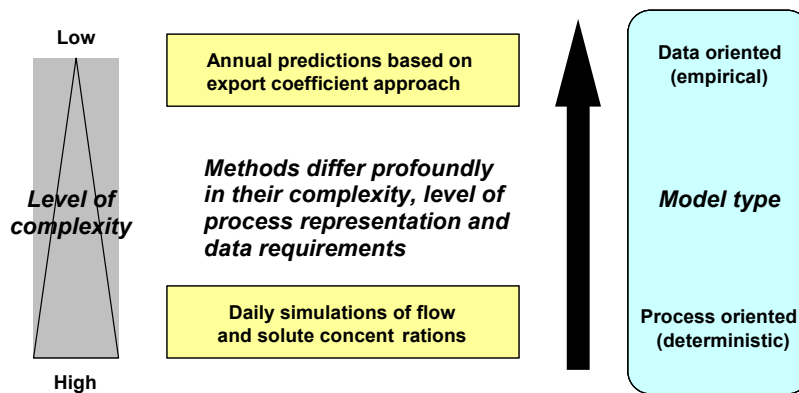
Figure 1. *A general relation between the complexity of models (left), model type (right) and the generated output.*

The reviewed modelling approaches are *examples* of different generic contemporary modelling solutions which can be used to predict nutrient pollution at catchment scale. Moreover, many models have only been applied within a relatively narrow climatic range of catchments in Europe, and may need further development or modification before they can respond to gradients in climate (e.g. frozen soils, water stress, temperature impacts on plant growth and soil nutrient cycling), hydrology (e.g. shallow groundwater), land use (new crop types) and/or agricultural practices in other parts of Europe. Problems with the acquisition of specific input data to the different models can also severely limit their application to different parts of Europe.

Table 1. *Models.*

No.	Name of the models and sub models including key references	Nitrogen (N) and/or Phosphorus (P) model
1	NL-CAT: ANIMO[b], SWAP[c], SWQN[d] and SWQL[e]	N, P
2	REALTA[a]	P
3	NLES-CAT[f]	N
4	MONERIS[g,h]	N, P
5	TRK: SOILNDB[i], HBV[j], HBV-N[k] and TRK[l,m]	N, P
6	SWAT[n,o,p]	N, P
7	EveNFlow[q,r,s]	N
8	NOPOLU[t]	N, P
9	Source apportionment (SA)[u]	N, P

[a] (McClure Morton, 2001); [b] (Groenendijk et al., 2005); [c] (Kroes and Van Dam, 2004); [d] (Smit and Siderius, 2005); [e] (Siderius et al., 2005); [f] (Simmelsgaard et al., 2000); [g] (Behrendt et al., 2003); [h] (Behrendt and Dannowski, 2005); [i] (Johnsson et al., 2002); [j] (Bergström, 1995); [k] (Pettersson et al., 2001); [l] (Brandt and Ejhed, 2002); [m] (Ejhed et al., 2003); [n] (Arnold et al., 1998); [o] (Di Luzio et al., 2001); [p] (Neitsch et al., 2001); [q] (Anthony et al., 1996); [r] (Lord and Anthony, 2000); [s] (Anthony et al., 2009); [t] (EEA, 2000); [u] (OSPAR, 2000)

Process-orientated dynamic models normally require large amounts of input data at a highly detailed temporal and spatial scale, but have the potential to provide dynamic response at a fine temporal and spatial resolution. In many cases, the required detailed input data may not be available, at least not for large catchments, which implies that a potentially large number of assumptions had to be made, and default values or transfer functions had to be applied. These problems can influence the model performance and require expert knowledge about modelling, especially with regards to the identification of plausible values or ranges for sensitive model parameters. This raises the issue of the associated difficulty of accurately identifying a large number of input parameters, many of which may be inter-dependent. Empirical and quasi-empirical approaches, *e.g.* in data oriented models, may in these cases be viable alternatives. Even in this category there is a large variability in complexity (Caraco and Cole, 1999; Grimvall and Stalnacke, 1996). However, many data based models have the limitation that they may not be able to describe dynamics in the modelled fluxes and the empirical functions may be limited to the specific catchment and climatic region in which they were developed. The trade-off between the complexity and applicability of these two approaches has been discussed (De Vries, 1994) and was an important consideration during the EUROHARP project. In recent years, initiatives have studied the linkage between more dynamic models and purely statistical ones. For example, Lidén et al. (1999) showed that the export coefficients from the Swedish HBV-N model (Arheimer and Brandt, 1998) were very similar to the export coefficients derived from the statistical MESAW-model (Grimvall and Stalnacke, 1996).

Nutrient models

A large number of nutrient loss models are used for research and policy support across Europe. Nine models were selected in the EUROHARP project as generic examples of the range of approaches used for estimating losses of nitrogen and phosphorus from agricultural land to surface freshwater systems in different European countries (Table 1). The approaches include: (1) NL-CAT (a combination of the models ANIMO/SWAP/SWQN/SWQL), (2) REALTA, (3) NLES-CAT, (4) MONERIS, (5) TRK (a combination of the models SOILNDB/HBV-N), (6) SWAT, (7) EveNFlow, (8) NOPOLU, and (9) Source Apportionment (SA).

The models 1, 5 and 6 require the largest number of data (highly process orientated). These models divide a catchment into unique combinations of land use, level of nutrient input, slope, soil type, hydrological situation/drainage system, and subsequently regard them as homogeneous areas. The location and area of each plot is known, and the model is applied to each plot. In the process-orientated tools, the dynamics of the fate of nutrient inputs in the soil are modelled in a (pseudo) two or three-dimensional way on a daily basis. All major biological and chemical processes that occur in soils are explicitly taken into account (e.g. volatilisation, mineralisation / immobilisation and phosphorus (de)sorption). Based on the representation of system processes, nutrient concentrations can be calculated (inorganic and organic components). Furthermore, the water flow, and overland particulate and nutrient flow is modelled (runoff, erosion, subsurface runoff/leaching) in order to assess the total nutrient load to surface waters. Model 5 supplies detailed process descriptions for a number of representative "type fields" with generalised parameterisations, and it subsequently transposes the results to all arable land after classification in a GIS. This reduces the input data demand. In model 5 the processes for phosphorus transport are only described for the topsoil, since runoff and erosion are assumed to be major sources of diffuse pollution in many catchments. The models 1 and 6 take all deeper layers into account separately, including the leachate from deeper layers to surface waters.

In contrast, models 3, 4 and 7 do not attempt a comprehensive representation of all individual system processes. Instead, they typically simulate nutrient losses by using a series of conceptual, (semi-)empirical or statistical functions and generally require less data (and hence time) as opposed to the demands of fully process based approaches, and therefore are potentially more readily applicable to catchment scale simulations (e.g. 10-3000 km^2). Such tools comprise parameters which may retain a physical basis (e.g. soil field capacity) or may use entirely empirical coefficients that have been found to reproduce observed field and river measurements in specific catchment typologies. These tools may include parameters such as nutrient load or surplus, soil nutrient

status, soil type, land cover, land use, and slope. Although such approaches usually have lower data demands than the highly process orientated models there are exceptions: for example model 3 requires the most detailed input concerning field activities and N-input of the nitrogen loss models compared to the other approaches in this study. In comparison, models number 4 and 7 explicitly model river flow entirely based on climatic input data (4 on an annual basis and 7 on a daily basis). Approach 3 requires river flow as input data, which limits the suitability for exploring specific instream river basin water management scenarios.

Models 2 and 8 relatively require low data input and can be described as balance approaches or risk assessment approaches. With respect to the balance approach (model 8) most of the complex bio-chemical reactions in soils are lumped into one retention coefficient for different types of soils and different levels of nutrient status. Nutrient losses by different pathways are often considered as a fraction of the nutrient input or related to the nutrient status of the soil. Finally, measured nutrient outlet loads are fitted to easily available geostatistical information and can be used to extrapolate losses under different conditions. The risk assessment approach (model 2), characterises risk areas within a catchment based on local circumstances (e.g. slope, soil type, crop type, fertiliser input). Each risk category requires surface water quality data in one specific area within the catchment, of which values can be extrapolated to areas with the same risk classification.

The source apportionment (SA) model (model 9) provides the simplest balance method to quantify diffuse nutrient losses and is one method currently included in the OSPAR HARP guidelines. In this model, diffuse nutrient losses are calculated by simply deducting all other sources and sinks from the total measured riverine load of nutrients. However, the SA method lumps all the uncertainty into the diffuse loss estimate of agricultural land, and does not characterise the spatial distribution of diffuse nutrient losses from agriculture across the catchment, because the application of the method is limited to the total catchment upstream of an existing monitoring station. The information on spatial distribution can be an important requirement for policymakers to support the targeting of mitigation measures at high and medium risk areas and for the development of abatement strategies, where Action Plans are to be designed in order to meet environmental targets (e.g. water quality and ecological status).

Finally, some of the 9 applied tools (model 1, 4, 5, 6, 7) are able to estimate retention of nitrogen and/or phosphorus in surface waters in order to reproduce nutrient loads and concentrations at a specific river gauging station. The complexity of describing the retention processes in the surface waters differs widely (Hejzlar et al., 2009). In models

2, 3 and 8 the retention is lumped together with other retention processes in soils. As a balance method, model 9 (SA) requires an estimate of net retention in the surface water system (such as OSPAR HARP guideline 9 or the approaches which are discussed elsewere (Hejzlar et al., 2009)).

Intercomparison

For the a priori intercomparison of the models 15 different assessment criteria have been established (Schoumans and Silgram, 2003):

(1) The original purpose/status and history of the model (maturity)

(2) The dependencies on previous models (scientific evolution)

(3) The reviews of pathways and processes described by the models

(4) A scientific description of the processes involved

(5) The spatial resolution and discretisation (horizontal and vertical)

(6) The temporal resolution and discretisation

(7) Forms of nutrient losses described by the model

(8) Data requirements

(9) The operational experience and skills requirement of users

(10) The participation in previous model comparison studies

(11) The sub-modules that can be independently checked

(12) An existing sensitivity analysis

(13) The cost indication (based on work load to set up and apply the model)

(14) The capability to evaluate nutrient and watershed management strategies (scenario analysis)

(15) The applicability to different catchment typologies (climate, land use, hydrology etc).

The synthesis of the intercomparison is presented in tables 2, 3, 4 and 5. Table 2 gives an overview of the discretisation of the models in space and time, the nutrientprocesses and pathways described by the different models.

Table 2. *Pathways and processes described by the models.*

Model pathway, process or characteristic	Model number								
	1	2	3	4	5	6	7	8	9
Spatial and temporal resolution of application									
Horizontal boundaries (km²); [Field (FD)]	1	10-15	FD	1; 50[1]	1	1	1	10-15	1
Temporal resolution of model output (Day, Year)	D	Y	Y	Y	D; Y[2]	D	D	Y	Y
Soil physical/chemical/biochemical processes									
N and P mineralization/immobilisation	Y	N	N	I	Y	Y	N	N	N
Linked to C cycle	Y	N	N	N	Y	N	N	N	N
Ammonia volatilisation	Y	N	N	I	Y	Y	I	N	N
Nitrification	Y	N	N	Y	Y	Y	I	N	N
Denitrification	Y	N	N	I	N	Y	I	N	N
P sorption/desorption	Y	N	–	I	N	Y	N	N	N
P precipitation	Y	N	–	N	Y	Y	N	N	N
Erosion (gross/net)	Y	N	N	I	Y	Y	N	N	N
1, 2 or 3D solute transport processes	1,3	N	N	N	1	3	1	N	N
Implicit lumping of N processes	N	–	N	Y	N	N	Y	Y	Y
Implicit lumping of P processes	N	Y	–	Y	Y	N	N	Y	Y
Pathways									
Overland flow	Y	N	N	Y	Y	Y	Y	N	N
Subsurface drainage									
- preferential	Y	N	T	N	N	Y	T	N	N
- matrix	Y	N	T	T	Y	Y	T	N	N
- tile drainage	Y	N	N	Y	T	Y	Y	N	N
- groundwater input / loss	Y	N	N	T	T	Y	N	N	N
- (S)hallow / (D)eep	SD	N	N	S	SD	SD	S	N	N
- Measured riverflow required as input	N	Y	N	Y	N	N	N	Y	Y
- in river retention of nutrients	Y	N	N[3]	Y	Y	Y	Y	N	N

If not defined in record: Y = yes; N = No; I = Implicit; T = Total or combined
[1]) Older versions operated at 50 km grid size; newer version of MONERIS is able to handle a 1 km grid size.
[2]) TRK produces daily output for water flow and nitrogen but annual output for phosphorus.
[3]) MONERIS river flow modelled on an annual base.

Spatial and temporal resolution.
The horizontal spatial resolution between the studied models increases from 0.1 km^2 to 15 km^2:
NLES-CAT < NL-CAT=SWAT = TRK < EveNFlow = MONERIS < NOPOLU = REALTA = SA

This classification reflects the original focus of the models' development, which ranges from field/farm studies (using models which have been subsequently generalised for upscaling purposes) to large river basin models. The models with a detailed spatial resolution are also able to describe large river basins, but in some cases a discretisation of the whole basin is necessary in order to limit the number of homogeneous areas (which are to be considered as a unique entity in the models) or the number of the studied catchments. Many models include discretisation routines or standard methodologies to divide the basin into homogeneous areas or sub catchments, based on available maps (geo-referenced input data). Assumptions made during the development of the model regarding (e.g. lumping of processes, input variable data) determine the smallest spatial unit for each model.

The models which model the fate of nutrients in soils have a lower vertical boundary which usually reaches at least to the water table. Models such as REALTA, NOPOLU and SA do not allow for soil/plant processes at all. REALTA uses a risk ranking system and NOPOLU uses an export coefficient for specific agricultural areas. NLES-CAT estimates the nitrate losses from the root zone, where nitrate is routed to surface waters through different pathways, which can be determined by a specific hydrograph separation technique.

With respect to the temporal resolution, all models are able to calculate annual nutrient losses from agricultural land to surface waters. The models SWAT, TRK, NL-CAT and EveNFlow have been specifically developed to predict the subannual nutrient losses to surface waters (daily loads and concentrations). These approaches are principally capable to explore the impact of changes in weather conditions, seasonal effects, or the impact of anthropogenic water management on the environmental losses from agricultural land during the year (modelling of peak flows, concentrations).

Hydrological pathways.
Modelling the water flow is often one of the most complex parts of many nutrient loss models. Moreover, the variations in flow are often correlated with wide variations in nutrient loads over time. An important limitation of four models (REALTA, NOPOLU, NLES-CAT, and SA) is that they are not able to quantify the water flow by different pathways by themselves. In some cases they require measured flow data for each of the pathways or combined information about the measured flows of these pathways. For MONERIS, the total river flow is calculated on an annual basis and subsequently

partitioned into surface runoff, tile drainage, urban runoff, groundwater, and interflow pathways. In contrast, the models NL-CAT, SWAT, TRK, and EveNFlow explicitly simulate the water flow on a daily basis. The Swedish model TRK (HBV) is the one approach which models in detail the effects of snow and snow-melt processes: in NL-CAT, EveNFlow and SWAT relatively simpler approaches are used.

Surface runoff.

In EveNFlow, the magnitude of surface runoff, as a proportion of annual rainfall, is estimated as a function of the mean rainfall intensity and topsoil air capacity (McClure Morton, 2001). The timing of surface runoff is determined by a dynamic version of the USDA-SCS curve number model, which has been constrained so that annual total surface runoff is equal to the runoff which is predicted by the Kirk equation. Surface runoff can also occur by saturation excess. Soil characteristics are used to estimate the mean proportion of effective rainfall that is lost as saturation excess surface runoff. The timing of this runoff is determined as a function of the catchment water store.

In SWAT the surface runoff is described by the USDA-SCS curve number model on a daily base. In NL-CAT runoff occurs in situations when rainfall intensity exceeds the infiltration capacity of the soil (defined by soil moisture conditions and soil hydraulic characteristics) and when the phreatic water level rises above the soil surface (such as in wet polder areas). When the water ponding exceeds a certain defined threshold level, surface runoff occurs according to a non-linear conceptual relation with the ponding depth. Furthermore, surface runoff is partitioned into overland flow and interflow. Within TRK, no distinction is made between surface runoff and root zone leaching from soils. The overland water flow component can be determined by a subroutine, based on either HBV groundwater conditions or the USDA-SCS curve number method.

Drainage volume.

Soil water balance and the water drained (drainage) through the soil to surface waters, are also described by the four models NL-CAT, SWAT, TRK, and EveNFlow.

For TRK, leaching occurs under circumstances when the soil moisture content exceeds the field capacity in the soil water balance. The primary hydrological unit in the semi-distributed HBV model are sub-basins, which are further divided into elevation zones with separate calculations of soil moisture. Percolation and drainage to surface water is calculated by means of a system of linear and non-linear groundwater reservoirs. The approach consists of one upper, non-linear, and one lower, linear, reservoir for each sub basin. These provide the components of the quick and slow (base-flow) components of the river hydrograph. Within EveNFlow leaching occurs under circumstances when the soil moisture content exceeds the field capacity value. The soil moisture content is

recalculated by a water balance for the soil system, with the amount of soil water increasing or decreasing based on net water input (precipitation minus actual evapotransporation minus runoff).

Within NL-CAT, the SWAP model solves the Richards equation numerically. The method takes into account the distribution with depth of the water retention curve and hydraulic conductivity. Preferential flow in macro-pores can be represented in considerable detail. Different types of drainage systems and water courses can be described by a linear relation between groundwater level and drain discharge. Drains can be defined as one of the drainage types, with the relation parameterised based on depth of drains and drainage resistance. In NL-CAT, the lower boundary of a field/plot consists of a boundary condition by which the influence of regional deep groundwater flow can be taken into account. For water flow the boundary condition can be a specific potential, a flux or a mixed condition and for solute transport the boundary condition is a concentration value.

The SWAT model does not solve the Richards equation but utilises a conceptual model for the soil water movement. SWAT separates the aquifer system into two different aquifer types (shallow and deep). Properties of the shallow aquifer, mostly defined by the user, determine the response of inputs to the deep aquifer that are subsequently considered to be lost from the system. Upward seepage and exchange with the vadose zone are also considered.

The NL-CAT soil moisture module describes the water movement through soil in considerable detail, including representation of macro-pore flow. The SWAT and TRK (HBV) models typically use semi-empirical relations to describe the percolation from the root zone to deeper soil layers.

Processes and modelled nutrient species.
One particular difference between the models that were tested in EUROHARP is presented in the way in which they describe biological and chemical processes.

The source apportionment (SA) method, REALTA and NOPOLU do not explicitly or implicitly take into account the specific internal soil processes. In the NLES-CAT model, which describes the statistical relationship between on the one hand nitrogen input, crop, soils, and climate characteristics, and on the other hand measured nitrate concentrations leaching out of the root-zone, the internal nutrient processes are implicitly accounted for. For all these four models (SA, REALTA, NOPOLU and NLES-CAT) soil processes are lumped and implicitly derived from measured monitoring data. In these procedures, direct extrapolation to other soil and climate or hydrological conditions may not be possible.

Within MONERIS the net balance between mineralisation and immobilisation is assumed to be negligibly small under all conditions. Furthermore, the net N surplus (input minus offtake) is assumed to be completely turned-over as dissolved inorganic nitrogen. The reduction of the nitrate concentration, due to denitrification, is a conceptual model based on comparisons of potential leachate concentrations in soils and observed average DIN concentrations in groundwaters for more than 300 German catchments with large gradients in hydrology, soil conditions and hydrogeological conditions. The procedure considers the residence time in unsaturated zones and in groundwaters and therefore needs to consider historical data on the nitrogen surplus. With respect to phosphorus, sorption and desorption processes are not explicitly considered. A general dependency between the P-saturation of soils and the P concentration in soil solution is applied for the calculation of the concentration of dissolved P of surface runoff. The P saturation of soils is estimated on the basis of long term P accumulation (sum of the P-surplus since 1950) in agricultural areas.

Within EveNFlow one particular module estimates the nitrate mass which is present in the soil at the onset of the winter drainage which is vulnerable to leaching. This calculation is based on empirical relationships between soil nitrogen supply and the nutrient balance under conventional cropping and grazing regimes (based on animal stocking densities and assumptions concerning manure management). A set of baseline coefficients has been derived for the UK for maximum potential N loss for each arable crop and for each category of livestock. EveNFlow uses a meta-model to estimate nitrate losses as a function of rainfall and soil water content in relation to these maximum potential nitrate losses.

The models SWAT, NL-CAT and TRK (SOILNDB) explicitly consider nutrient dynamics in soils (plant growth, mineralisation, immobilisation, denitrification, sorption, and desorption). In SWAT, for each process a lumped equation is used. TRK (SOILNDB) and NL-CAT are also comparable in their approach regarding nitrogen processes, which are described in more detail than in the SWAT approach. With respect to the mathematical description of the N processes, the differences are probably small due to the fact that both models are derived from detailed agricultural nutrient models. With respect to phosphorus, TRK has to be classified as an empirical (statistical) approach derived for Swedish conditions, because the sub-model SOILNDB is only applicable for nitrogen. In contrast, in NL-CAT the kinetics of phosphate sorption and desorption reactions are described in detail.

The level of representation of individual nitrogen processes in the soil decreases in the following order:

NL-CAT > TRK (SOILNDB) > SWAT>> EveNFlow = MONERIS > NLES-CAT > NOPOLU > SA

With respect to phosphorus the equivalent order is:
NL-CAT > SWAT >> MONERIS > TRK = NOPOLU = REALTA > SA

Cost indication.
The estimated time which the modelling institutes needed to apply their model to one new catchment (ca. 1000 km^2), assuming adequate input data were provided, varied from around 0.5 man-months up to 3 man-months per catchment per nutrient (N or P). Because computing power rapidly increases, the time that is actually necessary for running such models has become relatively unimportant, compared to the time it takes to prepare input datasets and identify model parameters (e.g. meteorological data, and summarise and analyse model output data.

For the nitrogen models, the anticipated time required increases in the order:
SA < NOPOLU < MONERIS < NLES-CAT = EveNFlow = TRK (SOILNDB) = SWAT < NLCAT

For phosphorus the total time input requirements increase in the order:
SA < NOPOLU = REALTA < TRK (P) < MONERIS < SWAT < NLCAT
So, SA, NOPOLU and REALTA are the least expensive models (in terms of time input, not necessarily in terms of data) while the NLCAT approach is the most expensive. This sequence also reflects the level of detail of the individual processes in each model.
The costs as well as the complexity of the models differ substantially. The suitability of a model for a particular application will depend on the purpose of the study (e.g. for identifying risk areas, detailed quantification of partitioning of losses from land, scenario analysis for mitigation options, etc.), the resolution (temporal and spatial), the quality (in terms of accuracy and precision of the model results and "cost-effectiveness"), the resource availability (data, time, funding), and a suite of factors dealing with catchment type, suitability to particular catchment types, implementation issues and evidence of satisfactory model performance for each individual catchment.

Restrictions for scenario analysis.
The potential suitability of the models (in terms of model formulation) for application into scenario analyses depends on the models' potential responsiveness to contrasting nutrient management strategies, land use changes, and hydrological measures.

With respect to scenarios dealing with nutrient management strategies, models which explicitly or implicitly consider agricultural practices such as land use and intensity of land use management (manure application, fertilisation) are potentially able to predict the impact of management strategies on nutrient losses to surface waters. All models (except model 9) are able to predict changes in nutrient losses due to changes in fertiliser application or the effect of livestock numbers.

In principle, the impact of water management strategies on nutrient losses from agricultural land to surface waters can only be determined by models which contain a hydrological component. Four of the nine models do not have an explicit hydrological module simulating river flow (REALTA, NOPOLU, NLES-CAT, and source apportionment) and are therefore not suitable for (independent) exploration of the effect of water management scenarios such as hydrotechnical measures (Table 3).

Applicability.
The potential applicability of the models has been considered as the most complicated question, because different criteria can be used to qualify the applicability, for example:

- Is the model valid for application under the specific catchment conditions?
- What are the temporal and spatial scales with which the model output has to comply, and which chemical species need to be modelled?
- What are the resource limitations (time and data costs) which may define a particular study (the models vary widely in their data input requirements and time needed for model application)?

The answers to these questions are clearly related to the different purposes of the application of these models, so no simple, single recommendation can be given. However, some guidance can be provided on the relative performance and costs (i.e. cost-effectiveness) associated with each of the different models when applied to a range of catchment typologies (Kronvang et al., 2009a).

The authors' assessments regarding potential applicability of models to different environments are presented in Table 5. The categories for climatic conditions entail subdivisions into the following regions:
- Northern Europe (NE): NO, SE, FI
- Mid Europe (M): DE, AT, SE, CZ., PL
- West Europe (W): GB, IE, DK, NL, BE, FR, LU
- Southern Europe (S): ES, IT, GR, PT
- Eastern and South Eastern Europe (SE): HU, SK, SI, RO, BA, HR, CS, BG, MD, UA
- North Eastern Europe (NE): EE, LV, LI, BY
Examples of the main characteristics of these regions are shown in Table 4.

Table 3. *Overview of the potential suitability of the models to assess the impact of nutrient losses from agricultural land to surface waters for different type of scenarios.*

Model	Nutrient Management	Land use Changes	Water Measures
EVENFLOW – N	o	+	+
MONERIS – N	+	+	+
MONERIS – P	+	+	+
NLCAT – N	++	++	++
NLCAT – P	++	+	++
NLES-CAT – N	+	o	–
NOPOLU – N	o	o	–
NOPOLU – P	–	–	–
REALTA – P	–	–	–
SA – N	–	–	–
SA – P	–	–	–
SWAT – N	++	++	++
SWAT – P	+	+	++
TRK – N	++	++	++
TRK – P	–	–	–

++	highly capable (e.g. dynamic effects on turnover are modelled)
+	capable (key processes are considered, at least in a lumped manner)
o	partially capable (e.g. only long-term effects assessed without recalibration)
-	not capable (model does not take account of management practices)

The slope for each landscape class is defined as follows:
- M: Mountainous slope > 10%
- H: Hilly 2-10%
- P: Plains 0-2%
- D: Deltas
- R: Riparian zone

Regarding the drainage conditions a subdivision is made between:
- R: Runoff / overland flow
- SS: Subsurface drainage
- AD: Artificial drainage (tile drainage)
- DG: Deep groundwater flow

The agricultural activity is defined as:
- I: Intensive: > 150 kg N/ha/y and/or > 10 kg P/ha/y
- M: Moderate: 50-150 and/or 0 - 10 kg P/ha/y
- E: Extensive: < 50 and/or < 0 kg P/ha/y

Table 4. Global climatic characteristics for the six European regions.

	N	M	W	S	SE	NE
Precipitation (mm/y)	300 - 3500	600 - 800	700 - 1400	400 -1800	500-800	550 -750
Average summer temperature (°C)	15	20	20	25	20	17-18
Average winter temperature (°C)	-5	0	5	12	0	-2
Period of frozen soils (months)	2 - 4	0 - 2	<1	0	< 1	3

Table 5. Potential suitability/applicability of the models different conditions within Europe.

	Climatic conditions						Landscape					Flow paths				Agricultural activity		
	N	W	M	S	SE	NE	M	H	P	D	R	R	SS	AD	DG	I	M	E
NLCAT - N	o	++	++	o	+	o	o	+	++	++	+	o	++	++	++	++	++	+
NLCAT - P	o	++	++	o	+	o	o	+	++	++	+	o	++	++	++	++	++	+
SWAT - N	o	++	++	+	+	o	o	++	+	o	+	++	++	++	++	++	++	++
SWAT - P	o	++	++	+	+	o	o	++	+	o	+	++	++	++	++	++	++	++
TRK - N	++	++	++	o	o	++	o	++	++	o	+	o	++	++	+	++	++	++
TRK - P	+	o	-/+	o	o	o	o	+	+	o	o	+	++	++	+	-	o	-
MONERIS - N	+	++	++	+	++	++	+	++	++	++	+	++	++	++	o	++	+	++
MONERIS - P	+	++	++	+	++	++	+	++	++	+	+	++	++	++	o	++	++	++
EVENFLOW N	o	+	+	o	+	+	+	+	+	-	-	+	+	+	o	++	++	o
NLES-CAT- N	o	++	+	o	o	+	o	+	+	o	o	-	-	-	-	++	++	+
NOPOLU - N	o	+	+	o	+	+	o	+	+	+	+	+	+	+	+	+	+	o
NOPOLU - P	o	+	+	+	+	+	o	+	+	+	+	+	+	+	+	+	+	o
REALTA - P	-	++	o	o	o	-	o	++	-	o	-	++	-	-	-	++	++	++
SA – N	+	+	+	+	+	+	+	+	+	+	-	+	+	+	+	+	+	+
SA – P	+	+	+	+	+	+	+	+	+	+	-	+	+	+	+	+	+	+

++	highly capable
+	capable
o	partially capable
-	not capable

111

Strength and weaknesses of the models.

It has been illustrated that none of the reviewed nutrient loss models appear to be ideally suited for application to all European catchments because of their wide range of specific soil, land use, climate, and hydrological conditions. This review also demonstrates that the EUROHARP models differ profoundly in their approach to predict the diffuse nutrient losses from agricultural land to surface freshwater systems. This is a reflection of differences in (i) their level of complexity, (ii) their representation of system processes and pathways, and (iii) their resource (data and time) requirements. The differences between modelling approaches are also a result of the original purpose associated with model development *i.e.* some models were intended as catchment scale screening tools, some for more detailed policy support work (such as pressure/impact assessments), and some were developed from detailed field scale models with a highly complex representation of soil-plant system processes. For example, the more complex process-orientated models like ANIMO (as part of NL-CAT), SOILNDB (as part from TRK) and SWAT originally have been developed for field or small homogeneous plots in order to assess the impact of nutrient management strategies under different conditions on the nutrients losses to the environment (nutrient accumulation in soils, nitrate concentrations in groundwater and nutrient losses to surface waters). The field-scale model NLES-CAT has a different history, as it was developed by comparing measurements of nitrate losses with local field characteristics (a statistical approach). Later on these models have been implemented in tools for regional/catchment applications and have become "data-driven" modelling tools. However, for large scale applications all these approaches use regional parameterisation which makes them suitable for scenario analyses at catchment scale.

In contrast, other less complex models (e.g. NOPOLU, REALTA) have been primarily developed at a large catchment scale to identify "high risk" areas within a catchment and estimate the magnitude of nutrient losses from those areas. These models do not attempt to predict changes in soil processes or interactions with the environment, but they do have the potential to provide an assessment of approximate changes in nutrient losses from agricultural land to surface water in a relatively cheap and fast manner. However, such approaches often need hydrological input data from other models or from flow measurements in order to be successfully applied which may limit their applicability in catchments with limited monitoring data.

Two models can be considered as medium complex models: MONERIS and EveNFlow. Both models have lumped representations of certain processes *e.g.* MONERIS assumes that the balance between mineralization and immobilisation is negligibly small. Compared to EveNFlow, the main processes which are lumped in MONERIS have been calibrated for a larger range of hydrogeological conditions and gradients in land use intensity, which explains the larger range of MONERIS applications (Kronvang et al.,

2009a). MONERIS has been developed especially for medium and large catchments/basins. Although MONERIS takes into account some soil processes, the model only calculates the total flow on an annual basis and only separates the different flow components over the same temporal scale. In contrast, EveNFlow uses a 1 km^2 spatial resolution and includes explicit representations of river flow (and hence concentrations and loads) on a daily basis, which permits the simulation of the frequency and timing of nitrate concentration peaks (e.g. for Nitrates Directive purposes) and seasonal effects (e.g. leaching/runoff of surface applied fertilisers or manures in the spring).

Conclusions

The final selection of a particular model for a particular catchment will depend on the intended questions, the data availability, the resource limitations, and the physical characteristics of the catchment in question (which limit the suitability of some models). The temporal resolution of the required output is likely to be a key factor in the identification of suitable models for specific policy support purposes. For example, under the EC Water Framework Directive (WFD), an annual time-step model may be sufficient as a "screening tool" for identifying high risk areas which are vulnerable to particular sources of diffuse pollution. In contrast, subannual models will be needed for determining the seasonal dynamics of eutrophication risk under WFD and for characterising the nitrate concentration dynamics (e.g. frequency of exceeding of threshold concentration) under the Nitrates Directive.

Since the models which were involved in the EUROHARP project vary widely in their complexity, degree of process representation, input data requirements, and temporal/spatial resolution, it is not possible to determine, a priori, the most suitable model for a particular application, although some broad recommendations can be given, considering:

(1) The precise aim of the study,

(2) The acknowledged limitations of specific model formulations,

(3) The quality, availability, time-step and record length of datasets needed for model parameterisation and performance assessment,

(4) Whether scenario analyses are required.

This a priori review of the mechanics of the different models tested in the EUROHARP project has provided a valuable overview of a representative cross-section of contrasting approaches adopted in contemporary modelling of nutrient pollution which may support catchment-scale policy in Europe. Further details of different model formulations are considered in greater detail in Schoumans and Silgram (2003) and in the reference source material cited in Table 1. One of the main criticisms in

recent years, originating from the political arena, has been about the lack of transparency and comparability of different model approaches used for policy support purposes. This review, together with the subsequent papers in this volume, has helped to overcome these issues and has promoted an exchange of scientific ideas which has led to the modification or refinement of several of these models during the course of the project, and has enabled a greater insight into the strengths and weaknesses and the potential suitability of different approaches for policy support across a range of catchment typologies.

In principle, the models with more complex levels of process representation and finer temporal and spatial resolution may be expected to have a larger potential capability to describe the dynamics and fate of nutrients in the soil-water system. Actual model performance of this cross-section of model types is reported elsewhere in this volume.[2-6] However, any potential for improved model performance (*i.e.* model outputs which match observations more closely, including perturbations in input data) must be tempered with the greater costs associated with the application of such models (due to input data requirements), and with the acute impact of the modellers' expert judgement and capability to identify the sensitive parameters in a particular study.

CHAPTER 7

PLEASE: A simple model to determine P losses by leaching

Abstract

Non-point phosphorus (P) loss from agricultural land to streams is caused mainly by overland flow and leaching. In many countries P-index methods are used to identify areas at risk of P loss to streams. In flat areas with shallow groundwater levels, where losses by leaching are important, these index methods have their limitations as leaching is often not described in detail. This paper presents a simple model to predict P loss at the field scale. This model called PLEASE (**P**hosphorus **LEA**ching from **S**oils to the **E**nvironment) is based on the well-known kinetics of P in soils and lateral water flux from soils to surface waters. PLEASE was applied using readily available information to a small catchment; a sensitivity analysis and comparison with two soil P indicators were done (soil P test and the phosphate saturation degree). The model predicted a total P load of 4187 kg P in the Schuitenbeek catchment. The result was also a predicted P discharge at the catchment outlet of 2973 kg P with account being taken of independent assessment of P retention in streams in the catchment (29%). This is comparable to the measured outflow (2770 kg P). The calculated P losses by leaching are highly sensitive to the soil Langmuir parameters, which means that it is important to determine the adsorption isotherm to obtain reliable estimated losses. The PLEASE approach has particular value compared to other soil P indicators for estimating actual P losses from agricultural land to surface water. These results suggest that PLEASE is a promising method for quantifying differences in P loss by leaching between fields within a catchment.

Keywords: phosphate, non-point pollution, kinetics, water flow, losses, surface water

Introduction

Non-point P loss from agricultural land to streams contributes substantially to the total transmission to the aquatic environment (EEA, 2005), resulting in pollution of streams and seas by nutrients with a consequential deterioration in biodiversity (Biggs, 2000; Smith, 2003). P losses from land occur due to transport by surface runoff and subsurface leaching through soil to surface waters such as field trenches and ditches, canals and small natural streams. Generally phosphorus enters aquatic ecosystems by erosion of soil particles during major storms events (Ernst, 1978; Daniel *et al.*, 1994; Sharpley *et al.*, 1994). However, in flat areas with shallow groundwater levels, P loss by leaching through soils contributes significantly to the phosphorus loads of streams (De Vries, 1975; Culley *et al.*, 1983; Heathwaite & Dils, 2000). Several approaches and models are used to estimate P loss from land to streams and these differ in complexity as well as in data requirements (Radcliffe *et al.*, 2009; Schoumans *et al.*, 2009). Often P indices are used to calculate the relative contribution of fields to P loads of streams (Eghball & Gilley, 2001; Sharpley *et al.*, 2003; Sharpley *et al.*, 2008). These methodologies focus mainly on P losses by surface runoff as the contribution of P loss by leaching is difficult to predict.

In the 1980s a simple risk indicator, the Phosphate Saturation Degree (PSD) of soil (Van der Zee, 1990; Van der Zee *et al.*, 1990; Van der Zee & Bolt, 1991; Schoumans, 2000) was developed to delineate potential source areas for increased P leaching. The PSD is an indicator of potential risk and gives no information on actual P loss to groundwater or streams. However, often such indicators are used to relate measured P loss to soil P levels and soil properties by statistical inference (Cox & Hendricks, 2000; Hooda *et al.*, 2000; Eghball & Gilley, 2001; Simard & Beauchenmin, 2002; Davis *et al.*, 2005; Vadas *et al.*, 2005). In this study a simplified process-oriented approach is developed to assess directly actual P loss by leaching at a field scale. This approach takes into account soil P kinetics which were used also to derive the Phosphate Saturation Degree and water flow from fields to streams.

Methodology

P loss by leaching from a field are mainly determined by the P sources (recently applied P and the P content of the soil which determine the total P concentration in the soil solution), rainfall intensity and duration (water sources) and drainage characteristics of the field which influence water flow within a field. In this study the focus is on fields on flat landscapes with shallow groundwater levels. As phosphorus accumulates in top-soil (Beek *et al.*, 1977, Schoumans, 2004; Walvoort *et al.*, 2011), leaching losses from deeper aquifers to local drainage systems are very limited.

Water flow is mainly horizontal since the ratio between field size and drainage length is much greater than depth of drainage in the saturated zone, (Kirkham, 1958; De Vries, 1975). As a result the amount of P leaching from a field to streams is determined

simply by the profile of average soluble total P concentrations in the soil during the year as a function of depth ($C(z)$) and the profile of horizontal total groundwater outflow from a field to the adjacent stream during the year as a function of depth ($J(z)$).

$$P_{loss} = \psi \int_{0}^{z} C(z) \bullet J(z) \, dz \text{, where} \tag{1}$$

P_{loss} = total annual P loss	(kg ha^{-1} yr^{-1})
$C(z)$ = phosphorus equilibrium concentration at depth z	(kg m^{-3})
$J(z)$ = annual lateral water groundwater outflow at depth z	(m yr^{-1})
Ψ = conversion factor from kg m^{-2} to kg ha^{-1} P = 10000	

The method for determining profiles C and J are described below.

Determination of the soluble P concentration profile

Measurement of the P concentration in a soil solution in the field as a function of depth is time consuming. Lysimeter cups have to be used or the soil has to be sampled and centrifuged to obtain soil solution samples. The ortho-P concentration in the soil solution is buffered by the amount of accumulated P in soils, which is described by a fast reversible adsorption reaction at the surface of soil particles (Q) and a slow diffusion precipitation reaction into soil particles (S). The phosphorus in the S pool is strongly bound compared to the phosphorus adsorbed on the soil surface and is often considered as "irreversible bound P" (Barrow, 1983a; Barrow, 1983b; Van der Zee & Van Riemsdijk, 1986a; Van der Zee & Van Riemsdijk, 1986b; Van der Zee & Van Riemsdijk, 1988; Freese *et al.*, 1995). These studies show also that the distinction between reversible and irreversible bound P explains the well-known hysteresis effect of phosphate sorption and desorption. Instead of measuring the ortho-P concentration in soil solution the P equilibrium concentration in the soil solution can be calculated by the sorption and desorption characteristics using the Langmuir isotherm (Van der Zee & Bolt, 1991):

$$C = \frac{Q}{K\,(Q_m - Q)} \tag{2}$$

C	= P equilibrium concentration in solution	(mol m^{-3})
Q_m	= adsorption maximum	(mmol kg^{-1})
Q	= amount of adsorbed P	(mmol kg^{-1})
K	= Langmuir affinity constant	(m^3 mol^{-1})

For different soil types the Langmuir affinity constant and the P adsorption maximum (Q_m) can be determined or assessed from soil characteristics such as the oxalate extractable Al and Fe content ($Q_m = \beta\,(Al_{ox} + Fe_{ox})$) (Van der Zee *et al.*, 1987; Koopmans *et al.*, 2006; Schoumans, 2004).

The actual amount of reversible adsorbed P (Q) in soils is rather complex to determine using the iron impregnated method (Van der Zee *et al.*, 1987; Menon *et al.*, 1989). However, Q is very much related to the amount of water extractable P. In The Netherlands the amount of water extractable P, the Pw-value (Sissingh, 1971), is used commonly for fertilizer recommendations. It has been shown that such a water extraction in combination with soil characteristics can be related to the P equilibrium concentration in soil solution and the amount of adsorbed P (Schoumans & Groenendijk, 2000):

$$Pw = 137.42 \ C_e \left(1 - 0.9722 \ e^{- K \ k_d \ \beta \ (Al_{ox} + Fe_{ox}) \ (1 - \frac{K \ C_e}{1 + K \ C_e}) \ t_e \ \lambda } \right) \tag{3}$$

Pw	= Pw-value	(mg P_2O_5 l^{-1})
C_e	= P equilibrium concentration in soil solution	(mg l^{-1})
k_d	= Langmuir desorption rate	(d^{-1})
t_e	= extraction time	(d^{-1})
λ	= conversion factor related to the soil solution ratio of the experiment	

Due to the high phosphate sorption capacity of soil, the phosphate penetration depth is usually <0.5 m, even in areas where manure applications rates have been high for decades as The Netherlands (Beek *et al.*, 1977; Schoumans, 2004; Walvoort *et al.*, 2011). The phosphorus concentration as a function of depth (P concentration profile) may therefore be assessed by the Pw in the upper 0.5 m in combination with data on oxalate extractable Al and Fe. Two topsoil samples (layer 0 - 0.2 m and 0.2 – 0.5 m) are recommended for characterising the phosphorus soil profile. However, more layers can be distinguished if necessary, and also the stated maximum depth of phosphate infiltration (0.5 m) can be changed. The first layer, in this example 0 - 0.2 m, is assumed to be homogeneous due to soil tillage. If the Pw-value of this homogeneous layer and extractable Al and Fe are determined, the P equilibrium concentration (C_e) in soil solution (Equation 3) and consequently the average amount of adsorbed P (Q) can be calculated according to the Langmuir equation (Equation 2). At the top of the second layer (at 0.2 m) the soil is in equilibrium with the average P concentration leaching out of the first layer and the amount of adsorbed P at the top of the second layer ($Q_{2,T}$) can be calculated from Equation 2:

$$Q_{2,T} = \frac{K \ C_{e,1} \ \beta \ \overline{(Al + Fe)_{ox,2}}}{1 + K \ C_{e,1}} \tag{4}$$

$(Al + Fe)_{ox}$ = average oxalate extractable Al and Fe   (mmol kg^{-1})

Index 1 and 2 refer to the layer and the index T to the top of the layer.

In the second layer, in this example 0.2-0.5 m, the distribution of P is not generally homogeneous as this layer is not ploughed. Because phosphate is highly sorbed to soil, a rather sharp front can be expected in soil columns and lysimeters. However at the

field scale the front will become more flattened due to heterogenic flow processes and bioturbation. As a result, we assume that the amount of adsorbed P will reduce exponentially with depth (Beek et al., 1977, Walvoort et al., 2011) according to:

$$Q(z) = Q_T \; e^{\; -k\,(z-z_T)} \tag{5}$$

Q_T = amount of adsorbed P at the top of the observed layer (at z_T)   (mmol kg^{-1})
z_T = depth of the top of the observed layer   (m below surface)
k = exponential component   (m^{-1})

The exponential component k (Equation 5) can be derived by integration of Equation 5 over depth (Equation 6) and substitution of the required information:

$$\overline{Q_{z_1-z_2}} = \frac{\int_{z_1}^{z_2} Q(z)\,dz}{\int_{z_o}^{z_2} dz} = \frac{1}{(z_2-z_1)} \int_{z_1}^{z_2} Q(z)\,dz = \frac{1}{(z_2-z_1)} \frac{Q_T}{k} \left(1 - e^{-k(z_2-z_1)}\right) \tag{6}$$

For the second layer Q_T (Equation 5) is equal to $Q_{2,T}$ (Equation 4). The average equilibrium P concentration (C_e) in the second layer is calculated from the measured Pw-value and oxalate extractable Al and Fe in the second layer (0.2 m – 0.5 m), similar to the calculations for the first layer (Equation 3). Consequently the average amount of adsorbed P in the second layer $\overline{Q_{z_1-z_2}}$ is known (Equation 2) and the exponential component k can be derived. As a result the amount of adsorbed P over depth (Equation 5) and variation in P with depth (Equation 2) can be calculated. Other functions can also be used to describe the shape of the phosphate penetration front in soils (Equation 5).

The P concentration profile in the soil below 0.5 m (the third layer) is derived simply by (i) the adsorbed amount of P at 0.5 m ($Q_{3,T}$), (ii) the natural background equilibrium concentration of P in the deep groundwater at greater depth (a few metres) and (iii) the sorption capacity of the soil below 0.5 m. Since the P concentration at 0.5 m is equal to the calculated P concentration leaching from the second layer, the total amount of adsorbed P at both depths (z_2=0.5 m and z_L = lower boundary level) can be calculated based on the Langmuir equation. The value of k for this layer can be derived by using the equation which describes the exponential decline in adsorbed P with depth (Equation 5):

$$k = \frac{1}{(z_3-z_2)} \; \ln\left(\frac{Q(z_2)}{Q(z_3)}\right) \tag{7}$$

where $Q(z_2)$ = amount of adsorbed P at the top of the third layer in equilibrium with the concentration leaching from the second layer   (mmol kg^{-1})

and $Q(z_3)$ = amount of adsorbed P at the bottom of the third layer in equilibrium with the background concentration. $\qquad$ (mmol kg^{-1})

As a result the amount of adsorbed P with depth (Equation 5) and P concentration with depth (Equation 2) in the subsoil (layer 3) are known.

To calculate the leaching of total P, assumptions have to be made with respect to the relationship between inorganic P and total P in the soil solution. In the protocol for the phosphate saturation degree (PSD) a fixed ratio between the ortho-P concentration and t-P concentration is used (ratio 2:3). However, it is known that the variation is huge. Chardon *et al.*, (2007) report an exponential relationship between t-P and ortho-P concentrations based on soil solution measurements, drainage water and surface water. In our study this equation is used to calculate the t-P concentration profile with depth:

$$TP = 1.1 \cdot orthoP + 0.1 \cdot e^{-orthoP} \qquad (8)$$

t-P = total-P concentration (mg l^{-1})

orthoP = ortho-P concentration (mg l^{-1})

Determination of the horizontal water flux profile

In PLEASE water fluxes from the field to surface water are calculated using data on:
1. Net annual precipitation surplus
2. Annual Seepage fluxes (upwards or downwards)
3. Long-term upper and lower height of the groundwater during the year.

It is assumed that the sum of the annual net precipitation surplus and upward seepage (or minus downward seepage), for the soil layer down to 1 m below the drainage level of the deepest local drainage system (z_L), will be drained to local trenches and ditches. This annual water discharge (WD; m yr^{-1}) should be equal to the sum of the annual horizontal water fluxes (J(z):

$$WD = \int_{z=z_L}^{z=z} J(z)\, dz \text{, where} \qquad (9)$$

J(z) = annual horizontal water flux at depth z (m yr^{-1})

The annual horizontal water flux as a function of depth, *J(z)* can be derived from the distribution of drainage fluxes with depth and duration of the groundwater level at depth z during the year (*D(z)*).

As a result the lateral flux with depth becomes:

$$J(z) = \int_{z=z_L}^{z=z} \left(\frac{q_{dr}(z)}{z_L - z} \right) \bullet D(z)\, dz \qquad (10)$$

where

$q_{dr}(z)$ = total daily drainage flux from the soil to surface water at groundwater level z (over the whole depth z to z_L), (m d^{-1})

$D(z)$	= duration of the groundwater level at depth z during the year	(d yr^{-1})
z	= groundwater level	(m below surface)
z_L	= lower boundary of the profile.	(m below surface)

Lateral drainage flux as a function of depth ($q_{dr}(z)$)

At higher groundwater levels the water discharge (q_{dr}) from the field to ditches and trenches will increase. The lateral drainage flux at groundwater level z ($q_{dr}(z)$) can be derived from a piecewise linear relation between groundwater level and drainage rates (Ernst, 1978; Van Bakel, 1986) as described with Equation 11 and visualized in Figure 1.

$$q_{dr} = \left(\frac{\max(0, h_{d1} - z)}{r_1} + \frac{\max(0, h_{d2} - z)}{r_2} \right)$$

(11)

where

h_{d1}	= drainage level of the deeper drainage system,	(m below surface)
h_{d2}	= drainage level of the shallow drainage system,	(m below surface)
r_1	= drainage resistance of the deeper drainage system,	(d)
r_2	= drainage resistance of the shallow drainage system.	(d)
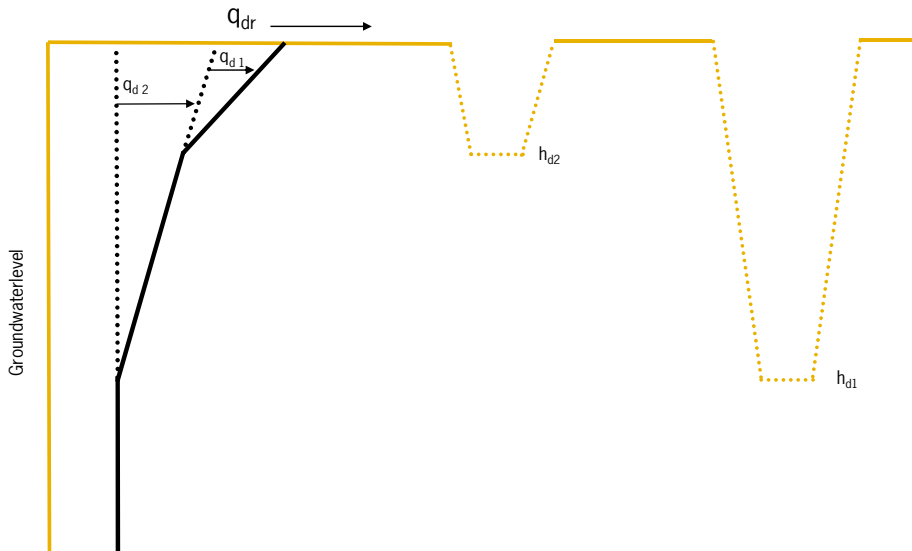
Figure 1. *Schematic illustration of the drainage flux (q_{dr}; m d^{-1}) as a function of groundwater level and two drainage systems (h_{d1}= depth of the local ditch; h_{d2} = depth of the local trench).*

Drainage levels h_{d1} and h_{d2} can be measured directly in the field (depth to the bottom of the ditches (h_{d1}) and trenches (h_{d2}) respectively, compared to the level of the surface of the field). The drainage resistance (r) can be assessed using the equation given by Ernst (1962) by summing vertical, horizontal, radial and entrance resistances. At the field scale, the radial and entrance resistance represent the major part of the total resistance r (Ernst, 1962) and therefore we can neglect the other terms, which result in a linear relationship between the resistance of the drains and their distance (L) respectively. ($r_1 = \kappa_1 L_1$) and ($r_2 = \kappa_2 L_2$). The data in Ernst's study (Ernst, 1978) result in a ratio of relative drainage resistance to rκ between κ_2 and κ_1 of 1.2 to 1.6 with an average of 1.4. The relationship for both drainage systems then can be given as:

$$r_1 = \kappa L_1$$
$$r_2 = 1.4 \kappa L_2$$

(12)

The κ factor is determined for each field by comparing iteratively annual water discharge (WD) with total horizontal water flux over depth (Equation 9). In order to solve Equation 9 data on the distribution of groundwater levels during the year (*D(z)*) are needed. Information of the groundwater level as a function of time is based on an equation describing the duration of the groundwater level at a certain depth (Van der Sluijs, 1982):

$$Gwl_D = \beta_{o,f} + \beta_{1,f} MHW + \beta_{2,f} MLW$$

(13)

where

Gwl_D	= depth of the groundwater level for the duration of T	
	month that the groundwater level is lower than this level	(cm below surface)
MHW	= mean highest groundwater level	(cm below surface)
MLW	= mean lowest groundwater level	(cm below surface)
$\beta_{o,f}$	= 8.9 + 1.025 D – 1.189 D^2 + 0.08882 D^3	
$\beta_{1,f}$	= 0.97 + 0.01333 D - 0.01583 D^2 + 0.00059 D^3	
$\beta_{2,f}$	= -0.23 + 0.1228 D	
D	= number of months that the groundwater level (Gwl) is below this depth (month)	

According to Van der Sluijs (1982) this relationship is valid for between 0.5 and 11.5 months. For each depth z the duration of the groundwater level (D) at this depth can be calculated (*D(z)*).

Since the relationship is only valid between 0.5 and 11.5 months (Van der Sluijs, 1982), an assumption has to be made for the periods each of 0.5 month duration that the groundwater level is very shallow or very deep. When the groundwater is very deep lateral water flux to the trenches and ditches is negligible. In very wet periods, when the groundwater level is shallow, overland flow and high lateral water fluxes through P enriched layers may occur resulting in high P loss. We assumed that in flat areas the

annual total lateral water flux under very wet conditions ($J_{0.5\ months}$) ranges from 5 mm in dry soils (MHW -> ∞) to 50 mm in wet soils with a MHW of zero (mean highest groundwater level at the surface of the field):

$$J_{0.5\ months} = 5.0 + 45.0\ e^{-0.015\ MHW} \tag{14}$$

$J_{0.5\ month}$ = total annual lateral water flow during 0.5 month of very shallow groundwater levels (very wet periods)   (mm.yr^{-1})

The coefficient -0.015 is based on the estimate that the runoff in moderately wet soils in The Netherlands (MHW of 40 cm) will be ca. 30 mm. Other parameters can be used depending on local precipitation.

Example of calculating P loss to streams

An example of applying the model to a typical wet grassland site is illustrated in Figure 2 using the parameter values in Table 1. The P concentration in the top layer (Figure 2) is constant and has a relatively high value (1.3 mg/l). The P concentrations reduce with depth below this layer because of the lower P status and the available phosphate sorption capacity. The precipitation surplus and the amount of upward seepage to surface water (trenches and ditch) is discharged in the zone between the upper groundwater level and 1 m below the lowest groundwater level. A large part of the drainage water flux is discharged from the deeper layers since these layers are permanently or for a large part of the year at these levels. The total annual lateral water flux from the field to streams decreases in the upper part of the soil as discharge from these soil layers is limited to wet periods. However, the lateral water fluxes increase again under very wet conditions, because at high rainfall intensities overland flow or shallow discharges through the plough layer may occur. It is the combination of the distribution of lateral water fluxes with the distribution of the P concentration that determines the distribution of the P fluxes to surface water. The highest P fluxes are in the upper 5 cm of the soil and these decrease gradually with depth (Figure 2).

Van der Salm *et al.* (2011) applied PLEASE to 31 sites and their results show that the model was able to predict accurately differences in P leaching between individual fields with a modelling efficiency of 0.92 for total P fluxes. In this study PLEASE was applied to a catchment to derive information on P loss, sensitivity of parameters and comparison with other approaches.

Table 1. *Model input parameters and values used in the example.*

Phosphorus status:		
Pw (layer 1)	80	mg P_2O_5 l^{-1}
$(Al + Fe)_{ox}$ (layer 1)	70	mmol kg^{-1}
Pw (layer 2)	35	mg P_2O_5 l^{-1}
$(Al + Fe)_{ox}$ (layer 2 and 3)	45	mmol kg^{-1}
P background concentration	0.05	mg l^{-1}
Hydrological information:		
Net precipitation surplus	257	mm yr^{-1}
Upward seepage	98	mm yr^{-1}
MHW	0.4	m below surface
MLW	1.1	m below surface
Parameters for the Langmuir equation		
K	35	m^3 mol^{-1}
β	0.167	(-)
k_d	0.2	d^{-1}

a

b

c
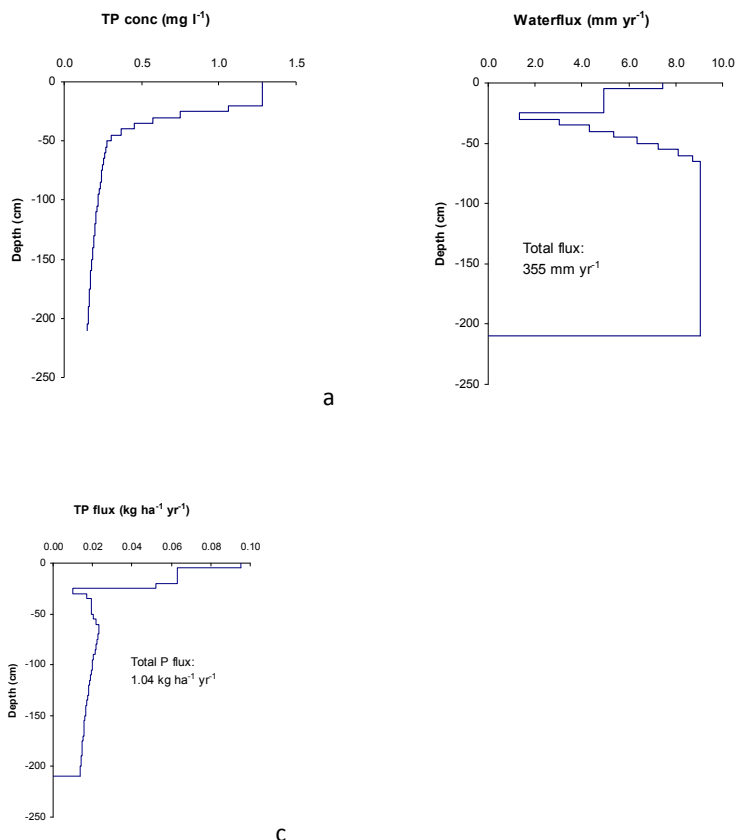
Figure 2. *Example of the distribution of the (a) total P concentrations (mg l^{-1}), (b) annual horizontal water flux (J; mm yr^{-1}) and (c) total P flux (kg ha^{-1} yr^{-1}) per 0.05 m layer.*

Application of PLEASE within a catchment

PLEASE was applied to a sub-catchment of Schuitenbeek (5030 ha) in the central part of The Netherlands in an area with sandy soils. About 70% of the catchment is in agricultural use, mainly grassland (80%) and the remaining 30% is forest and heather. In this catchment 260 sites were sampled using a stratified sampling technique (Breeuwsma *et al.*, 1989). For each site the amount of Al_{ox} and Fe_{ox}, and water extractable P (Pw) of the top soil layers (up to 50 cm) were measured. The average background concentration of P in the deeper layers (0.023 mg P l^{-1}) was derived from a national database of measured concentrations in deep groundwater (Rozemeijer *et al.*, 2005). The average Langmuir parameters (K and β) were derived from the relationships between measured concentrations and the amount of adsorbed P in 151 soil samples within the Schuitenbeek (Le Diot, 2008). The K and β values were 36.3 m^3 mol^{-1} and 0.085, respectively. The precipitation surplus for different crops was based on results from the national hydrological simulation model SWAP (Van Dam *et al.*, 2008; Kroes *et al.*, 2008). The amount of upward seepage was based on hydrological data for the catchment (Jansen *et al.*, 2006). The depth of the shallow and deep local drainage systems were set to the depth of MLW and MHW respectively. The distance between the trenches which were small depressions within the field for draining excessive precipitation was assumed to be 25% of the distance between the ditches which are used mainly for groundwater discharges (Ernst, 1978). The retention of phosphate in the streams of the Schuitenbeek catchment is 29% (Roelsma *et al.*, 2011). Application of the model to all 260 points gave a total P load of 4187 kg P. A P retention of 29% of P lead gave a predicted P discharge at the outlet of the catchment of 2973 kg P. This is comparable to the measured outflow (2770 kg P) of the stream during 1989-1994 when the soil samples were taken (Schoumans *et al.*, 2008).

Sensitivity analysis

In order to estimate the sensitivity of the calculated P loads for the Schuitenbeek, the effect of variation in the following input variables was considered: Langmuir affinity constant, phosphate sorption capacity, background P concentration, drainage characteristics and groundwater level characteristics. The impact of the Langmuir affinity constant (K) was assessed by changing the default value of 35 m^3 mol^{-1} to the 5% and 95% percentiles as reported for Dutch sandy soils e.g. 4 and 49 m^3 mol^{-1} (Pleijter *et al.*, 2012). The maximum adsorption fraction (β) in non-calcareous sandy soils was varied from 0.06 (5%) to 0.23 (95%) (Pleijter *et al.*, 2012). For background P concentrations the 25% and 75% percentiles of the measured P concentrations (c_3) were used, 0.006 and 0.046 mg l^{-1} respectively (Rozemeijer *et al.*, 2005). The MHW and MLW were increased or decreased by 0.1 m to account for uncertainty in the assessment. The depth of local drainage systems (h_{d1}) was assumed to be below the groundwater level for 6 or 9 months per year. The relative drainage resistance (rκ) was varied between 1.2 and 1.6 and Table 2 summarises the results from the sensitivity analyses.

Table 2. *Change in P load of the Schuitenbeek catchment due to changes in the main input parameters.*

Parameter	Change in P load (%)	
	Lower limit	Upper limit
Langmuir affinity constant (K)	21	-23
Maximum adsorption fraction (β)	39	-58
P background concentration (c_3)	-4	4
Groundwater level (MHW, MLW)	0	19
Depth of drainage systems (h_{d1})	1	5
Relative drainage resistance (rκ)	0	0
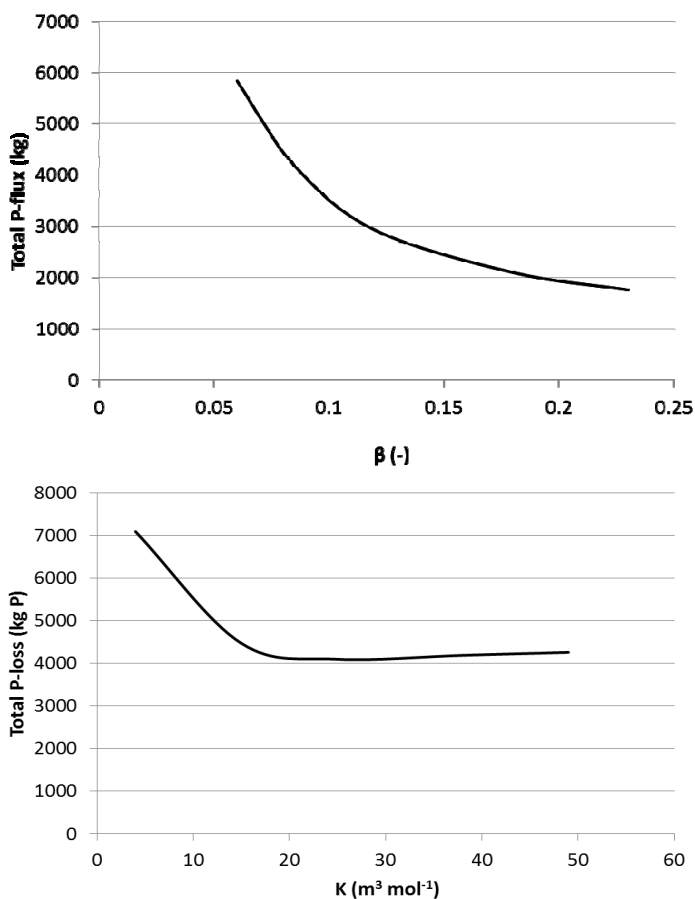
Figure 3. *The influence of the Langmuir parameters β and K on predicted P loss.*

The calculated P losses by leaching are highly sensitive to the soil Langmuir parameters. A decrease in the maximum adsorption fraction (b) resulted in a decrease in the phosphate adsorption capacity (Q_m) with an increase in P loss by 39%, while an increase would lower the P loss by 58%. The use of lower K values leads to an increase in P leaching by 21%, whereas a higher K value hardly influences P loss. Figure 3 shows the influence of both parameters on the predicted P losses from land to surface water in the Schuitenbeek catchment. An increase in b and K reduces P losses; however, the influence of the Langmuir affinity constant (K) is strong at K values up to 15 m^3 mol^{-1}. At higher values, the impact is relatively small with a minimum at 25 m^3 mol^{-1} occur. The increase is caused by fields with a high soil P status, where a higher K value leads to a much higher P concentration at the measured Pw values (equation 3). The influence of the uncertainty in the background concentration on the assessment of the total P loss was small (-4 to +4%). An increase or decrease in the groundwater level of 0.1 m (both MHW and MLW) increased or decreased the P load by 12% and 11%, respectively. Variation in the other parameters had a small or no effect on the predicted losses.

Comparison of PLEASE with methods to predict potential P losses
Soil P tests and the PSD are often used to estimate potential P losses to surface water (Cox & Hendricks, 2000; Hooda *et al.*, 2000; Eghball & Gilley, 2001; Simard & Beauchenmin, 2002; Davis *et al.*, 2005; Vadas *et al.*, 2005). However, these methods do not take into account hydrological information. The P losses calculated by PLEASE for the Schuitenbeek were related to the results from the soil P analyses and to the PSD to determine if these parameters could predict P loss with similar results which would give a 1:1 line. However, all relationships (Figure 4) were poor (R^2 = 0.062, 0.053 and 0.286 respectively). A specific value of the soil P test or PSD is related to substantial range of P losses as calculated by PLEASE. This suggests that the soil P test or the PSD are not accurate predictors of P losses. An important difference between the soil P test or PSD and the PLEASE model is that the hydrological aspects of P leaching are not taken into account, e.g. dry soils which have a high soil P status or phosphate saturation degree will have low leaching losses of P. Thus hydrological conditions seem to be important in determining actual P losses and not the soil P test value or PSD one. Similar conclusions have been made regarding the influence of hydrology on the assessment of P loss by surface runoff and erosion (Haygarth *et al.*, 2000).
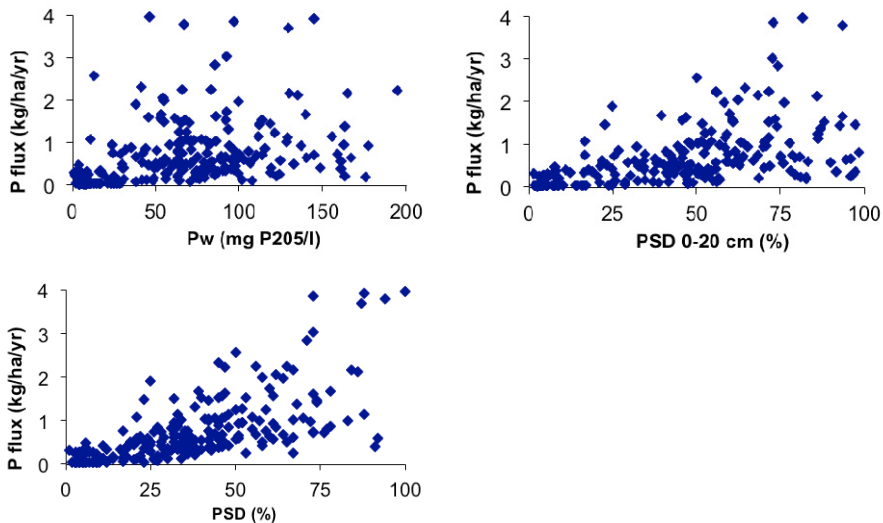
Figure 4. Relation between soil P characteristics and the actual P losses as calculated by PLEASE (soil P test Pw, phosphate saturation degree of the ploughed layer and phosphate saturation degree respectively).

Conclusion

In this study a simple model (PLEASE) is applied to assess the annual contribution of non-point P loss by leaching from agricultural land to surface water. The model calculates a phosphorus concentration profile on the basis of the P status of the soil, and a lateral water flux profile, which is based on the net water surplus, information of the mean highest and mean lowest groundwater depth, and the depth of drainage (trenches and ditches). The example shows that the method can be applied at the field scale and results can be aggregated to the catchment one. The simulated P from the land to Schuitenbeek was 4187 kg and the measured discharge value was 2770 kg and this included an independent calculation of P retention in the streams (29%). The result was a predicted P discharge at the outlet of the catchment of 2973 kg P. A sensitivity analysis of PLEASE parameters showed that the Langmuir affinity constant of the soil is one of the most important parameters with respect to the accurate assessment of total P loss. A comparison of PLEASE with other common methods for estimating potential P losses based on soil P tests or phosphate saturation degree (PSD), revealed a weak relationship between these indicators and the calculated P losses as these methods do not take into account differences in local hydrology. If such indicators are used to select fields with high P losses, mitigation measures might be applied to the wrong fields, because not all soils with a high soil P test or high phosphate saturation degree will lead to high P loss. On the other hand fields with a relative low soil P test or PSD can have

relative high P loss due to hydrological conditions. As a result, the PLEASE model approach seems to be a promising method for indicating differences in P loss by leaching between fields within a catchment.

CHAPTER 8

SIMPLE: Assessment of non-point phosphorus pollution from agricultural land to surface waters by means of a new methodology

O.F. Schoumans*, P. Groenendijk, L.V. Renaud & J. Mol-Dijkstra

Abstract

In the past, environmental phosphorus (P) parameters like soil P indices have been used to categorise the *potential* risk of P losses from agricultural land to surface waters. Assessment of actual risks of P pollution of groundwater and surface waters requires an approach that takes account of both sources and pathways. Dynamic process oriented soil and water quality models have been frequently used for such assessments, but they are data intensive and require high skills for successful application. Recently, an approximating model for phosphorus, called SIMPLE, has been developed that mimic the output from a complex dynamic water quality model by means of statistical relations to the most relevant input parameters that can be easily gathered from maps or soil survey. This simple meta model proves to be a powerful tool for quick assessment of the risk of P pollution from agricultural land to surface waters based on catchment characteristics.

Keywords: agriculture, modelling, phosphorus losses, surface water quality

Introduction

In many European countries, phosphorus (P) losses from agricultural land are seen as the main cause of eutrophication of rivers and lakes (Correll, 1998; Sharpley et al., 2000; Tunney et al., 1997b). The identification of risk areas ('hot spots') appears to be rather complicated because P loss from agricultural land depends on many factors, such as field position (slope, distance from surface waters), crop type, soil chemical and physical conditions and meteorological and hydrological situation. Depending on the local circumstances P loss can be transported to the surface water via runoff, erosion and leaching (subsurface runoff). In the Netherlands, the major transport route of P to surface waters at catchment scale is mainly caused by subsurface runoff (Groenendijk et al., 2013b; Oenema and Roest, 1998). Due to the facts that P is mainly transported through the soil to the surface waters, and that P is highly bound in soils, soil P parameters have become rather important as indices for P loss from agricultural land in the Netherlands (Schoumans, 1997; Schoumans, 2000; Schoumans et al., 1987; Schoumans and Groenendijk, 2000; Van der Zee, 1990; Van der Zee et al., 1989; Van der Zee et al., 1990a). In the early eighties only soil P fertility indexes were available and used to identify agricultural areas with a high P status. At the end of the eighties an environmental P index was developed, called the degree of phosphate saturation, which is defined as the ratio of the actual amount of P accumulated in the soil and the maximum phosphate sorption capacity of the soil (Chardon et al., 2000; Schoumans, 2000; Van der Zee et al., 1990a). The degree of phosphate saturation has been used to locate agricultural areas that are vulnerable from an environmental point of view (Breeuwsma et al., 1995; Breeuwsma et al., 1990; Breeuwsma and Schoumans, 1987; Schoumans and Chardon, 2015). Compared to standard soil P fertiliser tests, the degree of phosphate saturation is a better index for the risk assessment of non-point P pollution (Schoumans and Groenendijk, 2000). But in all these cases soil P indexes are still indexes of *potential P loss, i.c.* the hazard of P leaching at environmentally problematic concentrations.

The assessment of the *actual* risk of P losses from agricultural land is rather complex (Heathwaite, 1997) and therefore, sophisticated process oriented soil and water quality models are used (Boers et al., 1997; McGechan and Lewis, 2002; Neitsch et al., 2001; Nolan et al., 2005; Wolf et al., 2003). These models have several advantages, since they are very flexible and capable of describing the P losses from agricultural land to surface waters. Furthermore, they can describe the overall effect of nutrient and water management strategies on the changes in P losses. However, these models are rather complex. Dynamic modelling requires a large effort and a lot of input data, which are not always available (Radcliffe et al., 2009; Schoumans et al., 2009a). Therefore, a so-called meta model was developed, which is a simple approximation of a complex simulation model (Kleijnen and Van Groenendaal, 1992). It relates e.g. the predicted emissions from land to waters by means of the most relevant input

parameters that can be easily gathered from maps or soil survey. Meta models have been applied successfully in many studies in the Netherlands. The meta model that has been developed for phosphorus is called **SIMPLE**, which stands for "**S**mart prediction of the **I**mpact of **M**anagement strategies (nutrient and water) on **P**hosphorus losses by **Le**aching". The development of SIMPLE, its application on a national scale in the Netherlands and a sensitive analysis is presented and discussed in this article.

Material and method

Material

The input data and the results of the Dutch nutrient modelling approach to predict nutrient losses to groundwater and surface waters were used to derive the meta model. This model approach is used for national evaluations regarding the implementation of e.g. the Dutch Action Plans of the Nitrate Directive and River Basin management Plans (Boers et al., 1997; Groenendijk et al., 2012; Willems et al., 2007; Willems et al., 2005). The core is formed by the dynamic model ANIMO, which simulates the fate of nutrients in the soil and groundwater system. Figure 1 gives a schematic visualisation of the P cycle as described in the ANIMO-model.

The main soil related processes modelled in ANIMO are P mineralisation / immobilisation, crop uptake, adsorption / desorption, diffusion precipitation, precipitation/dissolution and leaching (incl. surface runoff) .

Depending on the assimilation ratio and the ratio between P content in parent fresh organic material and the P weight fraction of the humus/ biomass pool, mineral P will be released or incorporated.

Phosphate sorption is modelled by assuming a reversible adsorption reaction and a diffusion precipitation process. The Langmuir equation is used to describe instantaneous sorption of P to soil constituents, while the diffusion of P into aggregates, followed by precipitation, is described by a time dependent Freundlich sorption isotherm of three separate fractions (Schoumans et al., 1997; Schoumans and Groenendijk, 2000). Direct phosphate precipitation at high P concentrations (over saturation) is modelled as an instantaneous reaction when the P concentration in solution exceeds the pH dependent equilibrium P concentration. These precipitated P minerals dissolve immediately when the concentration of the water phase drops below this equilibrium concentration.
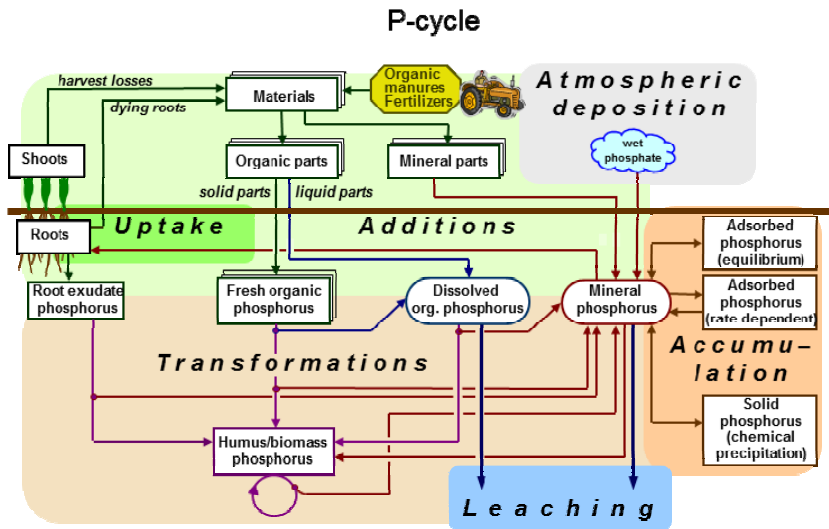
Figure 1. *Phosphorus inputs, pools, transformation and accumulation in the ANIMO-model (after Groenendijk et al., 2005).*

Phosphate uptake by crops is related to the P status of the soil and the actual P requirement of the plant. The P status of the soil is calculated according to Schoumans and Groenendijk (2000). The actual P requirement of the plant during the year is based on the difference between the potential crop production P requirements for maximum production and actual P content of the crop.

Based on nutrient fertilization of the soil and the water fluxes of the hydrological model SWAP (Van Dam et al., 2008), the ANIMO model calculates the *actual* amounts of different forms of P loss to the different water systems (trenches, ditches, brooks/rivers) within catchments and polders. This has been done on national scale for different national evaluations for Dutch Ministries (Boers et al., 1997; Groenendijk et al., 2012; Willems et al., 2007; Willems et al., 2005). Figure 2 shows the involved models and type of data used to assess the nutrient losses to groundwater and surface waters in the Netherlands on national scale. The model chain and data transfer is called the STONE (Wolf et al., 2003).

Annual P fluxes (kg ha^{-1}) for 6405 unique modelling units, so called plots, were computed for the period 1945-2045 with the ANIMO model (Groenendijk et al., 2012). A plot is a characteristic and unique combination of land use, level of nutrient inputs, soil type and drainage and seepage conditions. The long-term effect of different manure policies on the non-point P pollution was assessed by the mean value of the annual P losses calculated for the period 2031-2045 of each of the 6405 plots. This

period was selected because 15 meteorological years were used in the model runs and a stable state was reached by simulating the period until 2031-2045.
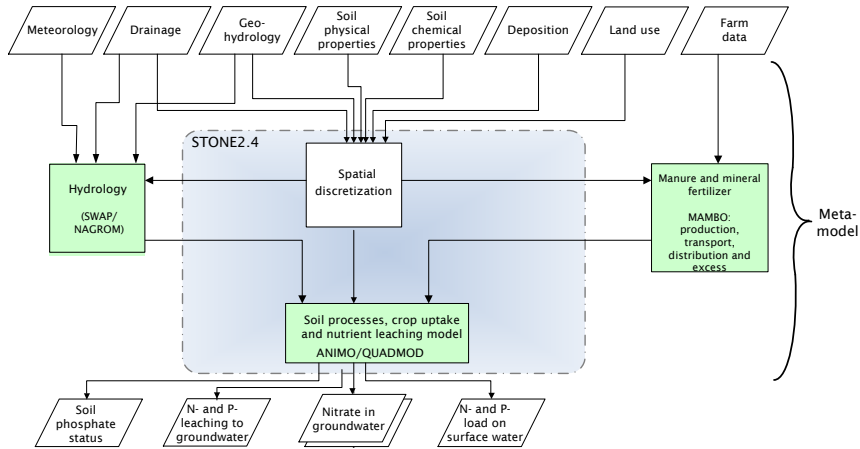
Figure 2. *Schematic visualisation of the data transfer and models used to assess nutrient losses to groundwater and surface waters in the Netherlands (Groenendijk et al., 2012).*

Method

The results of dynamic model simulations of the P losses from land to surface water of each plots as calculated by STONE are directly related to the input data of the model used for the plots. In this case P loss to surface waters under different circumstances, as applied in the latest national evaluation of the Dutch Manure Act (Groenendijk et al., 2012), is related to, amongst others, soil properties and land use (see figure 2). A non-linear multiple regression model was used to find the best-fitting relation between the model input variables, and the average annual P losses to surfaces in a period. Such a regression model between model output and model input is called a meta model (Kleijnen and Van Groenendaal, 1992). All unique modelling units (n=6405) were used to derive the parameters. In the P losses meta model only variables are used which can be rather easily collected in the field, derived from maps, or estimated. At first a multiple linear regression analysis was used, but after data analysis, a non-linear relationship (exponential functions) appears to be much better for two input parameters / factors, namely the influence of upward seepage ($P_{seepage}{}^{\tau}$) and mean highest groundwater level ($e^{\lambda * MHW}$). This observation leads to the following fitting procedure. First an objective function is defined as the sum-of-squared-errors (SSE) of the conditional linear meta model given λ and τ. Next, the objective function has been minimised for lambda and tau by means of the nonlinear optimization method (Nelder and Mead, 1965). This leads to optimal values for lambda and tau.

Given these optimal values, the conditional linear meta model can be fitted by means of ordinary least squares (OLS) to obtain the corresponding estimates of the other parameters in the model. A sensitivity analysis on some of the variables was carried out to get an expression of the effects on P losses to surface waters.

Results

The determined relevant factors to assess P losses from land to surface water are: (1) soil type, (2) land use (crop type), (3) mean highest ground water level (4) upward seepage quantity and quality, (5) net P surplus (P input minus P plant harvest), (6) amount of P accumulated in soils, and can be described by the following model equation:

$$^{10}\log (P_{loss}) = c_o + c_1[soil] + c_2[crop] + c_3[soil, crop] +$$
$$(c_4 + c_5[soil] + c_6[crop]) * e^{\lambda * MHW}$$
$$(c_7 + c_8[soil]) * P_{accumulation} + c_9 * P_{surplus}$$
$$c_{10} * P_{seepage}^{\tau} + c_{11} * J_{up}^{V} + c_{12} * J_{down}^{V} \qquad (1)$$

P_{loss}	= P loss to surface waters	(kg P ha^{-1} y^{-1})
c_i	= constant i	(-)
$c_i[s, c]$	= constant depending on combination of soil type and crop type	(-)
λ, τ	= exponential constants	(m^{-1})
MHW	= mean highest groundwater level	(m)
$P_{accumulation}$	= P accumulation in the topsoil (1 m)	(kg P ha^{-1})
$P_{surplus}$	= annual P surplus	(kg P ha^{-1} y^{-1})
$P_{seepage}$	= annual P input into the soil via seepage	(kg P ha^{-1} y^{-1})
J_{up}^{V}	= net seepage flux (upward)	(m y^{-1})
J_{down}^{V}	= net seepage flux (downward)	(m y^{-1})

In Appendix A the fitted regression coefficients are presented including statistical information of the significance of the coefficients (t-test and p-test values).The number of asterisks (***, **, *, none) represents directly the significances ($p < 0.025$, $0.025 < p \leq 0.05$, $0.05 < p \leq 0.1$ and $p > 0.1$ respectively). Based on the t-test values new groups of soil type and crop type or combinations of soil and crop type could have been defined to reduce the number of coefficients of the soils. This procedure has not been carried out because each time only one soil type or crop type or combination of both have to be selected and thereafter a complete new non-linear regression analyses have to be carried out which becomes very time consuming.

Figure 3 shows the relationship between the outcome of the meta model SIMPLE and the detailed dynamic model ($R^2 = 83.1\%$). At low P losses (10^{-2} kg P ha^{-1} y^{-1}) the relative differences are large, but the absolute differences are low and not relevant to locate areas with high P losses, so called 'hot spots'.
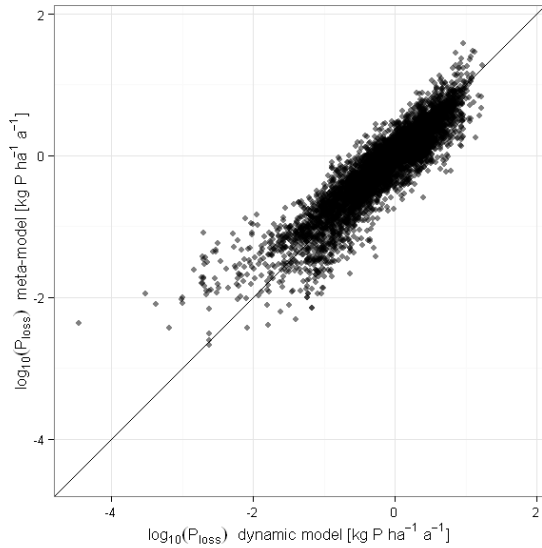
Figure 3. *Relation between P losses assessed by the meta model SIMPLE and results of dynamic modelling approach.*

In order to estimate the sensitivity of input parameters on the P loss from agricultural land to surface water, all input parameters have been changed separately on all 6405 plots. The P surplus was varied between plus or minus 20 P ha^{-1} y^{-1} as range of expected practical changes in P application rates The mean highest groundwater level (MHW) was changed from plus to minus 0.2 m and (e.g. as a result of more or less precipitation surplus). The other parameters were changed relatively in relation to the plot conditions. The changes in input parameters of the plots and the overall average effect on the P loss to surface water (sensitivity analysis) are shown in Table 1.

Table 1 shows that both the P accumulation in the soil as well as the annual P surplus on agricultural land are important driving forces for the P losses to surface water, but also the mean highest groundwater level (MHW) is an important factor. At high groundwater levels there will be frequently contact between groundwater levels and soil layers with a high P accumulation, and P leaching will occur from those layers to the surface water. The influence of upward seepage on P losses seems less relevant on a national scale.

Table 1. *The effect of changes in input variables for individual plots on the average percentage of changes in the predicted P loss from agricultural land to surface waters of all plots.*

	Change of input variable for individual plots			
P surplus (kg P ha^{-1} y^{-1})	-20	-10	10	20
MHW (m)	-0.2	-0.1	0.1	0.2
P accumulation	-50%	-25%	25%	50%
P seepage	-50%	-25%	25%	50%
J^v_{up}	-50%	-25%	25%	50%
J^v_{down}	-50%	-25%	25%	50%
	Average change in P loss of all plots (%)			
P accumulation	-19.8	-12.2	19.7	52.3
MHW	-18.3	-9.9	11.8	26.1
P surplus	-37.9	-21.2	26.9	61.1
P seepage	-6.2	-3.0	2.9	5.8
J^v_{up}	-0.9	-0.5	0.5	0.9
J^v_{down}	10.8	5.1	-4.5	-8.6

Figure 4 shows an example of an application of the meta model on the national scale for the Netherlands (left) and the *differences* with predictions of the original model (right). The same input data were used which were retrieved from geographic information systems concerning soil type, groundwater table, crop type, P manure and fertiliser rates, seepage and groundwater quality (Groenendijk et al., 2012).
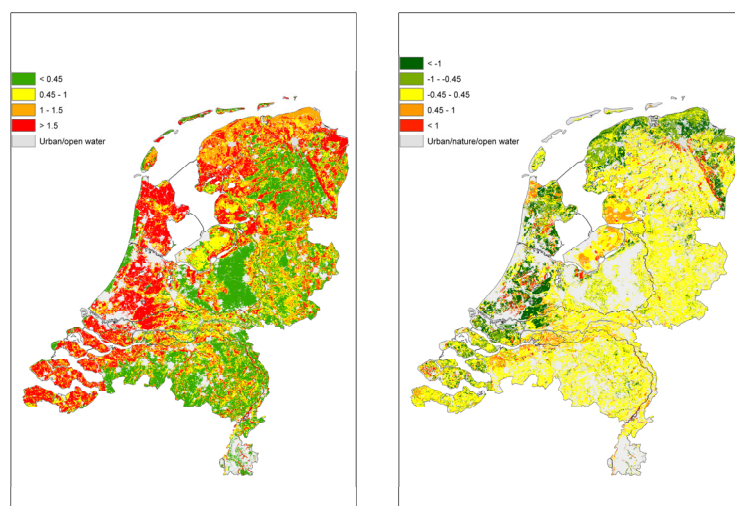
Figure 4. *Spatial distribution of the mean annual P losses (2031-2045) expressed in kg P ha^{-1} y^{-1} to the surface waters from agricultural land calculated by the SIMPLE meta model (left) and the differences between P loss estimated by SIMPLE and simulated by the dynamic model (right).*

High P loads to the surface water occur in the western part of the Netherlands and in some central, southern and eastern parts (figure 4). The central western part of the Netherlands is a peat polder area. In those areas high P and ammonium concentrations occur due to decomposition and mineralisation of peat under drained conditions. Furthermore, due to the reducing conditions Fe^{3+} is reduced to Fe^{2+} and P becomes more mobile (Hendriks and Van den Akker, 2012; Shenker et al., 2005; Van Beek et al., 2004), and consequently the P sorption capacity in the subsoil is low and sorbed P is highly reversible (Schoumans, 2013). In the North- and South-western part of the Netherlands, also polders, marine sediments (clay soils) are found, where high P concentrations are observed in the deeper groundwater (Groenendijk et al., 2013a; Groenendijk et al., 2013b) and sometimes also residual peat layers are observed in the subsoil. Especially, in situations which with substantial upward seepage fluxes additional P losses can occur.

The absolute differences ($kg\ P\ ha^{-1}\ y^{-1}$) between the results of the meta model and the dynamic model are relatively large in the western and northern part of The Netherlands (figure 4 right side; orange/red (estimated higher losses) and green colours (estimated lower losses)). Since, the green area is the dominated colour in those areas with high P losses (figure 4 right site), it seems that SIMPLE estimates lower P losses compared to the dynamic model especially in areas with high P losses. This is probably mainly caused by the log transformation used in the meta model and an upward shift of the regression line at low P losses (overestimation; figure 3) and consequently a downward shift of the regression line at high P losses. The difference between the SIMPLE estimates and the dynamic model at low P losses ($10^{-2}\ kg\ P\ ha^{-1}\ y^{-1}$; figure 3) is "oversized" due to the log transformation, but the differences are not relevant from an environmental point of view. In the sandy areas (southeast, central and eastern part of the Netherlands) with many vulnerable brooks, streams and lakes the match between the dynamic model and the meta model is much better. Although at low P losses the relative differences are large, but the absolute differences are low and not relevant to locate areas with high P losses, so called 'hot spots'.

Discussion

There are a number of advantages of using the SIMPLE meta model for the assessment of the *actual* risk of P pollution to surface water: (1) it is simple and can be used relatively fast as screening tool to locate P vulnerable soils/areas; (2) the simple relations focus us on the most important geographical data to be collected for the prediction of P pollution of surface waters; (3) in contrast to common regression analysis between monitoring data of P loss and characteristic geographical catchment data, meta models do not have the problem of lack of data, because simply different dynamic model runs can be used in order to produce data. However, a cautionary

remark on the application of such simple models should be made here. The reliability of the predictions of the meta model depends on the quality and validation of the process oriented model, the coverage of the (range of) input data in the original data set used for deriving the meta models, and the quality of the fit of the meta model. Application outside the input data range is of course not justified. Since this P meta model is based on a large number of typical Dutch situations it can, within these boundaries, be widely used to predict hot spot areas within catchments or other regions. Furthermore, if better regional input data is available, such as P accumulation or groundwater levels, also hot spots can be better localized with the same model description and parameters of the meta model.

The derived significant parameters of the meta model (Eq. 1), like soil type, land use, mean highest ground water table, upward seepage quantity and quality, net P surplus (P input minus P plant harvest) and amount of P accumulated in soils seems to be logical parameters. P losses by leaching are highly determined by the P saturation degree of the soil, which is defined by the ratio between the P accumulation in the soil and the P sorption capacity. The P sorption capacity of soils vary between soil types (Schoumans, 2013; Schoumans, 2014; Schoumans and Chardon, 2015), which explains the relevance of soil type in the meta model. Furthermore, P is often strongly sorbed in the topsoil, relative immobile and P leaching from the field to surface water is only possible if the groundwater has contact with the layers with P accumulation, therefore the mean highest groundwater level in the field is an important factor. Furthermore, the annual P surplus and the P flow in upward seepage water is important. The upward seepage concentration determines the base flow of P losses which can be large in some regions, e.g. with marine sediments in the subsoil and deeper layers. The net P surplus determines the increase of P concentration in the topsoil solution, or the decrease in P concentration at negative P surplus values. Finally, crop type is relevant because the net precipitation surplus differs between crops, determining the amount of P that is transported through the soil.

The model statistics (Appendix A) show the relevance (significance) of each parameter, which decreases in the order $P_{accumulation} >= P_{surplus} > MHW > P_{seepage} > J^{v}_{up} >= J^{v}_{down}$. This seems to be likely given the description of the P behaviour in soils as used in the dynamic model. The P concentration in soil solution is strongly determined by both the P content and the soil type (P sorption capacity). Increasing the P surplus will increase the P concentration in soil solution and large P losses can occur during wet periods by surface runoff and subsurface leaching. This also explains why the mean highest groundwater level is a relevant factor.

The P losses calculated by the dynamic model and the meta model are quite similar in large parts of the Netherlands (figure 3) especially in the sandy districts (central, south

and eastern part of The Netherlands). In the peat region (central western area) and clay region (along the Southwest and Northwest coast), the differences can be substantial. In those areas the largest P losses are calculated both by the dynamic model and the meta model. High P concentrations are found in those areas in the Dutch monitoring network of the surface water quality (Klein et al., 2012b). The absolute difference between the results of meta model and the dynamic model in the areas with large P losses is (probably) a consequence of the log transformation as used in the meta model. In fact, a log transformation gives also a good fit at high concentrations, but consequently, the mismatch can be huge after retransformation to the absolute P losses. This aspect needs more attention in order to increase the reliability of the model at large P losses. However, to locate hot spots the methodology of the meta model will still work under those conditions, but the estimated P loss is less reliable.

In the peat polders the large P losses are partly caused by manure and fertilizer applications. In those polders the whole area is intensively drained and decomposition of the peat is another important factor causing high P concentrations. The clay soils in the Southwest and Northwest coastal areas have also relative high P loads, which is related to the high P concentrations in marine sediments. However, in these areas, with mainly salt or salty groundwater and surface water, often nitrogen (N) is the limiting nutrient for eutrophication of the surface water. From that point of view there is less attention in the River Basin Management Plans on diffuse P pollution in those areas, but more attention on diffuse N losses. On the contrary, in the other parts of the Netherlands, mainly non-calcareous sandy areas with vulnerable fresh water systems, the focus is often on P. In this area the intensive animal husbandry is located and much of the excess of manure has been applied in the region. The largest P losses in the non-calcareous sandy districts are caused by high manure application on vulnerable soils with relative shallow groundwater levels (Breeuwsma et al., 1995).

The P losses calculated with SIMPLE change most remarkably if the P accumulation in the soil is changed, followed by the P surplus, mean highest water table (MHW) and upward and downward seepage fluxes (Table 1). These results of the sensitivity analyses are in line with the significance of the parameters as determined for the meta model (Eq. 1; Appendix A). Based on this model application it becomes clear which important parameters have to be collected in the region to locate hot spots and predict the diffuse P losses from agricultural land to surface waters.

Main purpose of the model: identification of risks for P-loads on surface waters, based on the consideration of both sources and pathways. But what about possibilities and limitations with respect to model applications for assessment of fertilization policy options?

Conclusions

In the Netherlands different methodologies have been used to assess non-point P pollution from agricultural land. In addition to simple agricultural (soil P tests) and environmental (degree of phosphate saturation) indexes to assess potential risk, also complex dynamic modelling approaches have been used to assess the actual risk of non-point P pollution. However, to apply a dynamic model many model input data are required. The use of a simple meta model, derived from a complex process oriented model, is cheap and especially suitable to detect 'hot spot areas' with high P losses to surface water within the catchment simply by using condensed information of land use, nutrient input, hydrological conditions and soil chemical conditions. Therefore, the SIMPLE model proves to be a powerful tool for a quick assessment of the risk of P pollution from agricultural land to surface waters.

Appendix A Parameter values of the model SIMPLE

Coefficients:	Estimate	t value	Pr(>|t|)	
(Intercept)	-9.33E-01	-4.632	3.69E-06	***
soil2	-1.43E-01	-0.602	0.547224	
soil3	-2.98E+00	-7.566	4.40E-14	***
soil4	-8.08E-01	-1.641	0.100859	
soil5	3.95E-01	1.851	0.064229	.
soil6	5.19E-01	0.772	0.440117	
soil7	-8.04E-01	-3.614	0.000304	***
soil8	-1.01E+00	-3.48	0.000504	***
soil9	-1.01E+00	-5.062	4.28E-07	***
soil10	-1.26E-01	-0.377	0.706193	
soil11	1.79E-01	0.788	0.430665	
soil12	-3.89E-01	-1.753	0.079623	.
soil13	-1.22E+00	-5.09	3.69E-07	***
soil14	-3.10E-01	-0.955	0.339811	
soil15	-1.18E-01	-0.576	0.564809	
soil16	-8.50E-01	-4.089	4.39E-05	***
soil17	-2.63E-01	-1.082	0.279453	
soil18	2.16E-01	0.851	0.394845	
soil19	-6.69E-01	-3.116	0.001839	**
soil20	-1.21E+00	-3.014	0.002591	**
soil21	4.24E-01	1.275	0.202238	
cropgras	-7.74E-02	-0.665	0.505986	
cropmais	-4.75E-01	-2.514	0.011976	*
cropnatuur	-2.90E-01	-2.32	0.020395	*
nl_MHW	5.62E-01	2.876	0.004045	**
P_accumulation	1.70E-04	13.238	< 2e-16	***
P_surplus	1.04E-02	8.646	< 2e-16	***
nl_P_seepage	2.81E-01	30.044	< 2e-16	***
Jv_up	8.34E-05	4.214	2.55E-05	***
Jv_down	-8.35E-04	-18.086	< 2e-16	***
soil2:cropgras	1.34E-01	1.32	0.18675	
soil3:cropgras	2.76E-01	2.211	0.027072	*
soil4:cropgras	8.79E-02	0.618	0.536696	
soil5:cropgras	-2.40E-03	-0.025	0.980016	
soil6:cropgras	4.39E-02	0.318	0.750526	
soil7:cropgras	-5.83E-02	-0.533	0.593884	
soil8:cropgras	1.55E-01	1.148	0.251052	
soil9:cropgras	-4.77E-02	-0.514	0.607119	
soil10:cropgras	-1.28E-01	-0.902	0.367161	
soil11:cropgras	7.05E-02	0.683	0.494674	
soil12:cropgras	-3.78E-02	-0.389	0.697023	
soil13:cropgras	2.65E-02	0.255	0.798684	
soil14:cropgras	-1.90E-01	-1.417	0.156467	
soil15:cropgras	8.00E-02	0.865	0.387042	
soil16:cropgras	3.27E-01	3.522	0.000432	***
soil17:cropgras	3.48E-01	3.54	0.000403	***
soil18:cropgras	2.66E-01	2.578	0.009963	**
soil19:cropgras	-1.16E-01	-1.225	0.220664	
soil20:cropgras	8.57E-02	0.531	0.595162	
soil21:cropgras	1.05E-01	0.728	0.466466	
soil2:cropmais	1.99E-01	1.092	0.274741	
soil3:cropmais	1.68E-01	0.783	0.433934	
soil4:cropmais	2.76E-01	1.059	0.289651	
soil5:cropmais	4.53E-01	2.579	0.00993	**
soil6:cropmais	4.17E-01	1.889	0.05895	.
soil7:cropmais	1.97E-01	0.632	0.527187	
soil8:cropmais	4.76E-01	2.293	0.021871	*
soil9:cropmais	3.86E-01	2.221	0.026373	*
soil10:cropmais	5.04E-01	2.637	0.008377	**
soil11:cropmais	4.69E-01	2.61	0.009071	**
soil12:cropmais	5.43E-01	3.074	0.00212	**
soil13:cropmais	4.20E-01	2.365	0.018081	*
soil14:cropmais	2.43E-01	1.008	0.313667	
soil15:cropmais	3.48E-01	1.958	0.050331	.
soil16:cropmais	1.60E-01	0.91	0.362894	
soil17:cropmais	3.41E-01	1.905	0.056805	.
soil18:cropmais	3.01E-01	1.606	0.108309	
soil19:cropmais	8.57E-02	0.488	0.625823	
soil20:cropmais	4.04E-01	1.858	0.063208	.
soil21:cropmais	5.92E-01	2.591	0.00959	**

Coefficients:	Estimate	t value	Pr(>|t|)	
soil2:cropnatuur	-2.76E-01	-2.389	1.69E-02	*
soil3:cropnatuur	7.72E-02	0.501	0.616303	
soil4:cropnatuur	-2.69E-01	-1.656	9.78E-02	.
soil5:cropnatuur	-3.34E-01	-3.011	0.002612	**
soil6:cropnatuur	-3.61E-01	-2.398	0.016492	*
soil7:cropnatuur	-4.85E-01	-3.656	0.000258	***
soil8:cropnatuur	-1.49E-01	-0.701	0.483639	
soil9:cropnatuur	-3.19E-01	-2.845	0.00446	**
soil10:cropnatuur	-7.32E-01	-3.037	2.40E-03	**
soil11:cropnatuur	-1.88E-01	-1.362	0.173175	
soil12:cropnatuur	-4.08E-01	-3.144	0.001677	**
soil13:cropnatuur	-2.15E-01	-1.485	0.13756	
soil14:cropnatuur	-5.27E-01	-2.401	1.64E-02	*
soil15:cropnatuur	-1.95E-01	-1.809	0.070523	.
soil16:cropnatuur	5.45E-02	0.501	0.616156	
soil17:cropnatuur	-1.13E-02	-0.099	9.21E-01	
soil18:cropnatuur	-1.26E-01	-1.049	0.294103	
soil19:cropnatuur	-2.76E-01	-2.494	0.012651	*
soil20:cropnatuur	-4.53E-01	-2.135	0.032812	*
soil21:cropnatuur	-4.44E-01	-2.29	0.022035	*
soil2:nl_MHW	6.74E-01	2.9	0.003743	**
soil3:nl_MHW	2.80E+00	6.834	9.06E-12	***
soil4:nl_MHW	9.48E-01	1.852	0.064117	.
soil5:nl_MHW	3.94E-01	1.908	0.056472	.
soil6:nl_MHW	9.67E-02	0.167	0.867421	
soil7:nl_MHW	1.51E+00	7.357	2.11E-13	***
soil8:nl_MHW	1.40E+00	5.716	1.14E-08	***
soil9:nl_MHW	1.82E+00	9.633	< 2e-16	***
soil10:nl_MHW	1.27E+00	5.651	1.67E-08	***
soil11:nl_MHW	2.16E-01	1.071	0.28433	
soil12:nl_MHW	1.10E+00	5.422	6.1E-08	***
soil13:nl_MHW	1.90E+00	8.453	< 2e-16	***
soil14:nl_MHW	1.41E+00	6.237	4.75E-10	***
soil15:nl_MHW	5.24E-01	2.536	0.011232	*
soil16:nl_MHW	3.72E-01	1.808	0.070709	.
soil17:nl_MHW	4.82E-02	0.193	0.846926	
soil18:nl_MHW	1.80E-02	0.066	0.94725	
soil19:nl_MHW	9.65E-01	4.505	6.76E-06	***
soil20:nl_MHW	1.79E+00	5.137	2.87E-07	***
soil21:nl_MHW	1.26E-01	0.515	0.606413	
cropgras:nl_MHW	-8.04E-02	-0.991	0.321913	
cropmais:nl_MHW	2.21E-01	2.567	0.010292	*
cropnatuur:nl_MHW	3.45E-01	4.475	7.78E-06	***
soil2:P_accumulation	-1.61E-04	-10.294	< 2e-16	***
soil3:P_accumulation	-6.13E-06	-0.302	0.763009	
soil4:P_accumulation	-8.49E-05	-2.204	0.027568	*
soil5:P_accumulation	-1.78E-04	-10.797	< 2e-16	***
soil6:P_accumulation	-1.95E-04	-6.64	3.41E-11	***
soil7:P_accumulation	-1.32E-04	-5.762	8.73E-09	***
soil8:P_accumulation	-1.41E-04	-4.854	1.24E-06	***
soil9:P_accumulation	-1.69E-04	-12.216	< 2e-16	***
soil10:P_accumulation	-2.39E-04	-9.165	< 2e-16	***
soil11:P_accumulation	-1.54E-04	-8.79	< 2e-16	***
soil12:P_accumulation	-1.82E-04	-12.139	< 2e-16	***
soil13:P_accumulation	-1.54E-04	-9.338	< 2e-16	***
soil14:P_accumulation	-1.95E-04	-6.195	6.2E-10	***
soil15:P_accumulation	-1.24E-04	-9.146	< 2e-16	***
soil16:P_accumulation	-6.67E-05	-4.915	9.12E-07	***
soil17:P_accumulation	-1.06E-04	-7.684	1.77E-14	***
soil18:P_accumulation	-1.33E-04	-9.201	< 2e-16	***
soil19:P_accumulation	-1.21E-04	-8.778	< 2e-16	***
soil20:P_accumulation	-1.83E-04	-6.457	1.15E-10	***
soil21:P_accumulation	-1.83E-04	-7.848	4.92E-15	***
tau	4.96E-01			***
lambda	3.94E-03			

CHAPTER 9

Mitigation options to reduce phosphorus losses from the agricultural sector and improve surface water quality: a review

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Abstract

The EU Water Framework Directive (WFD) obliges Member States to improve the quality of surface water and groundwater. The measures implemented to date have reduced the contribution of point sources of pollution, and hence diffuse pollution from agriculture has become more important. In many catchments the water quality remains poor. COST Action 869 was an EU initiative to improve surface water quality that ran from 2006 to 2011, in which 30 countries participated. Its main aim was a scientific evaluation of the suitability and cost-effectiveness of options for reducing nutrient loss from rural areas to surface waters at catchment scale, including the feasibility of the options under different climatic and geographical conditions. This paper gives an overview of various categories of mitigation options in relation to phosphorus (P). The individual measures are described in terms of their mode of action, applicability, effectiveness, time frame, environmental side-effects (N cycling) and cost. In total, 83 measures were evaluated in COST Action 869.

Keywords: diffuse pollution, water quality, phosphorus, nutrients, measures

Introduction

The role of an excess of nutrients phosphorus (P) and nitrogen (N) in the eutrophication of surface water was recognised in the mid-20th century (Redfield, 1958; Vollenweider, 1968). Among the negative environmental effects of eutrophication are reduced functioning and biodiversity of aquatic ecosystems and decline in surface water quality (Scheffer, 1998; Smith et al., 1999). The Harmful Algal Blooms (HABs) associated with eutrophication produce toxic algal substances that kill fish (Carpenter et al., 1969; Jaworski, 1981) and cause disease in animals (Kotak et al., 1994; Main et al., 1977) and humans (Falconer, 1989; Lawrence et al., 1994). Nutrient loads to waters must be reduced to control eutrophication.

The relative concentrations of total N and P together with bioassays have been used to estimate which of these nutrients is limiting the growth of algae in aquatic systems (Atkinson and Smith, 1983; Hecky et al., 1993; Redfield, 1958; Smith, 1983). For freshwater systems the indicative N:P weight ratios are ≤ 4.5 for N-limitation, 4.5-6 for intermediate conditions and ≥ 6 for P-limitation; the equivalent values for marine systems are respectively, ≤ 5, 5-10 and ≥ 10 (EC, 2002). In most freshwater systems P is the limiting factor and is the nutrient present in lowest amount in relation to phytoplankton requirements (Carpenter, 2008; Herath, 1997; Lee, 1973). By contrast, in marine systems, N has often been identified as the growth-limiting nutrient, especially in summer (Anderson and Glibert, 2002 ; Ärtebjerg and Carstensen, 2001). These findings should be interpreted with caution, however, as the N:P ratio may not correctly indicate the limiting nutrient of the system because of the role played by the absolute concentration and other factors such as light and physical conditions. Furthermore, the bio-availability of P can change over time due to redox processes, pH changes and enzymatically-mediated hydrolysis processes (Correll, 1998; FS13 Ekholm, 2008; Reynolds and Davies, 2001).

Since the mid-20th century, nutrient losses throughout Europe have been declining, partly as an epiphenomenon of processes such as industrial decline, but also because of targeted measures. Examples of the latter are increasing the number of homes connected to sewerage, introducing denitrification of N and precipitation of P in sewage water treatment plants, purifying industrial wastewater from industries and banning phosphorus in detergents. In many countries, P losses from easily identified and targeted point sources have been reduced. Yet despite these trends and the implementation of EU directives to reduce nutrient loads (EEC, 1991a; EEC, 1996; EEC, 2000), the water quality in many rivers, lakes and estuaries remains poor, largely due to diffuse pollution from land entering surface water systems (EEA, 2012b).

Nutrient losses from agriculture mainly enter water systems as a result of nutrients being transported by surplus runoff' as it flows over or under farmland. One of the most important pathways of P loss in hilly and mountain areas occurs when erosion

detaches soil particles during overland flow. In flatter or less hilly areas, the main pathways of phosphorus pollution to surface waters are leaching through the soil and artificial drainage (Chapman et al., 2005; Chardon and Schoumans, 2007; Grant et al., 1996; Heathwaite et al., 2005; Kronvang et al., 1997; Nelson et al., 2005; Ulén and Mattsson, 2003).

Organic or inorganic nutrient ions are transported by water flow, either in solution, associated with particles, or incorporated in microorganisms. In general, the amount of P bound to soil particles is much higher than the amount of bound ammonium. However, when organic particles are transported in dissolved form they carry more N than P, since the C:N:P ratio of soil organic matter is about 100:10:1 (Stevenson and Cole, 1999; Tilsdale et al., 1990). The concentration of soluble inorganic P in runoff water depends highly on the amount of adsorbed P. There is a good relationship between the amount of soluble inorganic P in surface runoff water and the soil P status of the plough layer (Allen et al., 2006), and in most cases there is a P enrichment of the fine eroded material (Schiettecatte, 2006). The magnitude of dissolved inorganic P losses by leaching seems to be strongly influenced by the phosphate saturation of the soil (Schoumans and Groenendijk, 2000; Van der Zee, 1990). The amount and composition of the soluble organic nutrients depend on factors such as the soil organic matter content, physical and chemical type of organic material, affinity of the nutrient to adsorb to the soil and soil pH (McDowell and Koopmans, 2006; Wilson and Xenopoulos, 2009). After manure or fertiliser applications, high nutrient concentrations can be found in runoff water (Allen and Mallarino, 2008; Smith et al., 2007), soil solution (Chardon et al., 2007; van Es et al., 2004) and tile drains (Schelde et al., 2006). These losses can generate high P fluxes and concentrations (Hahn et al., 2012; Preedy et al., 2001).

As significant P losses are known to occur via particles eroded from agricultural soils, soil erosion from arable land and grassland should be reduced. Since soil and crop management in the form of tillage strategies, application of soil conditioners, crop rotation, crop management and catch or cover crops directly impact on soil erosion, it is possible to reduce P losses by adapting these management strategies for this purpose in erosion-prone areas on arable land. On grassland, avoiding poaching by intensive grazing, and soil compaction by traffic are possibilities to reduce erosion (Newell Price et al., 2011). Clayey and silty soils are frequently important sources of loss of soil particles and attached P through erosion. Such soil types furthermore often demonstrate rapid water flow (preferential flow) via preferred pathways through a fraction of the soil pores (Jarvis, 2007), which enhances leaching of P through the soil profile and transport via tile drains. Soil and crop management strategies may also be adapted with the purpose of reducing this type of leaching loss.

A large proportion of arable land in north and northwest Europe has tile drainage: 30 % in UK, 40% in Denmark (Brown and Van Beinum, 2009), and over 90% in the clay/silty soil areas of Sweden and Finland (De la Cueva, 2006). The tile drainage systems channel water directly from farmland to streams and further to the sea. Reducing P transport from such drained agricultural fields will therefore effectively reduce the P transport in streams and the load on lakes and seas. Additionally, improvement of the actual drainage system may offer a possibility for reducing P losses under certain conditions.

The Water Framework Directive (EEC, 2000) obliges catchment management authorities of the EC Member states to improve the ecological status of surface waters by 2016 or at latest by 2027. When striving to meet the Directive's targets, the focus will be on reducing nutrient losses from agriculture, because this is becoming the main source of pollution. There is thus a need to have an overview of the options for reducing nutrient losses from the agricultural sector and empirically established effectiveness under different circumstances (Cherry et al., 2008; Withers and Haygarth, 2007). Focusing on P, here we give such an overview of mitigation practices that have been tested to varying degrees. Though the overview was conducted for Europe, it has relevance to regions elsewhere in the world where loss of P from farmland is an actual or potential problem.

Methods

From 2006 to 2011 the European Commission funded COST Action 869 in which 30 countries participated (Chardon et al., 2013). One of the main objectives was to undertake a scientific evaluation of the suitability and cost-effectiveness of different options for reducing nutrient loss to surface waters at river basin scale. This included reporting their limitations in terms of applicability under different climatic, ecological and geographical conditions. Based on information from literature and an inventory amongst participating countries, 83 measures were distinguished and grouped into eight categories: (a) nutrient management, (b) crop management; (c) livestock management; (d) soil management; (e) water management within agricultural land; (f) land use change; (g) landscape management and (h) surface water management. Each measure was described in a factsheet with the following sections:

- *Description*, including whether the mitigation effect targets P (or N).
- *Rationale, mechanism of action:* describes the mechanism to retain P (and N).
- *Relevance, applicability & potential for targeting*: describes under which conditions the option can be applied.
- *Effectiveness, including uncertainty*: estimates how effective the option can be, under which conditions it will be most effective and under which conditions it is least effective.

- *Time frame:* indicates if the option is assumed to be effective in the short, medium or long term.
- *Environmental side-effects / pollution swapping*: indicates unwanted effects in other environmental compartments.
- *Administrative handling, control:* describes the ease of applying and controlling the application of an option.
- *Costs:* since actual costs can vary greatly between and even within countries, only investment and maintenance costs are defined.
- *References:* the references given are preferably easily accessible, e.g. via a url.

All 83 mitigation measures are described individually on the website http://www.cost 869.alterra.nl/Fs/List_of_options.htm. The complete references, links and numbering of all factsheets are given in the Supplementary Material accompanying this paper. Many factsheets include information from other evaluation studies. Important sources of information included are (Cuttle et al., 2007; Newell Price et al., 2011), from the UK , (Schou et al., 2007) from Denmark and the SERA-17 group in the USA (SERA-17; http://www.sera17.ext.vt.edu/SERA_17_Publications.htm).

In order to structure the different types of mitigation options for reducing nutrient losses, a framework was created of systems influencing the surface water quality. It comprises four systems (Figure 1). At the farm scale, strategic socio-economic decisions are made about the production system, and often nutrient management and livestock management strategies are developed in order to comply with European and national legislation. Farm-gate nutrient budgets based on the nutrient and livestock management give valuable information about the potential pressure of nutrients in the region (I. farm system). The distribution of the available P sources over the fields in space and time depends on the crops and the soil P status, and gives more information about the soil balances and the potential risk of losses from the fields (II Field system). The actual P losses from the fields to surface waters strongly depend on the landscape and hydrological system in a given region, because those systems determine the transfer and buffer capacity for nutrients (III Landscape and hydrological system). The impact of nutrient loads on the ecology of the surface waters (IV Ecological system) depends on the actual nutrient pressure compared to the critical nutrient pressure.

Related to this framework of systems are the previously defined eight categories of measures relevant for reducing diffuse agricultural nutrient losses (see Figure 1). They represent a complementary set of options to mitigate nutrient fluxes in space and time. Below, we discuss the most important measures for each system in more detail. The final step in COST Action 869 was to develop a web-based procedure to assist national and regional governments, water managers, intermediaries, and innovative farmers to select the best measures under specific circumstances (http://www. cost869.alterra.nl/dbase). Acknowledging the importance of an integrated approach in

the design and implementation of mitigation options for reducing nutrient losses, the COST Action initially addressed both P and N. In this paper, however, we focus on P and treat N mainly as an important "side-effect".
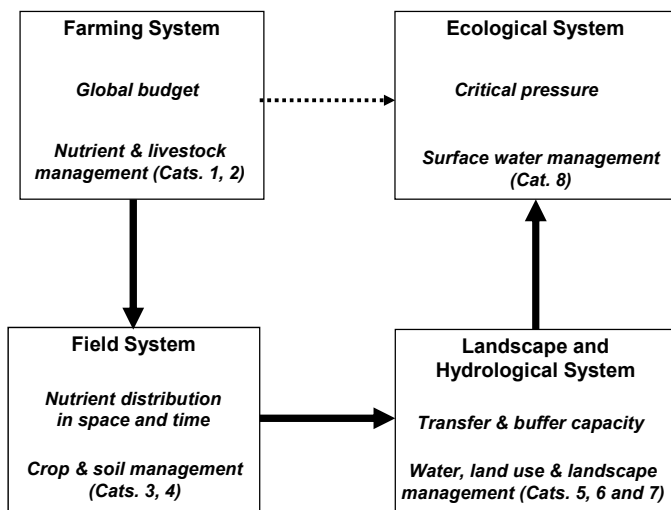
Figure 1. *Schematic visualisation of the systems determining the nutrient losses to surface water, with the defined categories of mitigation measures.*

Results

(I)   Farming system: nutrient and livestock management

Losses of N and P to surface waters are often a problem in regions with intensive agricultural and livestock production, due to the high availability of nutrients (Breeuwsma and Silva, 1992; Sharpley et al., 1994). Table 1 gives different mitigation strategies and associated measures related to farm management.

The EU Nitrate Directive is a crucial EU Directive: it stipulates the permitted amount of manure applications in the Nitrate Action Programmes (max. 170 kg manure N ha^{-1} unless so-called derogation permits apply more manure) and the period during which manure and fertiliser can be applied. The Directive also stipulates that total N application must be based on the balance between crop requirement and manure and fertiliser N supply, taking into account N release from the soil. No application standards for P are defined in the Directive, but it makes it obligatory for member States to prevent surface water eutrophication.

Table 1. *Mitigation strategies for nutrient management at farm scale.*

Strategy	Aim	Measure	Factsheets
Environmentally sound fertilizer application & nutrient handling	Incorporate soil P into management strategy to achieve moderate soil P levels	Make use of available P in soils to avoid high risk hot-spots	6 28 30 36 48 49
	Reduce P content of the soil at high risk hot spots	Don't apply manure and P fertilizer at high risk hot spots	82 28 30 34 35 45 4
	Increase P efficiency of crop uptake via appropriate placement and time of application	Use separated manure fractions and fertilizers with N:P-ratios in line with the N:P ratio required by crop	59 63
		Apply P near the roots instead of broadcast	8
		Avoid applying manure and P fertilizers before heavy rainfall or prolonged rainfall	81
		Phase nutrient fertilisation application over the year	24 25
		Create sufficient storage capacity	83
Change P input	Avoid high P content in fodder by increasing digestible P and lowering total P content in feed	Feed livestock refined fodder, taking account of their requirements given their growth phase	1 80
		Use feed with a lower content of phytate-P or add phytase to feed to increase digestibility of phytate-P	1 80
Change P output	Exploit the commercial value of the manure surplus	Make products for export or for arable farms.	46 *
		Produce secondary P resources for industries by incineration to P-ash	46

*) (Schoumans et al., 2010)

To derive agro-environmental nutrient management strategies, attention should be paid to the P balance at farm and field scales, by taking into account the amount of available soil P (FS28 Hofman, 2010). In many western European countries the amount of available soil P greatly exceeds the annual amount of P applied, because of the common agricultural practice of applying manure on the basis of crop N requirement. The average N:P ratio (w:w) of manures and composts often varies between 2 and 4, while the N:P uptake by major grain and hay crops varies between 4.5 and 9 (Eghball, 1998; Maguire et al., 2006). Thus, too much manure P is applied on agricultural land, and the P surplus accumulates in the soil. Soil samples taken in many regions with a high livestock density reveal that most of the soils sampled do not require further addition of P to support plant growth (Breeuwsma and Silva, 1992; Chardon and Schoumans, 2007; Lemercier et al., 2008; Sharpley et al., 1994).

At a high agronomic soil P status the P balance can be negative, and at low P status the P balance can be positive and this increases the soil P status to the level recommended to sustain optimal crop growth (Tunney et al., 1997a). Therefore, on farms with many fields with a high agronomic soil P status, the aim should be to have a negative P

balance at farm scale and to reduce the annual manure and/or fertiliser application on the fields with high soil P status, by taking account of soil nutrient status and crop response (FS06 Dana, 2010; FS30 Hofman, 2010; FS48 Newell Price, 2010; FS63 Turtola, 2010).

In so-called "critical source areas" (CSAs) (FS36 Krogstad and Bechmann, 2010; Heathwaite et al., 2000) – areas where sources and transport factors coincide with a high risk of P losses – integrated fertiliser and manure nutrient supply strategies are very important and can improve surface water quality by reducing the annual application rates of fertilisers (FS14 Garnier, 2010; FS35 Krogstad and Bechmann, 2010; FS45 Newell Price, 2010; FS49 Newell Price, 2010) and manure (FS60 Taylor, 2010; FS82 Taylor and Garnier, 2011). However, attention should also be paid to the N, P and K ratio of fertilisers in relation to the type and amount of manure that is applied to the fields and crop requirements (FS63 Turtola, 2010).

Not only should application rates and forms of applied nutrients fit with the crop requirement and the nutrient status of the soil; also important are the placement and the timing of manure and fertiliser spreading. Crops with large inter-row distances and/or a restricted root distribution, and crops which grow fast after fertilisation, show improved yields when fertiliser is applied in bands rather than broadcast. Depending on the crop, the recommended amount of P can be reduced appreciably (up to 75%) when P is band applied rather than broadcast (Van Dijk and Van Geel, 2012). The yield improvement is due to better nutrient availability; in addition, due to the increased uptake efficiency the nutrient losses are smaller (FS08 Delgado, 2010; Hofman et al., 1992). There are many options to deliver fertiliser nutrients in such a way that they meet the nutrient needs of different crops during the year. Strategies that are being increasingly used by farmers and should be encouraged still further are split nutrient fertiliser applications, and better timing of fertiliser applications or controlled release fertiliser, which result in more efficient nutrient uptake by plants.

Under the EU Nitrate Action Programme, EC Member States are obliged to restrict the period in which it is permitted to spread manure or fertiliser. To date, the closed period for manure and fertiliser application differs between the Member States[9]. Moreover, high nutrient losses can occur even during closed periods. A good agricultural practice guideline could be to avoid applying manure and fertiliser before predicted heavy or prolonged rainfall events (FS15 Garnier, 2010; FS16 Garnier and Harris, 2010; FS61 Taylor, 2010; FS81 Garnier et al., 2011), or to make it mandatory for the manure to be injected or ploughed in directly after application (FS25 Haygarth, 2010). This could affect the manure handling on the farm (FS24 Haygarth, 2010; FS27 Haygarth, 2010; FS44 Newell Price, 2010; FS59 Taylor, 2010) and the manure storage capacity required

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[9] http://ec.europa.eu/environment/water/water-nitrates/index_en.html

(FS26 Haygarth, 2010; FS50 Newell Price and Morvan, 2010; FS62 Taylor, 2010; FS83 Newell Price et al., 2011).

For farms with a large nutrient surplus, such as intensive livestock farms, additional specific measures should be taken. Total P in fodder often exceeds animal requirements and can be reduced to decrease the P content in excretions (FS80 Van Krimpen and Jongbloed, 2010). Reducing total P in animal diets will increase the manure N:P ratio. It will contribute to reducing a surplus in the P balance of a farm or region, and decrease the need for manure transport or processing. The main options for reducing P content in excretion are (Esmaeilipour et al., 2012; FS01 Bannink, 2010; FS80 Van Krimpen and Jongbloed, 2010; Maguire et al., 2005):
-   feed in accordance with the growth phase of the animal;
-   add phytase to feed (poultry and pig) to increase the ability to digest phytate-P;
-   feed with a lower content of phytate-P;
-   use or produce feed that is more digestible, and
-   maximise the use of available plant phytases to predigest phytate-P before feeding feed ingredients to the animals.

As a consequence of applying the options mentioned above (Jongbloed and Lenis, 1998) showed that in the Netherlands total P in feed for growing-finishing pigs fell by over 2.5 g/kg (33%) from 1973 to 1996, which led to P excretion falling from 1.62 to 0.67 kg P/pig. The introduction of microbial phytase in the last decade of the 20th century stimulated the further reduction of P excretion. Furthermore, it is possible makes it possible to remove phosphates from phytate-rich fodders, thereby making it possible to reduce the phosphate intake of pigs without adversely affecting their health and growth (Meesters et al., 2011).

A farm P surplus should be transported to neighbouring farms or to nearby less intensive agricultural areas (Lopez-Ridaura et al., 2009). Sometimes it is worthwhile separating a manure surplus into a liquid fraction (with high N and low P content) and a more solid fraction (high P and low N). The liquid can be applied to the land locally, and then only the more nutrient-rich solid fraction needs to be transported. Such an approach can be especially successful on a livestock farm with sufficient land of its own (Schröder et al., 2009). Instead of being transported over a long distance, the manure can be collected and processed in the region – e.g. via digestion (biogas production) – or the solid fraction can be incinerated to produce energy. Furthermore, the ash is rich in P that can be reused (FS46 Newell Price, 2010; Schoumans et al., 2010). Since over 80% of all P that is mined worldwide as rock is used in agriculture (in feed and fertilisers), this can contribute to sustainably closing the terrestrial P cycle. A more drastic step is to set a maximum permissible livestock density (as in Denmark) or animal production level. In general, the economic and social impacts of such severe measures make it difficult to restructure agriculture in order to create a regional /

national N and P balance that reduces the risk of surface water pollution (Senthilkumar et al., 2012a; Senthilkumar et al., 2012b).

(II)   Field system: soil and crop management
Soil and crop management affect the nutrient efficiency and nutrient losses directly, and many modifications to management have been suggested as mitigation options against P losses (Table 2).

The main purpose of soil management is to improve the soil's production potential for a certain crop. A number of soil management methods are available: they can be divided into soil tillage methods and soil amendments. Examples of soil tillage methods are direct drilling (no-ploughing and only minor disturbance of the topsoil, shallow cultivation and ploughing (FS02 Bechmann and Krogstad, 2010; FS77 Ulén et al., 2010). Examples of soil amendments are organic matter (FS66 Ulén et al., 2010) and chemical additives (FS05 Chardon and Dorioz, 2010; FS79 Ulén et al., 2010).

Cropping systems without ploughing are attracting much attention in Europe, for economic reasons (such as reduction in labour and energy consumption) and because of their potential to improve soil (Holland, 2004). In cereal cropping, soil tillage contributes to increased soil erosion risk, and thereby also to the risk of particulate P (PP) losses (Lundekvam and Skøien, 1998). The risk furthermore depends on slope and soil texture, with silty and low organic content soils being more vulnerable to soil erosion than clay and sandy soil types.

Table 2. *Mitigation strategies at field scale.*

Strategy	Aim	Measure	Factsheets
Change soil management	Avoid transport of particles or particulate P	No tillage/direct drilling: leaving more than 30% of the soil covered with plant residues or undisturbed stubble	3 69
		Shallow cultivation: Soil tillage to <10 cm depth. No inversion	73 76 71
		Contour ploughing	65
		Switch from autumn tillage to spring tillage	74
		Reduce soil compaction and improve soil structure	68 72 75 66 67
	Avoid leaching of dissolved P concentrations in soils	Conventional ploughing or interspersing periods of ploughless tillage with conventional ploughing	*
		Add chemical compounds to the soil to bind soluble P	5 79
	Reduce nutrient budgets and increase soil storage capacity by extensification and agro-forestry	Introduce crop rotation and include more years of grass or develop mixed (perennial and annual) cropping systems	21
		Set-aside for several years	21
	Avoid transport of particulate P in tramlines	Tillage to avoid tramlines	78
Change crop management	Avoid erosion and reduce surface runoff	Grassland instead of arable crops or grow deep-rooting crops	52
	Change cropping system	Introduce crop rotation and include more years of grass or develop mixed (perennial and annual) cropping systems	21 33
	Avoid leaching	Apply catch crops (and harvest the products)	51
		Crop production without fertilisation (P mining)	4

*) (Ulén et al., 2012a; Ulén et al., 2010; Ulén et al., 2012b)

The main soil tillage mitigation options are:

1. No tillage/direct drilling: Tillage leaving >30% of the soil covered with plant residues,
2. Shallow cultivation: Soil tillage to <10 cm depth without inversion,
3. Ploughing: Soil inversion at 20-25 cm depth, and
4. Contour ploughing.

For some sites, deeper and more intense soil tillage increases the erosion risk. In areas where the soil erosion risk is highest during autumn and winter, important options to mitigate soil losses in arable cropping systems are direct drilling in autumn (FS03 Bechmann et al., 2010) or leaving stubble undisturbed instead of mouldboard ploughing in autumn. In these systems, crop residues and an intact root system may trap and retain soil particles that would be removed by erosion. Furthermore, loosening soil by tillage will increase the risk of mobilisation of soil particles. However, improving aggregate stability by adding plant material will increase biological activity,

including earthworm activity, and reduce risk of erosion. The effect of soil tillage on phosphorus losses via surface runoff is related to the soil erosion processes, but the relationship between soil tillage and losses of P through leaching is much more complex. Here, in some cases ploughing may destroy macropores, thus hampering the transport of particles and dissolved substances via percolating water (Ulén et al., 2012a).

In a soil tillage system with direct drilling or shallow cultivation, the topsoil is not inverted. This has great potential for reducing soil erosion and PP losses from unstable, erodible clay loams, silty and clay soils under cereals (FS73 Ulén et al., 2010; Grønsten et al., 2007). Similar results have been reported for direct drilling of other crops, e.g. sugar beet (Strauss and Smid, 2004). However, if leaving plant material on the soil surface and surface application of P fertiliser are combined with no-till for a succession of years, P accumulates in the topsoil, increasing the risk of dissolved reactive phosphorus (DRP) losses in surface runoff (FS75 Ulén et al., 2010). In a Canadian study Gaynor and Findlay (1995) reported higher losses of DRP after reduced tillage compared to conventional ploughing. They suggested this was a result of P enrichment of the soil surface. Studies from the northern Mississippi in the US concluded that even though total P (TP) losses were considerably reduced when soil tillage was omitted, no-till DRP losses were eight times higher than with conventional ploughing (McDowell and McGregor, 1984). As DRP has a higher ecological impact than PP due to its higher bioavailability in the short term, direct drilling should preferably not be practised on areas where DRP losses from the soil are large, whether from surface water runoff or from leaching via preferential flow through the soil profile and/or tile drainage. However, since PP can at least partly be released and taken up by biota on longer term (Barko and Smart, 1980; Bole and Allan, 1978; Sharpley, 1993; Uusitalo and Yli-Halla, 1999), a balance has to be found between reducing PP loss and (the risk of) increased DRP loss.

In shallow cultivation, there is no inversion of the topsoil. The soil is usually tilled to a depth of 5-10 cm and remains covered with some crop residues. Based on field experiments reviewed in Scandinavia (Ulén et al., 2010), it can be concluded that, compared to ploughing, shallow cultivation reduces erosion and PP losses, though less so than direct drilling (FS76 Ulén et al., 2010). However, Nordic plot experiments showed large variation in the effect of shallow cultivation in autumn on soil losses between sites and years (Koskiaho et al., 2002).

Ploughing involves inversion of the topsoil, for instance by a mouldboard plough. In areas with a high runoff risk during autumn and winter, an important method for reducing erosion and PP losses is to plough in spring instead of autumn for a spring crop (FS74 Ulén et al., 2010). On erodible soils, spring ploughing rather than traditional autumn ploughing has been shown to decrease soil erosion by up to 80% (Lundekvam,

2007) and decrease TP losses by 60-80%. On less erodible soils, the effect on TP losses is smaller and may even be negative in surface runoff (Kværnø and Bechmann, 2010). Additionally, as for direct drilling, when soils are spring-ploughed, losses of DRP may be higher than during winter. The negative effect has to be weighed against the positive effect of reduced erosion and PP loss. On heavy clays, crop establishment in spring may suffer, because if these soils are not tilled in autumn their structure deteriorates.

Ploughing, cultivating and seed drilling perpendicular to slopes and along contours, is applicable for all areas at risk of surface runoff and erosion via rills (FS65 Ulén et al., 2010). In undulating fields, eroded particles in surface runoff may be trapped by grass and can settle in depressions. Therefore, grassed waterways (channels of grass within arable land, constructed in order to concentrate, control and slow down water flow) in combination with contour ploughing are desirable (FS65 Ulén et al., 2010). Another way to reduce erosion risk is reduce slope length by creating a grass buffer along the contour to break the slope (FS70 Ulén et al., 2010).

Besides alternatives for conventional tillage practices, special attention should be given to improving soil structure, especially on compacted soils (Batey, 2009; FS68 Ulén et al., 2010; FS72 Ulén et al., 2010) and in tramlines (Bailey et al., 2013; Deasy et al., 2009; FS78 Ulén et al., 2010; Silgram et al., 2007; Withers et al., 2006), because under such conditions high P losses by runoff and erosion can occur. Tramlines can be treated with a cultivator fitted with a ducksfoot tine used to disrupt the compacted surface of the tramline to circa 6 cm depth (Bailey et al., 2013).

Crop management encompasses the farmer's decisions on which crops and varieties to grow, when and how to sow or plant, and how to handle crop residues, pests and weeds. Principally, crop management options for reducing the erosion risk aim at: (1) increasing water infiltration to reduce runoff volumes and erosivity; (2) strengthening topsoil resistance against detachment of soil particles, and (3) protecting the soil surface against erosive forces with plant or residue cover (Govers et al., 2004). Cover crops can be grown in the interval between main crops to protect the soil surface against losses through erosion and surface runoff. A number of crop management options reduce the risk of nutrient mobilisation by surface runoff and soil erosion; most of these effects depend crucially on the crop type and growth stage as well as on crop rotation (Morgan, 2005).

Crop management strategies for reducing leaching losses of nutrient mainly involve associated catch crops: N is immobilised by being taken up by the catch crops in the interval between the growing seasons of two main crops (FS51 Rubæk and Jørgensen, 2010). The pronounced differences in cycling of soil P and N necessitate a different approach when using crop management to reduce P losses, because plant uptake of P

reduces the concentration of dissolved P only in the immediate vicinity of the root and this reduction is counteracted by desorption of a small fraction of the P retained on the soil particle surfaces. In other words, the soil solution P concentration is buffered by the large amount of P accumulated in the solid fraction. The concentration of dissolved P in soil solution is therefore less dynamic than for N, and even a well-established crop cannot significantly lower the P concentration in the soil solution and keep the concentration low. Reducing the leaching of dissolved P via crop management is possible only through long-term P mining (Delorme et al., 2000; Eghball et al., 2003; FS04 Chardon, 2010; Koopmans et al., 2004a; Koopmans et al., 2004b).

(III) Landscape and hydrological system

Despite the strong link between farm and field management and nutrient losses to surface water, losses at a catchment scale cannot be considered merely as the sum total of losses from farms or fields because of agricultural and environmental features and spatial and temporal constraints and interrelations. Diffuse agricultural pollution occurs in a complex and hierarchical matrix of fields and natural areas interacting with a hydrographical network (Forman and Godron, 1981; FS18 Gascuel-Odoux and Dorioz, 2010; Wang et al., 2004). As some areas in agricultural landscapes are nutrient sources and others are sinks, the catchment as a whole may have a net buffer capacity (Viaud et al., 2004).

A reduction in nutrient losses at catchment scale may be achieved by four means: (a) storage and trapping of water and/or sediment and nutrients within a buffer zone along watercourses; (b) water and dissolved nutrient uptake by vegetation and biota; (c) biogeochemical transformation (such as sorption, denitrification) and (d) dilution (by groundwater). The various management strategies that can be implemented to reduce nutrient losses at a catchment scale can be grouped into three main categories: field water management, land use changes and landscape management (Table 3).

Water-related measures mainly focus on changing the pathway length and the rate of the water flow from the source to receiving waters by changing the drainage conditions. The nutrient concentrations in the water flow will be reduced due to adsorption (P), denitrification (NO_3) and physical processes (steric effects; sedimentation) which also influence the water flow rate. However, it is important to note that changing the water flow will also change soil moisture, and can thus impact on the chemical (sorption and precipitation) and biological processes such as mineralisation or immobilisation of organic matter and nitrification/denitrification. As a result, pollution swapping can occur, e.g. if the groundwater level falls, P leaching will decrease but often the NO_3 concentration will increase because in dry soil less denitrification occurs. Water management measures aimed at reducing nutrient loss to

surface water can be grouped into two strategies (Table 3), related to the main pathways of water flow; (a) overland and (b) subsurface.

Table 3. *Mitigation strategies at catchment scale.*

Strategy	Aim	Measure	Factsheets
Water management	Change runoff flow by blocking or reducing overland flow	Create ponding systems	53
		Construct grassed waterways	52
		Create sediment boxes	56
		Improve surface irrigation	9
	Avoid subsurface losses through leaching	Remove trenches and ditches or allow to deteriorate	58
		Install drains	10 55 64
		Controlled drainage systems	7 54
		Let drainage water irrigate meadows	57
Land use management	Improve location of sinks and sources by changing agricultural use patterns	Alternate grassland and arable land Avoid certain crops in hilly areas	*
		Locate crops with high nutrient uptake on bottom lands	21
	Protect very vulnerable areas by nature development	Afforest or set aside agricultural land	*
Landscape management	Reduce direct losses from farm yards	Minimize volume of dirty water produced and collect farm yard runoff	47 44 27
	Reduce direct losses from livestock	Prevent contact with surface water: fences, bridges	11 19
	Reduce surface runoff and erosion from field to field within the catchment	Re-site gateways and paths: trails, roads, controlled access for livestock and machinery	12 19 20
	Intercept nutrients from runoff, erosion and subsurface losses to waters	Vegetated buffer strips	17 22

*) (Gascuel-Odoux et al., 2011)

Blocking or changing *overland water* flow can be achieved via various constructions, such as ponding systems (constructing bunds along ditches), grassed waterways and sedimentation boxes. It is important to slow down the flow rate and to increase the length of the flow path, as this will facilitate sedimentation (in lower parts of the field) and the infiltration of dissolved P. By retaining the water, sediment ponds at field edges will allow suspended material to settle and increase denitrification, resulting in reduced nutrient losses to surface water (Brown et al., 1981; FS53 Schoumans, 2010). The grass in grassed waterways acts as a filter, absorbing or taking up some of the chemicals and nutrients in runoff water (FS52 Schoumans, 2010).

During runoff events in an undulating landscape, surface runoff tends to flow preferentially towards depressions, creating rills that may result in gully erosion. To prevent this, wells for surface water can be dug in the depressions, backfilled with material that helps to collect the water efficiently. The aim is to avoid a concentrated flow of water from having so much energy that it will cause erosion in the depression (Aspmo, 1989; FS56 Schoumans, 2010).

In areas where nutrient losses are mainly caused by *subsurface drainage water* (e.g.in flat areas with shallow water tables; (Chardon and Schoumans, 2007) water management measures can be taken to reduce P losses. The most important measures are: allow field drainage systems to deteriorate, remove trenches and ditches or install drains. The removal of trenches and ditches will reduce the opportunity for groundwater transporting nutrients to enter surface water: the water has to flow a longer distance underground to reach other surface water bodies (ditches, brooks, rivers) and en route the buffer capacity of the soil filters out the P. By allowing field drainage of a trench or ditch to deteriorate such an effect will be achieved at longer term. However, during the deterioration of the trench (or ditch) the water quality improves if the residence time of the water in the ditches increases (FS58 Schoumans, 2010; Olli et al., 2009; Powell et al., 2007). Since trenches and ditches are constructed in wet areas and are necessary to ensure drainage of surplus precipitation, the impact of this measure will be that high groundwater levels will occur more frequently. Therefore, such measures should be evaluated at least at sub-catchment scale. Furthermore, more frequent wet conditions can have a negative effect on the agricultural productivity of the fields.

Subsurface transport of P to trenches and ditches can also be reduced by Installing artificial drains in undrained fields, because the groundwater will no longer reach the P-enriched layers and peak discharges will no longer occur from these layers (FS55 Schoumans, 2010; FS64 Turtola, 2010). Even greater reductions can be obtained via controlled drainage systems or deep controlled drainage systems (FS54 Schoumans, 2010). However, in cracking soils, artificial drainage increases nutrient losses because macropores connect the nutrient-rich topsoil with drain lines through which water and dissolved/suspended nutrients are transferred to water (FS07 Delgado, 2010). Artificial drainage is not recommended for peat areas, because when the groundwater level falls peat will oxidise and more P will become available than under anoxic conditions (FS55 Schoumans, 2010).

P losses via leaching can also be reduced by filling a mole channel, by mixing backfill, or enveloping a tile drain with a reactive material such as iron or aluminium hydroxides or oxides, or lime (CaO), depending on the soil pH (Groenenberg et al., 2013; Hanly et al., 2008; McDowell et al., 2008). A second option is to stop the water flowing through tile

drains and make it flow overland, irrigating meadows or riparian areas. The general idea is that water from tile drains that is polluted with particulate and dissolved nutrients is filtered by a meadow or a riparian area (FS57 Schoumans, 2010; Stutter et al., 2012; Stutter et al., 2009; Tanner et al., 2005).

Land use measures can be divided into three groups (Table 3). Changing the agricultural land use pattern by reallocating the land use or changing the crop can increase the buffer capacity of the catchment by rearranging the location of sinks and sources and decreasing the water flow (FS21 Gascuel-Odoux et al., 2009). Reallocating crops at farm scale, or collectively planning the land use for the entire catchment may cause changes in soil surface conditions (vegetation cover, roughness, soil structure) and therefore infiltration capacity downslope may increase, thereby reducing erosion losses (Souchere et al., 2005) and increasing nutrient uptake from the soil water. Vegetation management of buffer strips is also a critical factor in manipulating buffer conditions to remove stored P, increase buffer lifespan and prevent P being lost through leaching. Enhancing the plant uptake of the mobilised nutrients will have two benefits: removing pore water nutrients that would otherwise leach out (Lee et al., 2000) and providing a possible removal pathway via vegetation harvesting (FS22 Gascuel-Odoux et al., 2010).

Other important options available within the catchment are changing to a different agricultural land use (e.g. agro-forestry or extensification) or to a non-agricultural use. Unfortunately, catchment experiments cannot be easily performed to evaluate the effectiveness of such options, since it would take many years to test the effect of crop locations. The effectiveness of such options at catchment scale is mainly evaluated by hydrological and nutrient modelling that includes a detailed description of the agricultural landscape and its functioning. The modelling shows the effectiveness of the options on surface runoff and erosion, and thus on PP losses (Aurousseau et al., 2009; Cerdan et al., 2002; Jetten et al., 1996).

Interfaces between farm water and surface water regulate the surface flow connectivity between farm infrastructure, where wastewater is produced, and surface water. Outdoor manure heaps should not be sited over field drains or close to a watercourse because effluent from manure can contain very high concentrations of N and P (McDowell et al., 2005), and can reach surface water either directly or via the drains. Ideally, the heaps should be sited on concrete so the effluent can be collected; this is already prescribed by regulations in e.g. Switzerland (FS14 Garnier, 2010; FS26 Haygarth, 2010; FS44 Newell Price, 2010; FS60 Taylor, 2010). Although they are not considered as "agricultural", farm septic tanks can also contribute to P losses (Withers et al., 2011) and to avoid these losses, farms should be connected to the sewer system. To attenuate the transfer of nutrients from farmyard to subsurface it is desirable to: 1) minimise the volume of wastewater produced on the farm or regulate the storage

facilities; 2) separate runoff from farm roofs from runoff from farmyards and roads; 3) site waste storage facilities far from surface water drainage networks 4) introduce buffers (such as a farm pond or filter strips) (FS47 Newell Price, 2010).

Direct access of livestock to a stream can significantly damage river banks and local aquatic ecosystems and can also lead to direct pollution with organic and inorganic nutrients and faecal contaminants. Mitigation options aim to introduce physical barriers between grazing animals and surface water (Meals, 2004), to reduce cattle grazing (FS34 Jørgensen et al., 2009), or avoid high animal density in areas very close to watercourses (FS11 Dorioz and Gascuel-Odoux, 2010; FS12 Dorioz et al., 2010). This can be achieved by: 1) fencing off rivers and streams and leaving a protective zone of a minimal width (1 to 3 m) along the stream network; 2) creating designated livestock crossings of streams and rivers by means of bridges or paths; 3) re-siting pasture gateways away from watercourses and, if possible, upslope from the watercourse. These three measures are applicable to grazing land and livestock farms. Special attention should be given to parts of fields where animals congregate, such as drinking troughs, feeding places and shelter areas near watercourses. Such places can be considered as "pollution hotspots" on the farm, as excreta will frequently be deposited there. Trampling by livestock will increase soil compaction and runoff potential, creating areas at greater risk of P loss to water (Tunney et al., 2007). It is therefore advisable to move drinking and feeding places at regular intervals, in order to reduce uneven loading and physical damage (Wilcock et al., 1999)

Interfaces located along permanent streams and ditches control direct inputs to surface water. If they have a buffer effect, they are called riparian buffers. Two types of such riparian buffers can be distinguished in terms of their hydrological conditions: 1) unsaturated: vegetated buffer strips, and 2) saturated: riparian wetlands or wet meadows Riparian strips are generally considered to offer efficient protection against TP: much of the P transported to watercourses is bound to particles and the main physical process occurring within the buffer strips is sedimentation. Much is known about constructed vegetated buffer strips, as they have been widely studied and have been tested and calibrated with models. (Hoffman et al., 2009) have reviewed the efficiencies of riparian buffers for TP retention and report that the retention efficiencies varies between 41 and 92%. The effectiveness of riparian buffers depends on many factors, like the nature of contributing sources, slope, soil type, vegetation and local flow and hydrological soil conditions. Especially, under drainage conditions with tile drains the effectiveness of riparian buffers is relatively low, since buffers mainly target the surface delivery pathway. There is uncertainty about the true effectiveness, because most of the data used in the assessment were from short-term (even single rainfall event) plot studies (Liu et al., 2008 ; Schmitt et al., 1999).

In wet, shallow groundwater systems, small riparian wetlands are often created in the lowlands of headwater catchments, scattered in the rural landscape and often associated with wet meadows. They are the inescapable interface between groundwater, for which they are the non-point outlet, and the water bodies, and are often the interface between intensively cultivated hill slopes and plateaus and the water bodies. Wetland efficiency at reducing nitrate pollution has been extensively studied in natural (Fisher and Acreman, 2004; Machefert and Dise, 2004) and artificial wetlands (Kadlec, 2009; Vymazal et al., 2006). Wetlands can also trap particles and thus TP. But under anaerobic conditions, reductive dissolution of ferric compounds carrying P can be an important mechanism of seasonal DRP release (Khalid and Patrick, 1974).

Finally, field boundaries can be helpful as interfaces to control the connectivity of surface runoff and subsurface flows from plot to plot (FS19 Gascuel-Odoux and Dorioz, 2010). These interfaces are very diverse: e.g. simple field boundaries or margins, vegetated to various degrees; hedges and hedgerows, all acting as a filter for surface runoff. The effect of the boundary on subsurface flow depends on the local or hill slope conditions and on the vegetation type (hedges, trees, grass) (FS20 Gascuel-Odoux and Dorioz, 2010). The root systems of plants on field boundaries can take up water and chemicals from shallow groundwater (the root systems of trees extend to a depth of several metres), and thus may affect the subsurface flow. Gateways are effectively gaps in the field boundaries and are critical areas for surface runoff in all kinds of fields, not only in pastures. At the landscape level, gateways, livestock and tractor pathways form a network of preferential flow pathways that may be hydrologically connected to the water course. Consequently, re-siting gate and livestock and tractor pathways is a simple way to decrease local and global hydrological connectivity, thus reducing pollution via these preferential flow pathways (Cuttle et al., 2007).

(IV)   Ecological system
Surface water management is commonly deployed to retain sediment and nutrients transported to surface waters from land. The basic principles on which it is based include hydraulic retention (i.e. increasing the residence time of water in surface water systems), interaction between sediment and water, and biogeochemical processes such as denitrification and sorption. Surface water management also strives to re-establish lost biomes such as wetlands and lakes and to improve the ecological quality of streams and rivers (Kronvang et al., 2011). Three main types of surface water management can be distinguished (Table 4): (a) River maintenance and river restoration, (b) Lake re-establishment (lakes that have been drained for agricultural purposes) and (c) Wetland restoration and constructed wetlands.

Table 4. *Mitigation strategies in aquatic ecosystems.*

Strategy	Aim	Measure	Factsheets
River maintenance and river restoration	Increase nutrient retention capacity	Limit cutting of vegetation and reduce regular removal of gravel and impediments to flow	37
		Re-meander, restore flood plains and reconnect inundation areas	39 41
Lake rehabilitation and restoration	Reduce the P concentration of lake water	Control P inlet and prolong residence time of water	38
		Apply chemicals to bind P released from sediments	43
Wetland restoration and constructed wetlands	Retain nutrient loss from upstream fields in wetlands	Create wetlands in agricultural areas with substantial P losses	39 40 41 42

In order to facilitate fast drainage of water from fields, streams have traditionally been maintained by cutting back the vegetation several times per year and by removing gravel, stones and other physical barriers that impede water flow. Streams have thus been kept in canal-like state with a low capacity of nutrient retention (FS37 Kronvang, 2010). If maintenance is limited or abandoned, the physical conditions of the streams will change (FS23 Grizzetti and Bouraoui, 2010; Sand-Jensen, 1997). Aquatic and bank-side vegetation will quickly narrow the channel profile and promote denitrification and the deposition of sediment and PP (Kronvang et al., 2005; Veraart et al., 2011). The morphological and substratum diversity of watercourses that have been straightened and channelised in order to drain agricultural land can be improved in various ways. Active restoration is a quick and direct way of achieving the required physical improvement of the channel and restoring the interaction with the adjacent riparian areas through inundation during high flow periods. A study of 13 catchments in Western Europe found that the main factor for nutrient retention in the surface water system is residence time. This can be increased by restoring floodplains and reconnecting inundation areas (FS39 Kronvang, 2010; FS41 Kronvang and Lo Porto, 2010). As an example, increasing the water travel time in a catchment by 50% may result in 15-20% more N and P retention (De Klein and Koelmans, 2011).

The P loading of lakes is in the form of dissolved or PP. PP will be deposited in lakes as a result of sedimentation, whereas part of the DRP will be taken up by the biomass of phytoplankton or macrophytes produced in the lake. The amount of P that is recirculated and immobilised depends on local conditions in the catchment and the nature of the re-established lake. The factors and processes involved are: i) periods of anaerobic conditions in lake sediments; ii) ratio of iron to P in sediments; iii) residence time of water in lakes; iv) lake depth and v) inflow of P (Hejzlar et al., 2007; Kronvang et al., 2005). The most important factor for nutrient retention in lakes is the residence time for water: the longer the residence time, the greater the retention of nutrients

(FS38 Kronvang, 2010; Hejzlar et al., 2009; Hejzlar et al., 2007; Søndergaard et al., 2003; Windolf et al., 1996).

In principle a re-established lake will start to retain nutrients from its outset. However, a period with net release of P from the rewetted soils can occur if these soils contain large amounts of "old" agricultural P and are low in iron content. Another factor that may be important is a release of P from the former terrestrial vegetation and a hydrolysis of easily decomposable organic matter in the soils submerged by the re-established lake. On a longer time scale the re-established lakes will retain nutrients like natural lakes; the retention potential for N and P can be calculated from lake nutrient models. Phosphorus-enriched sediments can release P to the water through a process known as internal loading (Søndergaard et al., 2003). As a result, the total P retention can be very variable (-265% up to +91%) as shown by (Hoffman et al., 2006) for re-established Danish shallow lakes and wetlands. When sediments are contributing P to the lake, nutrient inactivation techniques called precipitation can be used to remove P from the water column and a process called inactivation can be used to retard its release from the sediments. In both cases, the aim is to prevent eutrophication or to rehabilitate water bodies that have become eutrophic due to high concentrations of soluble P, by binding the P and causing it to settle out on the lake or river bed (Svendsen et al., 1995). Aluminium, iron, or calcium salts are used to inactivate P in lake sediments. The chemical compound most commonly used to precipitate the P is aluminium sulphate (alum) $Al_2(SO_4)_3$: it is frequently used as a flocculating agent in the purification of drinking water and in wastewater treatment plants. The addition of alum helps reduce the DRP concentration in surface water (FS43 Lo Porto et al., 2010). Several studies have evaluated the effectiveness and longevity of treatments on several lakes in the USA and have concluded that in shallow lakes alum treatment effectively achieves P inactivation in most cases (Welch and Cooke, 1999). Applications in stratified lakes were highly effective and long-lasting (> 80%) (FS43 Lo Porto et al., 2010).

In recent years, interest in wetland restoration programmes has been growing throughout the world (Hoffman et al., 2009; Litaor et al., 2004). Restoration of riparian wetlands is conducted on low-lying, often former organic soils that were drained at some time in recent history, usually for agriculture. They are human-made wetlands, created on areas where the physical and chemical composition of the soil had changed as a result of many years of draining and farming. In most cases, restored wetlands are established with the principal aim of retaining nutrients lost from upstream agricultural fields by denitrification, P sorption, and sedimentation (FS17 Gascuel-Odoux and Dorioz, 2010; FS40 Kronvang, 2010). The restored wetland may be fed by groundwater or surface water and be adjacent to streams and rivers, or be located in estuaries along the coast. Wetlands dominated by surface water receive both dissolved and particulate

P forms that can be retained by sedimentation and sorption (Litaor et al., 2004; Litaor et al., 2005; Sade et al., 2010) and biological uptake (Hoffman et al., 2009; Kronvang et al., 2009b). Normally, restored wetlands are very effective for P sedimentation or uptake of P by vegetation. Experience with sedimentation of particulate P also shows that restored riparian wetlands can have a high retention capacity of 10-100 kg P ha^{-1} inundated wetland (Kronvang et al., 2009b). However, P retention is more certain for PP than for dissolved P, as some restored riparian wetlands experience a net leakage of dissolved P, due to iron-bound pools of former agricultural P in soils that is released under anaerobic conditions in amounts of up to 20 kg P ha^{-1} y^{-1} (Hoffman et al., 2009).

Wetlands are also constructed with the principal aim of retaining nutrients from neighbouring agricultural fields through processes such as sedimentation and sorption. Constructed wetlands are established either in small ditches and brooks or as an end-of- tile-drainpipe control. In all cases, nutrient-enriched water from fields flows through constructed wetlands for nutrient load reduction before entering surface waters downstream. The numerous configurations include: small sedimentation basins; infiltration basins with horizontal or vertical flow through the artificial substrate for sorption of P; shallow vegetative filters for storage of fine particles enriched in P and uptake of dissolved P; and small basins with material that increases the P sorption potential. The effectiveness of constructed wetlands for nutrient removal and storage is normally high, although most experience is from surface water systems in Norway, Sweden and the USA. Constructed wetlands established in brooks have been found to have an annual P retention of 1-50 g P m^{-2} yr^{-1} of constructed wetland (Braskerud et al., 2005; FS42 Kronvang et al., 2010). Usually the absolute and relative retention performance increases concomitantly with the load. However, the P retention is more certain for PP than for dissolved P, as some constructed wetlands experience a net leakage of dissolved P (Hoffman et al., 2006). Depending on the rate of wetland terrestrialisation constructed wetlands may last for 10-50 years before they need to be dug out again. In the long run, the P-binding capacity of constructed wetlands may also become exhausted and therefore it is important to maintain them by cutting vegetation and removing sediment.

Conclusions

The list of mitigation options that COST Action 869 yielded was produced by a diverse group of scientists from 30 countries in Europe, and therefore from a range of agricultural and pedoclimatic areas. For the four systems defined in Figure 1, the following main conclusions can be drawn:

(i) NUTRIENT & LIVESTOCK MANAGEMENT
- Nutrient management strategies, such as agro-environmental recommendations, are useful tools for setting up a more sustainable agricultural management practice.
- With respect to the selection and placement of fertilisers (NPK), the surplus of all components has to be minimised in relation to nutrient uptake of the crop and the composition of the applied manure.
- Reducing the N and/or P content of animal feed, or increasing the uptake availability, can greatly reduce a farm's nutrient surplus and the risk of losses due to over-application.
- Transport of manure from a farm with a nutrient surplus is costly; manure separation can reduce these costs if the liquid fraction with a relatively low P content can be applied locally.

(II) SOIL & CROP MANAGEMENT
- Direct drilling and shallow cultivation reduce erosion and total phosphorus losses from high risk areas more than ploughing that results in soil inversion.
- Compared to autumn ploughing, on average a spring tillage reduces erosion risk and P losses during winter.
- Accumulated surplus P fertiliser and organic matter on or near the soil surface pose a risk of P release and therefore increased DRP concentrations in surface water.
- Cover crops can protect the soil surface against nutrient being lost through surface runoff and erosion.
- P losses related to the high P status of a soil can be reduced by using crops to mine P from the soil over several years.

(III) WATER, LAND USE & LANDSCAPE MANAGEMENT
- Controlling the water flow from fields to surface water is one of the most important options to reduce nutrient pollution of the surface water, because nutrients from agricultural land are mainly transported to surface water via flowing water.
- The P concentration of infield overland water flow can be directly changed by creating ponds or grassed waterways or by installing sediment boxes.
- Subsurface nutrient losses from agricultural land can be changed by changing the drainage system (trenches, ditches and tile drains). Controlled tile drainage systems are especially effective at changing the depth of the water discharge to surface waters.
- Buffer areas act by storing and trapping water and/or sediment and nutrients, the uptake of dissolved nutrients by vegetation and biota, biogeochemical transformation (such as sorption and denitrification) and dilution. To be effective, they have to be properly structured and managed.

(IV) SURFACE WATER MANAGEMENT

- Surface water management to increase nutrient removal and storage processes is often applied in River Basin Management Plans because it is cost-effective for both N and P.
- River maintenance and restoration can assist in increasing nutrient retention and improving stream ecology.

CHAPTER 10

Phosphorus management in Europe in a changing world

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Abstract

Food production in Europe is dependent on imported phosphorus (P) fertilizers, but P use is inefficient and losses to the environment high. Here, we discuss possible solutions by changes in P management. We argue that the use of P fertilizers and P additives in feed could be reduced by fine-tuning fertilization and feeding to actual nutrient requirements. But also P from waste has to be completely recovered and recycled in order to close the P balance of Europe regionally and become less dependent on the availability of P-rock reserves. Finally, climate-smart P management measures are needed, to reduce the expected deterioration of surface water quality resulting from climate-change-induced P loss.

Keywords: Phosphorus, European P balance, resource cycle, P recovery, climate change

Introduction

Phosphorus (P) is a life-essential irreplaceable element and the Earth's biomass potential is P limited (Asimov, 1959; Filippelli, 2008; Smil, 2000). As P is often in short supply for optimal plant and animal growth and development, farmers use P fertilizers, and add P additives . P also has many industrial applications, including household detergents. However, excessive use of P leads to deterioration of the water quality, eutrophication and loss of biodiversity.

Essentially, all chemical fertilizer and feed P is derived from phosphate-rich rocks which are located in a few places on Earth and are finite. As Europe has no significant phosphate mines, it is highly dependent on the import of phosphate ore (De Ridder et al., 2012). The current worldwide P reserves are estimated at 67 000 Tg P[11] and the world mining production in 2013 was 220 Tg P (Survey, 2014). About 75% of the known reserves are located in Morocco (Western Sahara), which is the main exporter of phosphate ore. China and USA also have significant reserves but the phosphate ore is not sold on the global market, which further limits the source of supply for other countries.

Geopolitical changes can cause the price of P fertilizer and hence of food to rise, as happened in 2008 (Cordell and White, 2011). Moreover, the challenges related to population increase, increasing urbanization and changes in diets are putting further pressure on the P demand, as agricultural production will have to increase further to meet food demand. Meanwhile, the burgeoning biobased economy and growing demand for bio-energy are increasingly competing with the food production sector for scarce land, fresh water and other natural resources. These changes may have increasing impacts on climate change, water resource depletion, soil degradation and air pollution, and could ultimately further constrain food production in the future. These trends and issues can be expected to affect P use efficiency and water quality too.

Recently, it has been proposed to implement a coherent package of nutrient management strategies and measures: the 5R strategy (Withers et al. 2015). This strategy is intended to close the P cycle in Europe. The five Rs are: Realign P inputs, Reduce P losses to waters, Recycle P in bio-resources, Recover P from waste, and finally if necessary Redefine our food system. Many Best Management Practices (BMPs) have been developed to increase P use efficiency and reduce P losses (Schoumans et al., 2014a). Here, we build on the 5R strategy and BMPs to discuss the prospects for the two main options for closing the P cycle (reduce the inputs and recover/recycle P from food processing waste, non-food waste, municipal waste and manure) against the background of the changing world. We start with a brief overview

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[11] 1 Tg = 1000 million kg

of the P balance in Europe followed by a discussion of the options to close Europe's P balance and the options for recovering P from waste streams. Although the P losses to surface water are relatively low in terms of the inputs and outputs of the P balance, they still need to be reduced since P losses have a relatively large impact on Europe's freshwater systems. We therefore close by discussing the possible impact of climate change on P losses to surface waters, in order to evaluate the long-term consequences for the water quality.

P balance of the European Union (EU-27)

Farmers in Europe began using P fertilizers before farmers in other continents (Fig. 1). Until the 1980s, about half of the annual total P fertilizer consumption in the world was in Europe. Thereafter, consumption in Europe fell sharply in response to the political and economic changes in Eastern Europe and the increasing soil phosphorus status and improved utilization of manure P in the European Union (EU). In Asia, consumption has been increasing rapidly since the early 1980s; that continent now accounts for over half of the world P fertilizer use annually. Consumption in America, Oceania and Africa is rising slightly.
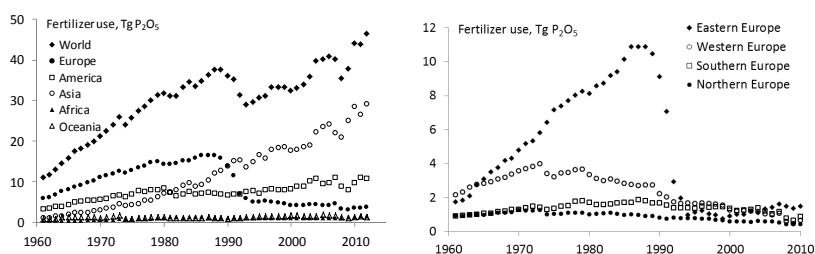
Figure 1. *Consumption of phosphate fertilizers in teragram P$_2$O$_5$ (1 Tg = 10^{12} g =1 million ton) in the world per continent (left) and per European region (right) during the period 1960 – 2012 (FAOSTAT, 2014). Note the large drop in fertilizer use at the end of the 1980s and beginning of the 1990s in Europe (left) and especially Eastern Europe (right), which resulted from the eastern countries in the former Soviet Union achieving independence and being reassigned (together with their fertilizer use) to Asia rather than Europe.*

The picture changes slightly when the consumption of P fertilizers is expressed per unit of agricultural land. Western Europe was the largest consumer during the period 1961–2012 (Table 1), despite the drop in use from the 1970s onwards. During the period 2008–2012, average consumption in Western Europe was at a similar level as the world's five-year average (Table 1). Mean annual consumption in Europe was 5.2 kg P per ha (equivalent to 12 kg P$_2$O$_5$ per ha) during 2008–2012. Consumption of P fertilizer in the EU fell appreciably after the price peak in 2008–2009 and has never fully recovered. This contrasts with the rapid recovery in, for example, Asia and

America (Fig. 1). Fertilizer use is low in Africa, although most African soils are very low in P, which severely limits crop production (Syers et al., 2008b; Van der Eijk et al., 2006).

Total P fertilizer consumption in the world quadrupled during the period 1961–2012 (Fig. 1). However, consumption per ha of agricultural land increased less, as the agricultural area increased too, notably in Africa, Asia and Latin America.

Table 1. *Mean, minimum (min) and maximum (max) values of annual chemical phosphorus (P) fertilizer use per ha of agricultural land per continent and for four regions in Europe (in kg P2O5 per ha per year) during the periods 1961 – 2012 and 2008 – 2012 (based on FAOSTAT, 2014).*

	Period 1961-2012			Period 2008-2012		
Region	Mean	Min	Max	Mean	Min	Max
World	6	2	10	9	7	10
Africa	1	0	1	1	1	1
Asia	6	3	9	8	6	9
America	8	1	22	17	13	22
Oceania	3	2	4	3	2	3
Europe - Northern	13	6	21	7	6	7
Europe - Eastern Europe	23	11	35	12	11	14
- Eastern Europe	8	2	18	4	3	5
Europe - Southern	18	10	25	13	10	15
- Western Europe	39	8	65	10	8	12

The use of P fertilizer was a major factor contributing to the increase in crop production during the second half of the 20th century; other important factors were the increased availability of N fertilizers, improved crop varieties and improved crop husbandry. The use of P fertilizer has also contributed to an increase in soil P status in many regions, especially in Western Europe (Reijneveld et al., 2012; Tóth et al., 2014), and thereby has led to a decrease in crop response to P fertilizer application. It is well known that responses in crop yield diminish greatly with an increase in soil P status (Hinsinger, 2001; SCOPE, 1995; SCOPE, 2014), making it uneconomic to apply P fertilizer. This partly explains the large decrease in P fertilizer use in, for example, Western Europe during recent decades.

Few studies have examined the social implications over time of the fate and efficiency of P inputs, and so little data are available on P use efficiency at the level of the entire food chain (e.g. (Ma et al., 2013; SCOPE, 1995). Table 2 presents the P input–output

balance for the EU-27 for 2005 (Van Dijk et al; unpublished). The main input is chemical fertilizer P, followed by imported food products, animal feed and non-food products. These inputs were used (i) to supply households with food and non-food products, and (ii) to export food and non-food products. Consequently, the apparent efficiency of P use is 57% (EU food and non-food consumption and P export compared to total P inputs)([664+272+544+17+31]/[2659]). However, most food and non-food products to households end up in wastes (691 Gg P) and only part of the P in these wastes is recycled (240 Gg P). If we assume that the output consists solely of the export of products containing P, the P use efficiency falls to 22% ([544+17+31]/2659), or to 53% if we assume that the accumulated P in the root zone of cropland (817 Gg P) is available to growing crops in the long term ([544+48+817]/2659). The remaining 47% (1250 Gg) is considered to be waste streams (mainly organic waste and P losses to surface waters).

Table 2. *Inputs and outputs of phosphorus (P) (in Gg P) in the European Union (EU-27) in 2005 (Van Dijk et al; unpublished).*

Inputs	Gg P	Outputs	Gg P
Imported fertilizers	1487	Exported food	544
Imported animal feed	417	Exported non-food	17
Imported food products	625	Exported manure	31
Imported non-food products	130	Leaching losses	164
		Manure losses	67
		Food-processing waste	275
		Non-food waste	53
		Municipal waste	691
		Accumulation in agricultural soil	817
Total	2659		2659

Ott and Rechberger (2012) arrived at slightly lower estimates for the P use efficiency in the EU-15 during the period 2000–2010 than we show here for 2005. The main reason is that we have included the new Member States in central Europe, which have higher P use efficiency in crop production than the 'old' Member States of the EU-15. However, considerable uncertainty surrounds the data presented in Table 2, which we have compiled from statistics (FAOSTAT, Eurostat), expert interviews, literature and additional model calculations. The uncertainty in the input and output flows is estimated at roughly between 10 to 50% for the EU (Ott and Rechberger 2012).

Given the current P inputs (Table 2) and high soil P status (Tóth et al., 2014) the risk that P is limiting crop and animal production in Europe is low, although there is huge spatial variation in P inputs and soil P status across Europe (Csathó and Radimszky,

2009). The spatial variation in P inputs is strongly related to animal density and associated P inputs via animal manure. Although the Nitrate Directive (EEC, 1991b) restricts the annual manure application rate in terms of amount of nitrogen, there is no European policy on P legislation, although some EC Member States have introduced limits to P application (Amery and Schoumans, 2014).

Options to close the P balance in Europe
The legacy of past fertilizer and manure applications in soil P reserves can be used for crop nutrition during subsequent decades (Sattari et al., 2012), though for how long depends on how effectively the accumulated soil P is used. In areas with high soil P status, the P application can be greatly reduced. In the long term, P fertilizer should match P removed in harvested crops, and P import should match P exports plus inevitable P losses. Also, P supplementation of animal feed should be reduced so that the P content matches animal requirements, and efforts have to be made to increase the digestibility of P in feed, especially in the case of feed for monogastric animals (Van Krimpen et al., 2012). Our analysis indicates that European P inputs via chemical fertilizers and animal feed can be reduced but that the European P cycle can be closed only if P from waste streams is recycled back to the soil into the food chain (Table 2). A main challenge is therefore the recovery and subsequent recycling of P from wastes (domestic and industrial) and manure (from intensive livestock farming). Another challenge is to transfer P from regions with excess P (for example, regions with high densities of livestock and/or of people) to regions with the greatest need to replenish depleted soil P pools. Further, decreasing the diffuse pollution of surface waters (P leaching losses from cropland and farmyards) would also contribute to solving the 'P challenge'.

P recovery from waste streams
Awareness of the scarcity of P and of the need to close the P cycle has stimulated research on the P recovery from waste streams. As indicated in Table 2, the waste streams in the EU-27 are substantial: the biggest is domestic wastewater, which is mainly collected at waste water treatment plants (WWTPs).

Figure 2 illustrates the main points for interventions for P recovery in the stream flow of wastewater at a WWTP. Direct application of stabilized and dewatered sewage sludge on arable land is the traditional path to valorize the nutrients from WWTP in agriculture (no. 1 in Fig. 2). But, due to increasing concerns about pollutants, whether known (heavy metals) or unknown (organic contaminants and pathogens), this route is being increasingly questioned by the public and authorities, and some European countries have banned the application of sewage sludge in agriculture (e.g. Switzerland). Therefore, solutions for technically advanced P recovery and recycling have been investigated and in some cases are already being implemented. These

alternative routes for nutrient recovery provide safe products or raw materials suitable for reuse in the nutrient cycle of the food chain.
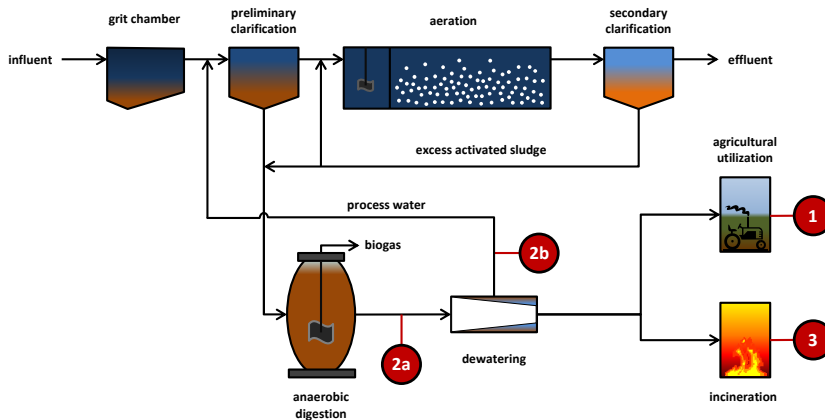
Figure 2. *Hotspots for phosphorus (P) recovery from the wastewater stream (in centralized sanitation systems) Source: (Kabbe, 2013) Legend: 1 – direct sludge application in agriculture; 2a – P recovery from aqueous sludge phase prior to dewatering; 2b – P recovery from sludge liquor after dewatering; 3 – P recovery from mono-incineration ash.*

If sludge is incinerated in a mono-incineration plant (no. 3 in Fig. 2) a high P concentrate (P ash) can be produced from waste streams (Adam et al., 2009; Kabbe, 2013; Schipper and Korving, 2009). The P content in municipal sludge ash ranges between 4 and 13% (Krüger et al., 2014). But, due to low plant availability of the nutrient within the ash, further treatment is needed before it can be fully utilized as a P resource. Due to lack of ash treatment facilities and interim storage capacities, most of the P in the ash is not recovered as easily soluble mineral P. The production of fertilizer from ash via a thermochemical method such as in the AshDec process (Outotec) (Adam et al., 2009; Stemann et al., 2014) involves treating the ash at approximately 1000 o C to remove the heavy metals and to increase the bio-availability of P in the ash. The process produces a magnesium-enriched dicalcium phosphate that can be marketed as chemical fertilizer. An alternative is wet chemical extraction developed in cooperation with companies with experience in treating low-quality phosphate ore (De Ruiter, 2014). This process (EcoPhos) would allow the production of phosphates suitable for use in animal feed. Looking at the Mephrec process, thermal valorization and phosphorus recovery in one single step are not mutually exclusive (Scheidig, 2009). This technology even offers prospects of recovering precious metals as well as P. The resulting P-rich slag is suitable for fertilizer production and comparable to the well-known Thomas phosphate, a by-product of steel production.

Depending on the wastewater treatment scheme, phosphorus can be recovered from the aqueous phase of the sludge before (no. 2a in Fig. 2) or after the sludge dewatering process (no. 2b). Many mature techniques are available and being developed for sludge treatment (Kabbe, 2013; Rulkens, 2004; Stemann et al., 2014) and, more specifically, for recovering P from municipal or industrial waste streams (Table 3). Examples of well-known P-recovery techniques are AirPrex, NURESYS, PEARL, PHOSPAQ, the Gifhorn process and the Stuttgart process (P-REX EU Project, http://www.p-rex.eu/). Phosphorus is often recovered as magnesium ammonium phosphate (struvite), mono ammonium phosphate (MAP) and dicalcium phosphate (DCP) (Greaves et al., 1999; Kabbe, 2013; Le Corre et al., 2009; Tan and Lagerkvist, 2011).

The crystallization of struvite tends to be a favoured approach and is the final step of many P recovery technologies (Table 3), yielding a slow-release fertilizer with excellent plant availability (Römer, 2013). By crystallizing struvite directly after the digestion (no. 2a in Fig. 2) within the sludge but prior to dewatering, the efficiency of the sludge dewatering can be increased dramatically, thus substantially reducing operational costs (Heinzmann and Lengemann, 2013). These benefits are mainly achieved by lower sludge disposal costs, reduced demand for chemicals (flocculation aid), lower maintenance costs (pipe clogging and abrasion of centrifuges) and a higher overall energy efficiency. An option (LysoGest, PCS GmbH) (Kabbe, 2014) to enhance the yield of struvite is being demonstrated at WWTP Lingen in Germany, where thermal hydrolysis is being applied to break down excess activated sludge. As well as improving biogas production in the subsequent digester, the treatment also transforms insoluble or hardly soluble polyphosphates into soluble ortho-phosphate available for struvite crystallization in the sludge water (no. 2b in Fig. 2).

The struvite recovered from the sludge might include more impurities than the material crystallized from the process water after dewatering. But the end products are two registered fertilizers (Berliner Pflanze (BWB), Crystal Green™ (OSTARA)) and every WWTP operator needs to choose the treatment process that best fits expectations, needs and infrastructure. Unfortunately, most of the technologies available are suitable only for WWTPs with biological P removal (Bio-P). If the P is removed by precipitating hardly soluble iron or aluminium salts, direct struvite crystallization is not a sensible option. The P needs to be remobilized, e.g. by lowering the pH, as done in the Stuttgart and Gifhorn processes. A very promising and green alternative is the Budenheim process (Schnee, 2014); it applies carbon dioxide under pressure as dissolving agent, which is internally recycled, to reduce the pH and thereafter the released phosphates are precipitated as dicalcium phosphate.

Table 3. *Phosphorus (P) recovery in wastewater treatment plants (WWTPs). Sources: (Kabbe, 2013; Stemann et al., 2014).*

Process	Scale	Product	Reference
Sludge / process water			
AirPrex	full	struvite	http://www.nutrientplatform.org/business-cases/bedrijfsnaam/a-tm-z/41-waternet.html
ANPHOS	full	struvite	http://www.nutrientplatform.org/business-cases/bedrijfsnaam/a-tm-z/81-aa-en-maas.html
Aarhus Water	full	struvite	http://www.phosphorusplatform.eu/images/download/ScopeNewsletter102.pdf
Budenheim	pilot	DCP	Schnee (2014)
Crystalactor	full	CaP	http://www.nhm.ac.uk/research-curation/research/projects/phosphate-recovery/Nordwijkerhout/Piekema.pdf
EkoBalans	pilot	struvite and NPK	http://www.ekobalans.se/en/kretslopp/i-helsingborgs-stad.html
Fix-Phos	full	CaP/CSH	Petzet and Cornel(2012)
Gifhorn	full	struvite	http://www.asg-gifhorn.de/docs/2007-08-flyer-klaerschlammbehandlungsanlage.pdf
LysoGest	full	struvite	http://beta.eliquostulz.com/de/lysogest.html
Nuresys	full	struvite	http://www.nuresys.org/content/references
PEARL	full	struvite	http://www.ostara.com/sloughUK
Phospaq	full	struvite	Abma, W.R., Driessen W., R. Haarhuis en Van Loosdrecht, M.C.M. (2010) Upgrading of sewage treatmentplant by sustainable and cost-effective separate treatment of industrial wastewater. Water Science & Technology, 61(7), p. 1715-1722
P-RoC	pilot	CaP/CSH	http://kit-neuland.de/2012/uebersicht/die-phosphor-philosophie/
REPHOS	full	struvite	http://www.remondis-aqua.de/aq/industrie/leistungsspektrum/abwasserbehandlung/leistungen/
STRUVIA	pilot	struvite	http://phosph-or2014.irstea.fr/wp-content/uploads/2014/01/Nveau_Procede_Recyclage_P-Veolia.pd
Stuttgart	demo	struvite	http://www.recyclingmagazin.de/rm/news_detail.asp?ID=15423&SID=617061192168100100&NS=1
During or after incineration			
AshDec (Outotec)	planned	P mineral	http://www.outotec.com/en/Products--services/Energy/Phosphorus-recovery/
EcoPhos	demo	DCP	http://www.ecophos.com/#/en/operations/
Mephrec	planned	P mineral	http://www.nuernberg.de/internet/klaerschlammverwertung/
LeachPhos	planned	Struvite or DCP	http://www.bsh.ch/de/news/news-detail.aspx?nwsid=9
Thermphos	No longer in operation	P4	Schipper and Korving (2009)

In regions with intensive livestock farming, P recovery from manure has received much attention. Poultry manure is often incinerated because of its high organic matter content (high energy production) or is dried and exported. Dairy farmers often apply the manure from their cows on their farmland. Consequently, manure processing is mainly focussed on the treatment of pig slurry. Figure 3 gives an overview of the main routes for recovering P from manure slurries.

Nowadays, the most important route of pig slurry treatment is pelleting or composting the dried separated solid manure fraction and exporting the products to other regions. However, the transport costs are still high, and much pig slurry is rejected by crop farms because it has a low N:P ratio which does not match the requirements of most arable crops. This being so, it is more interesting to valorize the components of manure into valuable products.

The solid manure fraction can be used for bio-energy production through incineration and subsequent P recovery from the ash. Both the wet and dried solid fractions of manure can be incinerated depending on the specifications of the incineration plant. The advantage is that manure has a lower iron content than most sewage sludge, and therefore, P ash will contain less iron and is a better as a resource for elementary P production (Schipper and Korving, 2009). In addition, also commercial fertilizer industries are able to produce chemical P fertilizers from the P-rich ash.

Another option is to produce a P rich biochar via pyrolysis (Shafizadeh, 1982; Wang et al., 2014; Weber et al., 2014) or gasification (Schmieder et al., 2000; Wu, 2013). Pyrolysis is a process in which organic matter is heated indirectly to a temperature of 300–550 °C in the absence of oxygen. The organic matter is then converted into a char, pyrolysis oil, water phase, and a gas phase (syngas). The percentage of carbon that was originally present in the manure cake and remains in the char of the pyrolysis process is in the order of 60–70 %. Gasification involves the organic matter being broken down into a P rich biochar and combustible gases at temperatures of usually about 800–1000 °C in a low-oxygen environment. The fraction of the original amount of carbon present in the manure cake that remains in the char is relatively low, in the order of 10%, resulting in more CO_2 being produced than in the process of pyrolysis. Pyrolysis and gasification have potential advantages compared to incineration. A main advantage is that the combustible gases of both systems can be converted into electric power more efficiently. Due to the lower temperatures, the plant-availability of the P tends to be higher in pyrolysed biochar than in untreated P ash (after incineration) or in biochar produced via gasification. The growing interest in producing biochar is in response to the claim that biochar is a soil conditioner and may contribute to fewer emissions of greenhouse gases (Lehmann, 2007; Sohi et al., 2009; Spokas and Reicosky, 2009).
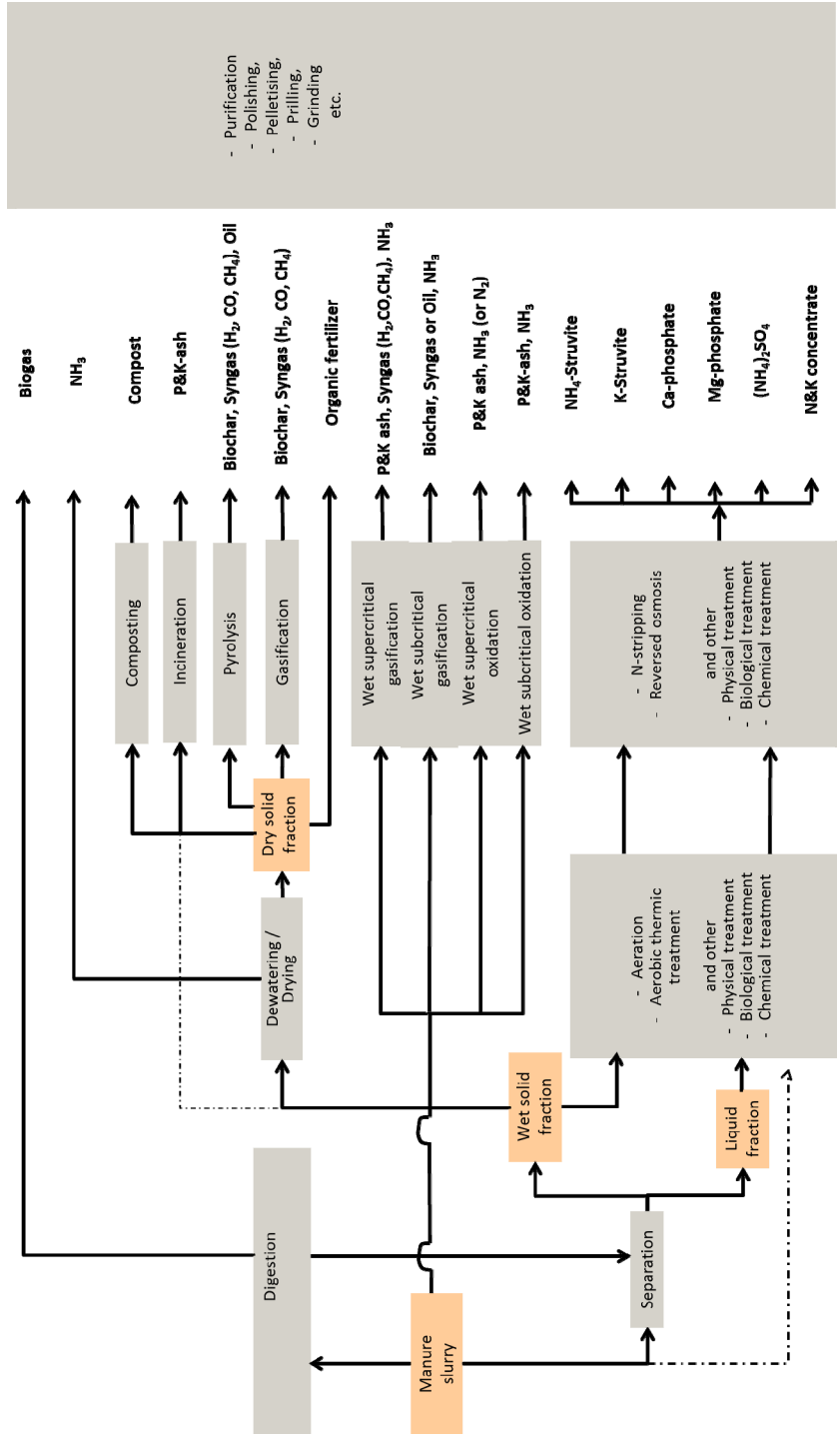
Figure 3. Schematic overview of the main options to recover nutrients from manure in different steps.

The complete P recovery from solid manure fractions via incineration, gasification and pyrolysis is attractive because of this manure's high organic matter content and energetic value. However, there should be also a solution for the disposal of the liquid fraction, since the techniques using whole manure as source are still in development (wet supercritical and subcritical gasification, and wet supercritical and subcritical oxidation; see Fig. 3). In regions with intensive livestock farming there is simply too little land available for applying the liquid fraction (with a high N content, and low organic matter content) and the cost for treatment of the liquid fraction is expensive, resulting in overall treatment costs of manure of €15–30 per ton pig slurry (Schoumans et al., 2010).

More attention has to be drawn to the development of simple precipitation techniques to recover only a part of the P in manure through precipitation of calcium phosphates and /or magnesium phosphates (e.g. struvite) as secondary resource for the fertilizer industries. In principle, the approaches and techniques are the same as for wastewater treatment, but the organic matter content is much higher, which negatively influences the precipitation and crystallization process (Cerrillo et al., 2014; Liu et al., 2013; Zhang et al., 2014). Nevertheless, P recovery via struvite precipitation gives good results in different types of manure (fractions), and high P recoveries (50–90%) can be obtained from the manure or liquid manure fractions, such as calf manure (Schuiling and Andrade, 1999; Siciliano and De Rosa, 2014), dairy slurry (Huchzermeier and Tao, 2012; Qureshi et al., 2008; Qureshi et al., 2005; Rico et al., 2011; Uludag-Demirer et al., 2005; Uysal and Kuru, 2013; Zhang et al., 2010)), pig slurry (Capdevielle et al., 2013; Jordaan et al., 2010; Nelson et al., 2000; Schoumans et al., 2014b; Shepherd et al., 2009; Suzuki et al., 2006) and even poultry manure (Yetilmezsoy et al., 2013; Yilmazel and Demirer, 2013; Zhang and Lau, 2007). High P recoveries (up to 80%) from manure or the solid manure fraction can also be obtained using a technique in which acid is applied to release P from the solid fraction into solution, filtering the solution followed by addition of calcium(hydr)oxides to cause calcium phosphates to form (Schoumans et al., 2014b). Since most of the P is in the solid manure fraction, the absolute P recovery is high, but the cost of recovering P is higher than in the case of struvite production (Schoumans et al., 2014b). The main advantages of partial P recovery from manure are that the ratio of N and P in manure becomes more in line with the crop requirements, the organic matter can still be used as a soil conditioner, less chemical P fertilizer is needed and less needs to be spent on exporting manure from areas with a mineral surplus.

Improving the Utilization of P Stored in Soils
In general, not more than 10–20% of the applied P is taken up by crops in the first year following application. The remainder is accumulated in the soil, and is a source for crop uptake in the next years (Nuruzzaman et al., 2005; Syers et al., 2008a). When a

certain target soil P status has been reached, the P application rate should not exceed the P withdrawal with the harvested crop. In several areas in Europe, soil P status is higher than the target soil P status, especially in regions with intensive livestock production and with vegetable productions. In these regions, P applications can be withheld or the P application rate can be less than the P withdrawal with the harvested crop, because the crop can utilize the residual P of previous applications.

Tunney (2002) and McDowell (2012) argue that there is a small agro-environmental target zone of soil P contents where optimal crop yields and limited P losses can be achieved (Fig. 4). Increasing the soil P status above that target zone would be economically and environmentally unwise. In case the soil P status is above the target range, efforts should be made to decrease the soil P status, through lowering the P application below the level of the P withdrawal with harvested crop, resulting in mining of the soil. It has been argued that the relationship between soil P status and the risk of soil P losses exhibits hysteresis, which means that the relationship between P sorption and P desorption versus the P equilibrium P concentration differs (Barrow, 1983) and consequently, loading the soil with P to a high soil P status is associated with a higher risk of P losses than mining the soil P (Schoumans and Chardon, 2015) as expressed with the dotted lines in Figure 4. However, it is unclear whether growing crops will be able to access the residual soil P at a sufficiently high rate to meet the demands at all growing stages under mining conditions. A main challenge will be to manage the residual P in soils and the recycled P fertilizers in such a way that optimal crop growth can be achieved with minimal P losses at reduced soil P levels. If so, the availability of residual P in soil for growing crops and the availability of recycled P fertilizers have to be reconsidered in the fertilizer recommendation schemes for farmers.
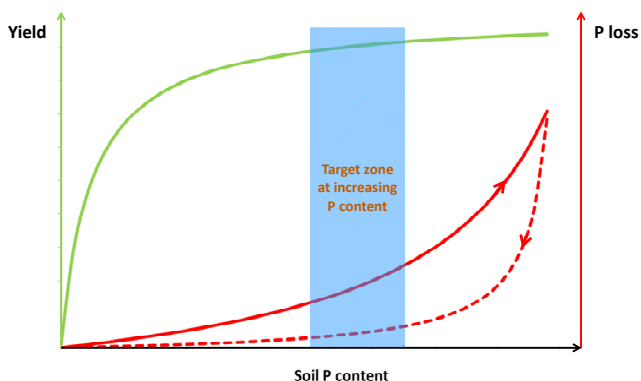
Figure 4. *Conceptual representation of yield and phosphorus (P) loss at increasing soil P content (solid lines) and associated optimal agro-environmental target zones, according to Tunney (2002). Dotted line represent the expected P loss at decreasing soil P content due to mining according to Schoumans and Chardon (2015).*

Impact of Climate Change on P Fate and Losses

The impact of climate change on the fate of P is difficult to evaluate, due to the multitude of antagonistic and synergistic processes involved in P cycling and transport from source to the fresh waters and finally to the sea. Expected climate change will impact P fate not only directly but also indirectly through effects on the hydrology, on land use and land management – including increased water abstraction, increased fertilization and changes in ecosystems' composition and functioning. Phosphorus cycling will be affected by changes in temperature and soil moisture regime, and P losses will be affected by changes in the timing and intensity of precipitation.

It is predicted (IPCC, 2013) that Europe will experience a significant rise in temperature, while precipitation will increase in Northern Europe and decrease in Southern Europe, with large seasonal variation. Furthermore, it is predicted that extreme climatic events will become more frequent, including heavy precipitation events, heatwaves, extended low flow periods and droughts. Consequently, climate change will impact the hydrology of most European catchments and will affect the dilution and concentration of phosphorus in surface waters. Recently, the observed increased rain amount during the intense rain events in the Lake Erie has led to an increased phosphorus loading to the lake through runoff, enhancing algal blooms (Sharpley et al., 2015).

Climate change will affect residence and travel time, leading to increased deposition of particulate phosphorus in streams during summer low-flow periods (Whitehead et al., 2009). On the other hand, in Northern Europe, climate change will lead to greater and more frequent flooding, with more interactions between the streams and riparian areas, leading to higher deposition rates of sediment and particulate phosphorus in these areas. Furthermore, extreme high flows and flood events will reduce the retention of phosphorus in streams and will enhance the degradation and transport of particulate phosphorus from stream banks; additional phosphorus loads are expected from more frequent flushing of sewer overflows (Withers and Jarvie, 2008).

It is predicted that P loads will increase in Northern Europe, due to increased surface winter runoff and associated sediments (Arheimer et al., 2012), but with large inter-annual variability which might mask the long-term changes expected at the end of the 21th century. An increase of total phosphorus load to the Baltic Sea by 15% is expected in the upcoming 100 years due to climate change (Hägg et al., 2013). An increase of total phosphorus loading by 2050 is predicted for the whole Europe but mostly due to increase discharge from waste water treatment plants and manufacturing (Reder et al., 2013). However, a decrease in river discharge due to climatic change will reduce total P concentration in European streams (Reder et al., 2013). This phenomenon is

expected to occur in Ireland, where wetter winters and drier summers with decreased flow are predicted (Jordan et al., 2012).

In Southern Europe, higher evapotranspiration, reduced precipitation and thus a lower water flow are also expected to result in increased concentrations of nutrients, including phosphorus, particularly in river basins dominated by WWTP discharges or by high background P losses. In addition, despite the predicted decrease of annual runoff, very intense rainfall events will be more frequent in Southern Europe, and therefore erosion rates and phosphorus loads will increase (Molina-Navarro et al., 2014).

Higher temperatures are associated with higher mineralization rates (Withers and Jarvie, 2008), resulting in soluble phosphorus being more available in the soil profile. The higher water temperature in streams will boost and prolong biological activity, leading to higher primary productivity and higher phosphorus uptake. Similar processes are expected to occur in rivers and lakes. Higher temperatures will increase the release of P from bottom sediment (Feuchtmayr et al., 2009) because the biological activity is higher and continues for longer in the warmer waters, the stratification of organic matter continues also for longer, and higher temperatures increase mineralization of the organic matter in these sediments. Due to prolonged stratification and lack of mixing in lakes, nutrient concentration will decrease at the top of the water column and increase at the lower end of the water column (Jeppesen et al., 2009).

Discussion

Europe has a long history of net P accumulation due to the large import of P fertilizers (Fig. 1, Table 1) over the last decades. In 2005 a total of 2569 Gg P has been imported to the EU-27, of which 1487 Gg P in P fertilizers and the remainder in food and feed, whereas only 592 Gg P has been exported (Table 2). Currently, overall P exports from the EU-27 are only 22% of the amount imported, resulting in high P accumulation (in waste and soil; Table 2). Since Europe does not have many phosphate mines and global phosphate rock reserves are limited, there is a need for Europe to close the P cycle.

There is limited scope for reducing the import of P fertilizers by reducing or temporarily abandoning the chemical fertilization of agricultural land with a high P status. That is because such soils are often located in regions with large manure surpluses where the use of P fertilizer is already low. The prospects for reducing the import of P via animal feed seem to be better. Because the feed components are cheap, the P content in the feed exceeds the requirements of the livestock; it seem to be possible to reduce P imported in feed by 20–25% (Esmaeilipour et al., 2012; Maguire et al., 2005; Van Krimpen et al., 2012) without consequences for the health of

the animals. However, such a reduction would have a limited effect on the total P import to Europe.

A substantial part of the net P accumulation in Europe is applied on agricultural land as manure (817 Gg P) and can contribute to the maintenance or improvement of the soil P fertility in areas with a relatively low soil P content. However, P tends to be applied mostly in regions with intensive farming (livestock and/or crop production), where the soils already have high soil P status, thereby increasing P losses to groundwater and surface water (EEA, 2012a).

The European P cycle could be completely closed and European water quality could be improved if imported chemical P fertilizers were fully replaced by chemical and organic P fertilizers recovered from waste streams (from non-food, food, households and manure; maximum about 1900 Gg P; see Table 2), which can be transported cost-efficiently within Europe (SCOPE, 2014). Several techniques are available for recovering P from non-agricultural waste streams (1000 Gg P; Table 2). The incineration of domestic and industrial sludge into P ash and the production of struvite or calcium phosphate from wastewater streams seem to be reliable techniques and are already operating at full scale in North-Western Europe (Table 3). P recovery from manure (potentially about 900 Gg P as amount of P accumulated in soils and amount of manure losses, see Table 2) and conversion into chemical fertilizers is less developed. There are currently no financially attractive options which can compete with the production of fertilizers based phosphate ore, especially if the organic matter (with a low P content) needs to be retained as soil conditioner. However, a number of initiatives and research projects have started studying simple low-tech options for recovering P via different techniques as shown in Figure 3. The economic success will depend on the overall costs of recovering P and the cost savings for farmers who have to transport the solid P-rich fraction of manure over long distances from regions with intensive livestock farming to areas with low soil P content.

Especially, in the intensive livestock regions the soil P status is higher than the target soil P status and, from an economical and environmental point of view, the P applications can be less than the P withdrawal with the harvested crops. A main challenge will be to manage the residual P in soils and the recycled P fertilizers in such a way that optimal crop growth can be achieved with minimal P losses at reduced soil P levels. If so, the availability of residual P in soil for growing crops and the availability of recycled P fertilizers have to be reconsidered in the fertilizer recommendation schemes.

The P losses from agricultural land to surface water are small compared to the total P balance (164 Gg, which is 6% of 2659 Gg P; Table 2). However, the consequences for

the ecological quality of Europe's fresh surface water systems are substantial, because diffuse P pollution is seen to be one of the most important factors affecting the eutrophication status of freshwater systems. Losses from agriculture have to be reduced in order to meet the objectives of the Water Framework Directive (EEC, 2000). The Nitrate Directive (EEC, 1991b) regulates the total amount of nitrogen (N) applied on agricultural land, but in most European countries the amount of P applied is not regulated (Amery and Schoumans, 2014). In addition, climate change will affect the nutrient losses from land to waters and could undermine the effectiveness of mitigation options. Only a few studies have focussed on the consequences of climate change on diffuse pollution to surface water. The assessment of climate change impact on the surface water quality is complex, because temporal and spatial changes in temperature and precipitation directly influence the crop–soil system and all biological, chemical and physical processes, leading to changes in P concentrations, water flows and pathways. It is expected that due to excess P the surface water quality will decrease, but the causes differ regionally in Europe. In Northern Europe more frequent freezing-thawing of the soil will further accelerate P losses since this will negatively influence resistance again soil erosion and enhance P leaching (Blackwell et al., 2010) in combination with less retention in surface water In Southern Europe the P concentration in surface water will increase due to higher evapotranspiration, reduced precipitation and thus lower flow, and to greater erosion losses due to more frequent rain events. However, it is important to mention that the current large inter-annual variability might mask the long-term changes (Arheimer et al., 2012). Nevertheless, the options to reduce P losses to surface water (Schoumans et al., 2014a) have to be evaluated in terms of Water Framework Directive measures that are 'climate-change proof', because the costs (investments and maintenance) of reducing P losses are often high. Such an evaluation should be part of all national action plans to reduce nutrient losses to groundwater and surface water.

For achieving progress towards a circular P economy, active involvement of all actors and stakeholders in the P use chain is required. Several platforms and initiatives at European, regional and national levels have already been established involving all relevant stakeholders. This will contribute to an integration of the options for P recycling and valorization of P waste streams. Involvement of policy makers in these platforms is a prerequisite to ensure that any possible legal barriers are not obstructing possible sustainable solutions. Further, a broad public awareness is needed, as consumers should become more involved in the public debate about minimizing P losses and wastes and the recycling and reuse of wastes.

Conclusions

The management of P in Europe has to change because global reserves of P are running out, Europe is very dependent on the import of P, and also because climate

change will affect Europe's freshwater quality. The import of P can easily be reduced by (i) applying P fertilizers only where required, (ii) taking into account the amount of P forms in the soil (fast and slow release), and (iii) by reducing the P content in feed to meet the actual dietary requirements of the animals. The biggest reductions can be obtained by reducing or even stopping the import of chemical P fertilizers by recovering P from waste streams and manure and by cost-efficiently transporting the resulting fertilizer products to regions with less P. There are many options to recover P, but many techniques still have to be tested in practice at pilot and full scale, especially those for recovering P from manure. Such effective strategies will increase the efficient use of P and consequently reduce the P losses to the environment, especially when fertilizer P application is fully adjusted to the actual release of P in soils. This P source approach will also help to reduce the rise in P concentrations in surface water that climate change is expected to bring about. Although many measures are available to reduce P losses from agricultural land, they need to be re-evaluated in terms of their climate-proof effectiveness for addressing the objectives of the Water Framework Directive in the long term.

CHAPTER 11

General discussion and synthesis

Introduction

Diffuse nutrient losses from agricultural land to surface waters are a major and important source of eutrophication of inland fresh water systems. The water quality is especially poor in Northwest Europe (EEC, 2012) and P is often considered as the limiting nutrient in freshwater systems (Carpenter, 2008; Herath, 1997; Lee, 1973). The main aim of the European Water Framework Directive (EEC, 2000) is to improve water quality. An important aspect is a reduction of P loads from agriculture because the P load of surface waters from point sources has been reduced remarkably in recent decades (EEA, 2012b).

In order to reduce the diffuse P losses from agricultural land, information is needed on the contribution of each field (area) within a catchment to P losses to surface water. In the Netherlands most of the rainfall surplus flows through the soil to groundwater, or via tile drains to surface water bodies. Phosphorus is mainly present as inorganic P in manure (Bril and Salomons, 1990; Gerritse, 1977; Gerritse and Vriesema, 1984) and in mineral fertilisers that are applied on agricultural land. These phosphate components in the applied P are often easily soluble, leading to high P concentrations penetrating the soil or to high P concentrations in surface runoff.

In this thesis the main focus is on the risk assessment of P losses to surface waters in flat areas caused by leaching of P through the soil, and on options to reduce P losses from agricultural land in order to improve the surface water quality. In the Netherlands the main soil types are non-calcareous sandy or clay soils, peaty clay soils, and calcareous sandy or clay soils. Much information is available on the behaviour of P in non-calcareous soils where aluminium and iron dominate the extent and kinetics of P (de)sorption. Less information is available on the kinetics in peaty clay soils and in calcareous sandy soils, while in the Netherlands relatively high P concentrations are observed in surface waters in regions with these soil types (De Klijne et al., 2007; Groenenberg et al., 2013; Klein et al., 2012b; Portielje et al., 2002). Therefore, the first research question was to study the vulnerability of Dutch peaty clays soils and calcareous sandy soils to P losses.

In order to predict the potential risk of P losses to surface water and to evaluate options to reduce this, information on the behaviour of P in those soil types is needed and that the behaviour of P in those soil types can be described. The second research question focussed on the development of P risk indicators for easily assessing the potential and actual risk of P losses to surface water at local (field) and regional or catchment scale. These indicators will be helpful for selecting areas which contribute substantially to the P losses to surface waters. First, I used the approach of the P saturation degree (Van der Zee et al., 1990a) to determine the potential losses from agricultural land to groundwater from different soil types. Secondly, methods were developed to determine the current P losses from land to surface water. The information of sources ad pathways of P losses to surface water was used to develop

management strategies to reduce P pollution of the surface waters (third research question).

In order to acquire evidence-based information the following objectives of this thesis were addressed (par. 1.6):
- To quantify the capacity of peaty clay soils and calcareous sandy soils to bind and release mineral P, the main P form in manure and in mineral P fertilisers;
- To estimate the area of phosphate-saturated soils in the Netherlands as indicator of the potential risk of P leaching;
- To develop new methods for quantifying the actual risk of P pollution;
- To give an overview of mitigation measures to reduce P pollution from land to surface waters and strategies for a better closure of the P balance.

Phosphate kinetics in peaty clays soils and calcareous sandy soils

Peaty clay soils are located in the polders in the west and northwest of the Netherlands. Their organic matter content is high and clay material is mainly observed in the upper 60 cm of the soil profile. The P sorption capacity of lowland peaty clay soils is determined by a fast reversible reaction and a time-dependent poorly reversible reaction (Chapter 2). The fast reaction can be described by the Langmuir equation and the slow sorption reaction by means of the time-dependent Freundlich equation. The P sorption capacity (PSC) of peaty clay soils is related to the oxalate-extractable Al and Fe contents, just as in acid sandy soils, and even the maximum phosphate sorption capacity is similar ($PSC_{max} = 0.5*(Al+Fe)_{ox}$). Hence, since the aluminium and iron contents often decrease with depth, the capacity to bind P also decreases with depth. The amount of easily reversible bound P (Q) is also related to the amounts of oxalate-extractable Al and Fe. However, the maximum amount of P that can be easily reversibly bound (Q_m) varies with the depth of the soil profile. In the upper layers of the soil profile (about 40 cm), the maximum of Q_m is about one third of the maximum P sorption capacity (PSC_{max}), while in the subsoil (80-120 cm below surface) the proportion is about two thirds. In layers with a high organic matter content, all the sorbed P is readily available. This means that P that has been leached from the upper layers will be poorly bound because of the lower P sorption capacity in the subsoil, in combination with the fact that most of the P is reversibly bound. It can be concluded that peaty clay soils are indeed vulnerable to P leaching.

The calcareous sandy soils in the Netherlands are located in the western coastal area. They are mainly coarse sandy soils: the $CaCO_3$ content in the soil samples studied ranges from 0.2 to 2.7% and the Al and Fe contents are lower than in non-calcareous soils. It is known that in calcareous soils three reaction mechanisms are important (1) a fast reversible surface adsorption reaction, (2) a fast precipitation reaction of easily soluble calcium phosphates on the surface of calcite ('nuclei growth'), and (c) a time-

dependent precipitation of a poorly soluble calcium phosphate caused by calcium phosphate cores clumping into crystals (Chapter 3). As the first two reactions cannot be studied separately with laboratory batch experiments, the fast and easily soluble overall reaction of P (Q) was measured, which could be described well with the Langmuir equation. The slow precipitation reaction of the poorly soluble calcium phosphate was described by the time-dependent Freundlich equation. It was found that the maximum capacity of the soil to bind P was not related to the $CaCO_3$ content of the soil samples. The maximum P sorption capacity of the samples ranged from 6 to 11 mmol P kg^{-1}. Compared to non-calcareous soils and peaty clay soils, in these calcareous sandy soils only a small part of the maximum total P sorption capacity consists of reversibly bound P (5%–15%), and the sorption strength (K) of this fraction is very low. If the amount of easily soluble P varies between 0.1 and 0.5 mmol kg^{-1}, the concentration in soil solution will already range between 3 and 8 mg P L^{-1}. Over time, these high P concentrations will be found in groundwater and drainage water. Such concentrations leaching from the topsoil far exceed the target P concentrations in surface waters. Consequently, coarse calcareous sandy soils can be considered as vulnerable to P leaching, especially if the P content in the soil increases.

Relationship between soil fertility P parameters and soil chemical parameters

In the Netherlands, two soil P fertility indexes have been used most often during recent decades: the Pw value (based on a water extraction of the soil (1:60 v/v) and mainly used for arable land) and the PAL value (based on an ammonium lactate extraction of the soil and mainly used for grassland). When a process description of P sorption and desorption in the soil is used for calculating the P concentration in soil solution, the soil fertility parameter Pw can be described adequately (Chapter 5). The parameter PAL can be assessed using a linear regression equation depending on the following variables: (1) the amount of reversibly bound P (Q_o) measured with the infinite sink method, (2) the total amount of hardly soluble P (S_o, which equals the amount of oxalate-extractable P (P_{ox}) minus Q_o) and (3) the oxalate-extractable Al and Fe contents of the soil (respectively Al_{ox} and Fe_{ox}). In this way the agronomical parameters Pw and PAL can be related to the parameters that determine the P concentration in soil solution and the potential risk of P losses to groundwater and surface water. However, in order to assess the actual risk, the hydrological conditions also need to be taken into account.

P risk assessment

The potential risk of groundwater pollution with P can be determined with the so-called Phosphate Saturation Degree (PSD) approach developed for non-calcareous sandy soils (Van der Zee et al., 1990a). The P concentration in the leachate at a certain reference depth (L_{ref}) depends on the soil's affinity to bind P reversibly (determined by the Langmuir adsorption constant K) and on the ratio between the maximum amount of reversibly bound P (Q_m) and the maximum total P sorption capacity (PSC_{max} or F_m). If a maximum acceptable P concentration for the reference depth is set, the critical PSD can be determined. In the Netherlands the Technical Committee on Soil Protection (TCB) has advised the Dutch Government that it is necessary to ensure that P losses do not cause an increase of the natural background concentration of P in groundwater. For acid sandy soils a background concentration of 0.1 mg L^{-1} ortho-P was chosen, resulting in a critical PSD (PSD_{crit}) of 25%. This means that in the soil layer from the surface to reference depth L_{ref}, the total amount of accumulated mineral P in the soil should not exceed 25% of the total P sorption capacity. The TCB advised using the mean highest groundwater table as reference depth. Using this approach, a PSD_{crit} could also be set for other soil types in the Netherlands (Chapter 4). For this purpose, background concentrations were determined based on concentration in deeper groundwater, and the soil-specific P sorption and desorption characteristics were used. As a result of these conditions and parameters, the soil-specific PSD_{crit} increased in the following order: peaty clay soils (5%), calcareous sandy soils (23%), non-calcareous sandy soils (23%), non-calcareous clay soils (31%), and calcareous clay soils (78%). Based on information from a stratified soil survey (performed in the period 1992 – 1998), the area of P-saturated agricultural soils was determined. At that time about 43% of the agricultural soils had a PSD higher than the PSD_{crit} for their soil type, and high P accumulations were measured in soils, ranging from 2000 to 10 000 kg P_2O_5 ha^{-1}. Since that survey, the average P accumulation in soils has increased by about 300 kg P ha^{-1} (CBS, 2013), which is equivalent to approximately 700 kg P_2O_5 per ha. Consequently, the average PSD of the soils and the P-saturated area in the Netherlands must now be even greater. The distribution pattern of this excess of P accumulation over agricultural land is unknown, and therefore the current PSD and area of P-saturated soils cannot be accurately calculated. However, this approach does show that there is a potential risk of long-term P pollution of groundwater, and consequently of long-term increased P losses to surface water bodies, which is probably underestimated.

Modelling approaches can be used to assess the geographic distribution of areas at high risk of P losses. Different modelling approaches are available, from process-oriented (mechanistic of deterministic) to data-oriented, and have been used to assess the P losses at catchment scale. In the EUROHARP project, different model approaches were compared (Chapter 6). Most of the models are able to give valid results of the P

losses at catchment scale, after model calibration at catchment scale. The advantage of process-oriented models is that they are better able to assess the effect of management strategies on the P losses via scenario analysis. Their disadvantage is that these deterministic models are quite complex and need many input data. In this study, two simplified methods were developed to assess the actual risk of P pollution. The first approach is based on soil fertility and environmental parameters and on the hydrological characteristics of a field, and is called the PLEASE method (Phosphorus LEAching from Soils to the Environment) (Chapter 7). The calculated P leaching losses at catchment scale are highly sensitive to the Langmuir parameters used, which determine the reversible sorption behaviour of P in soils. The PLEASE approach is a promising method for quantifying differences in P loss by leaching from fields within a catchment. The second approach is called SIMPLE (Smart prediction of the Impact of Management strategies on Phosphorus losses by LEaching) (Chapter 8). The SIMPLE model mimics the output of a complex dynamic water quality model used in the Netherlands (ANIMO). It does so using statistical relationships between the predicted P losses and the most relevant input parameters that can be easily gathered from maps or from a soil survey. This simple meta model has proved to be a powerful tool for a quick assessment of the risk of P pollution from agricultural land to surface waters by leaching and surface runoff, based on catchment characteristics.

Comparison of the P risk assessment approaches developed in this study
In chapter 7 the results of PLEASE were compared with the PSD approach in the Schuitenbeek catchment and it was shown that even at low PSD values the P losses can be greater than the background losses. On the other hand, at high PSD values the P losses can still be relatively small, because most of the water fluxes in the field originate from deep layers. To show how the risk assessment approaches presented in this thesis differ from each other, the results were compared for the Schuitenbeek catchment. The data collected from this catchment to calculate the PSD and run PLEASE can also be used to assess the P losses with the SIMPLE approach. However, it was too complex and time-consuming to apply the NL-CAT dynamic model to calculate the daily P losses for the Schuitenbeek area, so the results of the STONE model (Wolf et al., 2003) are presented below. The soil and hydrological parts of the STONE model are the same as those described for the dynamic NL-CAT model (Chapter 6). The results of the latest application of the model at national scale (Groenendijk et al., 2012) were used to calculate the annual average P losses within the Schuitenbeek catchment. This means that the dynamic model was not applied using regional information on the Schuitenbeek area.

Since the PSD of the soils in the Schuitenbeek catchment was calculated from stratified soil samples for combinations of mean highest groundwater level (MHW), the average P loss for those combinations was also calculated. The following highest groundwater

level groups were distinguished: groundwater tables (GT) II/III with a mean MHW in the layer 0-25 cm deep (very wet soils); GT V (MHW: 25-40 cm; wet soils); GT IV/VI (MHW: 40-80 cm; moderately dry soils) and GT VII (MHW: > 80 cm; dry soils). Figure 1 shows the overall results of the measured average PSD and the annual P losses predicted with PLEASE, SIMPLE and STONE, taking into account the groundwater groups and land use.
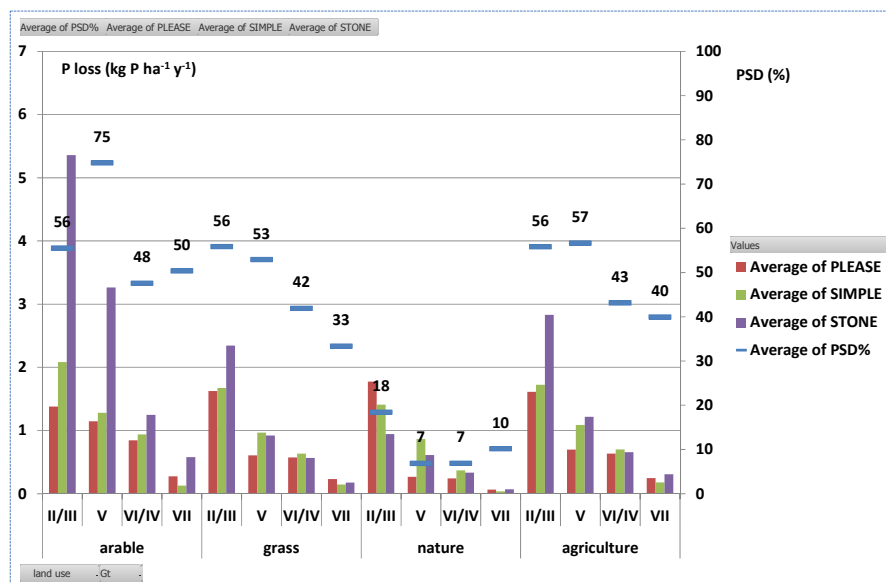
Figure 1. *The measured average PSD, and estimates of the average annual P losses according to the PLEASE and SIMPLE approaches and the STONE dynamic model.*

The average PSD of the arable land (57%) is higher than the PSD of grassland (46%) because much of the manure surplus was applied on maize land in the past. The PSD of the nature conservation area (11%) is on average below the value of 25% that has been set as critical value for acid sandy soils. As expected, the PSD of dry soils (VI/VI & VII) is lower than the PSD of rather wet soils (II/III and V), because in the definition of the PSD the MHW is taken into account. If the MHW is deeper, the P sorption capacity of the soil is greater, and consequently the PSD will be lower (assuming a similar P accumulation in the soil).

For all types of land use there is a clear tendency for the calculated actual annual P loss to be lower with deeper mean highest groundwater (Figure 1), regardless of which of the methods is used to assess P loss. The differences in predicted annual P loss are small between the PLEASE, SIMPLE and STONE approaches under relative dry conditions. For wet to very wet soils the STONE model calculates substantially larger annual P losses, because during the year there are large P losses when rainfall is very

intense or conditions are very wet, especially on soils with large P accumulation. Finally, by comparison with the STONE dynamic model, the PLEASE and SIMPLE approaches seem to over-estimate the P loss for wet to very wet nature areas. Although there are differences in the absolute value of the estimated P losses, the sequence in P loss estimates between land use and groundwater table groups is very similar. This emphasises that the simplified approaches PLEASE (field scale) and SIMPLE (regional scale) are powerful tools for assessing the P risk of agricultural areas in a catchment.

Figure 2 shows the regional distribution of the PSD and the assessment of P loss for the groundwater table (GT) groups according to the three approaches (PLEASE, SIMPLE and STONE).
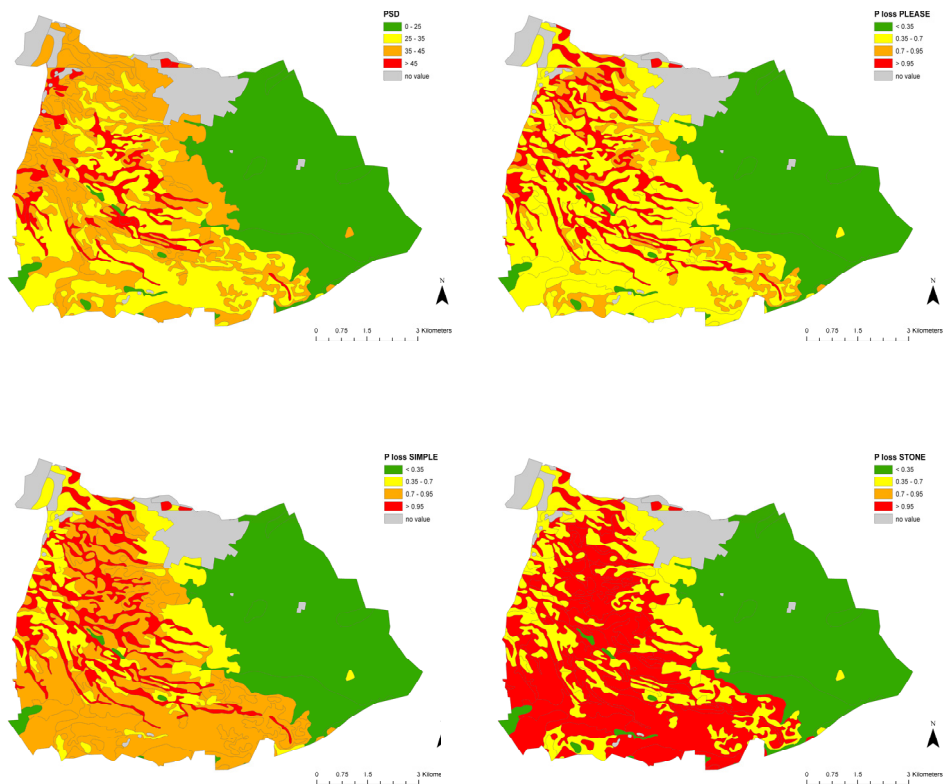
Figure 2. *Maps of the average PSD (%), and estimates of the average P losses (kg P ha^{-1} y^{-1}) for the Schuitenbeek catchment according to PLEASE, SIMPLE and STONE.*

In the eastern part of the Schuitenbeek area the main land use is forest, which has a low PSD and low P losses. The highest PSD values are located in the centre and west of the Schuitenbeek catchment, partly in the valleys of the Schuitenbeek. The P loss estimates by the PLEASE and SIMPLE approaches show that there are probably high P losses in the stream valleys of the Schuitenbeek (red areas). The main difference between the results of the SIMPLE and PLEASE approaches is that a large part of the areas that are yellow when the PLEASE method is used shift to orange (higher P losses) when SIMPLE is used. This is in line with the results presented in Figure 1, i.e. the P losses predicted by SIMPLE are higher than those predicted by PLEASE. The highest P losses are calculated with the STONE approach (Figure 1) and consequently a larger part of the Schuitenbeek catchments is assumed to contribute strongly to the P losses to the surface water (Figure 2). It is evident that there are differences in the calculated P losses between the three models, mainly because of differences in their underlying concept, the data they require and the uncertainties in their parameters and data.

Unfortunately, no measurements are available of the spatial distribution of P losses within the Schuitenbeek, so no hard evidence can be presented on the goodness of fit of these approaches, merely an illustration of their differences and similarities. However, if different methods/approaches give similar results, there is stronger proof that there is an identifiable risk of P losses from land to surface waters. Such an ensemble modelling approach (using several models for the same catchment) is an important methodology for distinguishing areas at risk for high P losses, as demonstrated in the EUROHARP project (Kronvang et al., 2009a). From these model applications it is clear that the main risk areas for P losses are the stream valleys of the Schuitenbeek catchment. Although the total P loss estimated by PLEASE for the whole catchment (chapter 7) agrees reasonably well with the P discharges measured downstream (after taking into account the estimated P retention in surface water), there is still uncertainty about the level of P losses from a part of the agricultural area in the Schuitenbeek catchment. However, using the maps shown in Figure 2, some sub-catchments can be selected in which the surface water quality could be measured to ascertain which of the model approaches fits best in the areas of less certainty. By combining model approaches and surface water measurements much more information will become available on the contribution of agricultural areas within a catchment than when only routine surface water measurements are used, since to measure is to know, but only if it is known what is being measured. Clearly, models are helpful tools for interpreting the surface water quality data.

Management strategies to reduce P losses from agricultural land
Approaches for the assessment of the risk of P losses based on soil characteristics and hydrological circumstances are important instruments to quantify which areas need further attention for reducing P losses from agricultural land to surface water. Within

COST Action 869 (2006-2011) an inventory was made of mitigation measures to reduce diffuse P pollution. As described in Chapter 9, in total, 83 measures were evaluated in terms of their suitability and cost-effectiveness in reducing nutrient loss from rural areas to surface waters at catchment scale, including the feasibility of the options under different climatic and geographical conditions. The measures were grouped according to whether they related to the management of farm, field, landscape, or surface water systems. The mechanisms underlying most measures can be well described, but data on their effectiveness under different conditions is still poor and needs further attention.

Management options dealing with measures in surface water are often able to improve the surface water quality in the short term, but it is important to continue implementing the measures. Furthermore, such measures are end-of-pipe measures, and a more sustainable approach requires more source-oriented measures, such as the original P saturation 'strategy'. Surface water measures associated with landscape management mainly focus on the settling of eroded, which is less relevant in the Netherlands but will be effective in hilly and mountainous areas.

The most promising measure to decrease the P losses in the long term is to reduce P application rates, and even better, to lower the P content of fields that contribute to the P load of surface water. The soil P fertilisation recommendation system used in the Netherlands advises that at a high soil P status, no P should be applied to agricultural land. However, under the Dutch Manure Act, P may still be applied on these soils, mainly because of the high manure surplus in the Netherlands. This policy will delay the improvement of surface water quality, especially in agricultural areas that contribute substantially to the P load of surface water. However, for the further development of P management of agricultural land, a more agro-environmental approach is needed, which should take into account the actual risk of P pollution of the surface water. From the findings on the application of the tools for assessing P risk that have been presented in this thesis, it is clear that such an agro-environmental approach can be developed. For example, a more efficient P application standards regime which also takes account of the hydrology aspects could be introduced, instead of general application standards based solely on the soil P status. Furthermore, via the '4R farmer stewardship' (right P source, right amount, right place and right time) the P efficiency can be increased and P losses can be further reduced.

By improving the infiltration capacity of the soil, P losses via surface runoff can be reduced, contributing to less P loss to surface water in the short term. Reductions in P losses in the short term can also be achieved via active water management such as controlled drainage. However, attention has to be paid to pollution swapping, because

nitrate losses may increase if the denitrification capacity of the soil is reduced as a result of lowering the groundwater table.

Many of the mitigation measures studied in this thesis are no-regret measures, such as preventing farmyard losses, and runoff losses caused by trampled and compacted soils (feeding places, farm tracks, etc.), and should be implemented as part of Good Agricultural Practice (GAP). An important prerequisite for a sustainable agro-environmental P approach is that the soil P balance of each field is based on the P status of the soil or, even better, on the soil's carrying capacity for P or on actual P losses. On farms with a high soil P status this reduces the amount of P that can be applied on agricultural land and increases the farm's P surplus. The need to export manure from the farm can be minimised by reducing the farm's import of fertiliser P and of feed with a high P content that exceeds the P requirements of the livestock, as discussed in chapter 10. Furthermore, a smaller volume of manure has to be exported if it is separated into a liquid fraction rich in nitrogen and potassium that can be applied on the land, and a P-rich solid fraction that can be exported. Since P is an important and irreplaceable finite source for food production and for the functioning of all living species on Earth, there is a need to increase the re-use of residual agricultural P biomass products (e.g. plant residues and animal manure). Furthermore, P has to be recovered from waste streams, for use as a secondary resource for industries. There are many options for recovering P from manure and industrial and domestic waste streams (chapter 10).

The steps described above need to be taken in order to reduce Europe's high dependency on the import of P fertiliser and feed, since Europe has no significant P rock mines, and also in order to develop a strategy to close Europe's P balance. The recently published EUROPE2020 strategy will facilitate such a sustainable development, since a resource-efficient Europe is one of the aims of the EUROPE2020 strategy. This can also be beneficial for introducing an agro-environmental P-sound approach, which is needed if we are to meet the objective of the Water Framework Directive: to improve the surface water quality in freshwater systems that are P-limited for most of the time. The expected negative impact of climate change on the surface water quality (chapter 10) emphasises the urgency of introducing such an agro-environmental P-sound approach, via recovery of P from waste streams, and the implementation of climate-proof mitigation options (chapter 10).

Recommendations

- In order to improve the surface water quality, more attention should be paid to soils which are vulnerable to P losses due to their low P sorption capacity and/or release relatively large amounts of P at a low phosphate saturation degree (PSD). Examples in the Netherlands are peaty clay soils and coarse calcareous sandy soils.

- In order to implement mitigation measures to reduce P loss at the right places within a catchment, risk assessment approaches which can assess the actual P load to surface water should be used instead of the commonly used PSD as measure of the potential risk of P loss. The PLEASE and SIMPLE P risk approaches to determine the actual P losses have been developed for the ranking of fields or areas within a catchment with low to high P loads, and are powerful tools for identifying areas at high risk of P loss.

- Although many measures are available for reducing P losses to surface waters, there is a need for a differentiation in P application standards that takes account of the environmental carrying capacity of the soil or the actual P losses from the soil to surface water. This would facilitate the development of sustainable agricultural practice that contributes to meeting the Water Framework Directive objectives.

- Besides the need to reduce P losses to surface water, there is also a need to close the P balance at national and European scales. Recovery and valorisation of all or part of the P in animal manure so that it becomes a secondary raw material for industry would enable the agricultural sector in Europe to reduce its dependence on the import of fertilisers, and consequently would mean more manure and organic matter could be applied on agricultural land as soil conditioner. In this way, the P balance could be better closed at farm, regional, national and European scales.

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Summaries

Summary
Samenvatting

Summary

Introduction

Phosphorus (P) is a finite irreplaceable element for all living species on earth. The use of P has greatly contributed to the increase of food production for two reasons: (1) the import of P in feedstuffs for the increased numbers of livestock and (b) the import of fertiliser P to raise the soil P content and to meet the crop-dependent P requirements in order to boost crop yield. In the Netherlands and in many other Western European countries or regions, the import of P exceeds the export of P. Since agriculture is the main consumer of P, much of the P has accumulated in agricultural soils, causing environmental losses to surface waters and having major ecological consequences such as eutrophication.

Successful P management strategies are needed to improve the surface water quality. In the first place, quantitative information on the spatial distribution of P losses to surface water is needed. In the Netherlands, the phosphate-saturated soils protocol is used to assess the *potential risk* of increased P concentrations in groundwater in the long term in acid sandy soils because intensive husbandry is concentrated on these soils. For these soils, the parameters of the protocol were determined. However, no information was gathered for other soil types in the Netherlands. Consequently, the potential risk of increased P concentrations in other soil types was unknown and no spatial information was available on the degree of phosphate saturation in the Netherlands. Furthermore, new and simple methods are needed for assessing the actual risk of P losses to surface waters, because information is needed on the areas that already contribute substantially to the current water quality and eutrophication status of these waters. Finally, information is needed on effective measures to reduce P losses from agricultural land to surface water.

The main aims of this thesis were:
- (a) to determine the vulnerability of lowland peaty clay soils and coarse calcareous sandy soils for P losses, by quantifying their capacity to bind and release mineral P as main P source in manure and chemical P fertilisers;
- (b) to determine the so-called critical phosphate saturation degree of Dutch soil types and the spatial distribution of phosphate-saturated soils in the Netherlands;
- (c) to develop methods to quantify the actual risk of P losses from agricultural land to surface water;
- (d) to give an overview of mitigation measures to reduce P losses from agricultural land to surface waters and to determine options to close the P balance.

Phosphorus behaviour in soils

The P sorption and desorption kinetics of lowland peaty clay soils can be described by a fast reversible reaction and a time-dependent poorly reversible reaction. Both the maximum P sorption capacity and the maximum amount of reversibly bound P are related to the sum of the oxalate-extractable aluminium and iron contents of the soil. The maximum phosphate sorption capacity of the soil horizons decreases with depth, while in the subsoil the fraction reversibly adsorbed P increases. The P that is accumulated in lowland peaty clay soils can easily leach out to surface water as a result of the shallow groundwater levels and the large fraction of reversibly adsorbed P. In calcareous sandy soils the P sorption can also be described by a fast reversible reaction and a time-dependent slow reaction of P. The P sorption maximum is smaller than that of other Dutch soil types. A small part (5-15%) of the P sorption capacity is reversibly bound P. Nevertheless, this small amount is easily soluble as it is weakly bound, and consequently relatively high P concentrations are observed in solution even at a low soil P content.

Due to the high amount of reversibly sorbed P in lowland peaty clay soils and the weak P binding in calcareous sandy soils, both soil types can be considered as vulnerable to P losses.

P risk assessment

The so-called phosphate saturation degree (PSD) of non-calcareous sandy soils was introduced in the Netherlands in a protocol in the early 1990s as a simple index to determine the potential risk of increased P concentrations in groundwater that exceed the background concentration in the long term. The critical PSD of non-calcareous sandy soils was found to be 25%, which means that the actual amount of phosphate in the soil layer between the soil surface and the mean highest water groundwater level (MHW) should be less than 25% of the maximum phosphate sorption capacity of this soil layer.

In the research described in this thesis, the same approach as developed for the determination of the critical PSD of acid sandy soils, which is based on the sorption characteristics and the natural background concentrations, was used to determine the critical PSD for the other main Dutch soil types. The soil type specific critical PSD increases in the order: peat soils (5%), calcareous sandy soils (23%), acid sandy soils (25%), non-calcareous clay soils (31%) and calcareous clay soils (78%). The relatively low critical PSD emphasises the vulnerability of both peaty clay soils and calcareous sandy soils. Based on the chemical characteristics of soil samples from a stratified soil

survey, the agricultural area of phosphate-saturated soils was determined. In about 43% of the agricultural land in the Netherlands, the critical PSD for the given soil type was exceeded at the time of the soil survey. Consequently, a large area of agricultural land contributes or will contribute in the near future to the P pollution of surface water.

The *actual risk* of P losses from land to surface waters can be determined by a process oriented dynamic modelling approach based on the behaviour of P in soils and on water transport. In the Netherlands, the ANIMO soil–water quality model is used at a national scale, as part of the STONE model instrument[12], for evaluating the efficacy of the Manure Act and the Water Framework Directive. Although dynamic models have many advantages for scenario analyses, they are time-consuming (data collection and data input) and thus costly and are therefore not commonly used. Therefore, in this study two new simplified P risk assessment approaches were developed for assessing the *actual risk* of P load to surface water: one at local (i.e. individual field) scale and one at regional scale.

The first approach is based on the relationship between measured soil fertility parameters and the P sorption and desorption parameters of the soil, in combination with the hydrological characteristics of a field. It is called the PLEASE method (Phosphorus LEAching from Soils to the Environment). The PLEASE approach is a promising method for quantifying differences in P losses from fields to surface waters within a catchment. The main advantage of the method is that soil data measured in the field are used to estimate the P losses from that field. The second approach is called SIMPLE (Smart prediction of the Impact of Management strategies (nutrient and water) on Phosphorus losses by LEaching). It is an approximating model for P, which relates the P load to surface water calculated with the dynamic process oriented STONE model instrument with the most relevant and easily available geographical input data of the model instrument, by means of statistical relationship. This simple meta model proves to be a powerful tool for quickly assessing the risk of P losses by leaching and surface runoff from agricultural land to surface waters by using catchment characteristics that can be easily gathered or are already available in maps or databases. Examples of such characteristics are historical P surpluses and actual P application rates, soil type, crop type, groundwater table depth, precipitation surplus, and seepage fluxes. The most important or sensitive input variables for the assessment of P losses are the historical P surpluses, groundwater table and actual P application rates.

It is evident that all approaches have their pros and cons, and that the same areas will not always be designated as at risk of P losses. Nevertheless, as a result of the

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[12] The STONE model instrument consist of a discretisation of the Netherlands into about 6400 unique plots including the input data to run the manure and fertilizer distribution model MAMBO, the hydrological model SWAP/NAGROM and soil process, crop uptake and leaching model ANIMO.

simplicity of PLEASE and SIMPLE, the data availability and their low operational costs make it possible to apply and compare the efficacy of several approaches for the same catchment (ensemble model approach). By combining different approaches it becomes clear in which areas unacceptably high P losses are always predicted and in which areas the model predictions disagree. Because of the transparency of the methods it is relative easy to derive information on the reason for these differences and which input data have to be collected in more detail.

Mitigating phosphorus losses

Within COST Action 869[13], which ran between 2006 and 2011, an inventory was made of mitigation measures to reduce the diffuse P pollution in order to meet the objectives of the EU Water Framework Directive (WFD). In total, 83 measures were evaluated in terms of their suitability and cost-effectiveness for reducing nutrient loss from rural areas to surface waters at catchment scale, including the feasibility of the options under different climatic and geographical conditions. The measures were grouped according to whether they are related to the management of farm, field, landscape, or surface water systems. The underlying mechanisms of most measures can be described well; however, the data on their effectiveness under different conditions is still inadequate and needs further attention. On the other hand, many mitigation options are no-regret measures and should be implemented as part of Good Agricultural Practice (GAP). Management dealing with measures in surface water or at landscape scale can often improve the surface water quality in the short term. However, source-oriented measures, such as reducing P application rates or lowering the P content of the soil, are needed to decrease P losses in the long term. A more agro-environmental approach that takes account of the actual risk of P pollution of the surface water is needed for the further development of P management of agricultural land. The results of applying the P risk tools presented in this thesis show good starting points for developing such an agro-environmental approach.

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[13] COST stands for **CO**operation in **S**cience and **T**echnology. COST actions are subsidised by the EU RTD Framework Programme

Closing the P balance

The management of P in Europe has to change for three important reasons: (1) global reserves of P are running out, (2) Europe is very dependent on the import of P, and (3) climate change will negatively affect Europe's freshwater quality. The import of P can easily be reduced by applying P fertilisers only where required, taking into account the amount of P in various forms in the soil, and by reducing the P content in feed to meet the actual dietary requirements of animals. The largest reductions of P imports can be obtained by successful and economically feasible P recovery from waste streams and manure and from re-using the resulting secondary raw P materials in the food chain. There are many options for P recovery, but many techniques still have to be tested in practice at pilot and full scale, especially for recovering P from manure.

Such strategies will increase the efficient use of P and consequently reduce P losses to the environment, especially when fertiliser P applications are fully adjusted to the actual availability of P in soils. This P source approach will also help to reduce the rise in P concentrations in surface water that climate change is expected to bring about. Although many measures are available to reduce P losses from agricultural land, they need to be re-evaluated in terms of their climate-proof effectiveness for addressing the objectives of the Water Framework Directive in the long term.

Conclusions and recommendations

Based on the outcome of the studies described in this thesis, the following conclusions and recommendations were made:

- In order to improve the surface water quality from agricultural land, attention should be paid not only to acid sandy soil where most of the intensive husbandry is located, but also to soils which are vulnerable to P losses due to their low P sorption capacity and high release of P at low PSDs. Examples are peaty clay soils and calcareous sandy soils.

- In order to implement P-reducing mitigation measures at the right places within a catchment, it is important to have information on the spatial distribution of P losses from agricultural land to surface waters. In addition to applying time consuming process-oriented dynamic models, the derived simple P risk assessment tools (PLEASE at field scale and SIMPLE at regional scale) could be used to rank fields or areas within a catchment that show low to high P loads.

- Although there are many measures for reducing P losses to surface waters or the impact of P in surface waters, there is a need for a differentiation in agricultural P application standards that meets the environmental carrying capacity of the soil in terms of risk of P losses, in order to develop long-term sustainable agricultural practices that contribute to meeting the Water Framework Directive objectives.

- Besides the need to reduce the P losses, the P balance should be better closed at regional, national and European scales. Large-scale P recovery and valorisation of all or some of the P from manure so that it becomes a secondary raw mineral resource for fertiliser and feed industries would allow agriculture to reduce its dependence on the import of P.

Samenvatting

Inleiding

Fosfor (P) is een onvervangbaar element voor al het leven op aarde, waarvan de beschikbare voorraad eindig is. Het gebruik van P in de landbouw heeft geleid tot een hogere voedselproductie door (a) import van P in veevoer om de zich uitbreidende veestapel te voeden en (b) import van kunstmestfosfaat om de fosfaattoestand van de bodem op peil te brengen en om aan de gewas-specifieke fosfaatbehoefte te voldoen, waardoor de opbrengsten konden stijgen. In Nederland en veel andere West-Europese regio's en landen is de import van P groter dan de export van P. De meeste P die in Nederland wordt geïmporteerd, wordt in de landbouw gebruikt. Het overschot aan fosfaat kwam in het verleden vooral in de vorm van dierlijke mest op de landbouwgronden terecht. Dit heeft uiteindelijk geleid tot een verhoogde fosfaatuitspoeling naar het oppervlaktewater waardoor een belangrijke bijdrage werd geleverd aan de verslechtering van de waterkwaliteit (eutrofiëring van het oppervlaktewater).

Er zijn succesvolle management strategieën voor P nodig om de waterkwaliteit te verbeteren en daarvoor is allereerst kwantitatieve informatieve nodig over de ruimtelijke verdeling van de fosfaatbelasting van het oppervlaktewater vanuit landbouwgronden. In Nederland is een protocol fosfaatverzadigde gronden ontwikkeld om het potentiële risico van verhoogde fosfaatconcentraties in het bovenste grondwater (op termijn) te voorspellen voor kalkarme zandgronden, omdat in deze gebieden veel intensieve veehouderij voorkomt. Voor deze grondsoort zijn de parameters voor het protocol vastgesteld. Echter, voor de overige grondsoorten is geen informatie verzameld, waardoor er voor Nederland als geheel geen ruimtelijke beeld bestaat van de mate van fosfaatverzadiging en van het potentiële risico van verhoogde fosfaatconcentraties in het bovenste grondwater. Daarnaast is er behoefte aan eenvoudige methoden om het (huidige) *actuele* risico van de fosfaatbelasting van het oppervlaktewater in kaart te brengen, zodat inzichtelijk gemaakt kan worden welke gebieden nu al substantieel de oppervlaktewaterkwaliteit en de eutrofiestatus beïnvloeden. Tot slot is informatie nodig over de effectiviteit van maatregelen om de fosfaatbelasting van het oppervlaktewater vanuit landbouwgronden te verminderen.

De hoofddoelstellingen van deze thesis zijn:

(a) de kwetsbaarheid van laagveengronden en kalkrijke zandgronden voor fosfaatuitspoeling aan te geven door de capaciteit te kwantificeren om mineraal

(anorganisch) fosfaat te binden en weer af te geven; dit is de belangrijkste vorm van fosfaat in mest en kunstmest;

(b) het vaststellen van de kritische fosfaatverzadigingsgraad van Nederlandse grondsoorten en de ruimtelijke verdeling van het areaal fosfaatverzadigde gronden in Nederland;

(c) methoden te ontwikkelen om het actuele risico voor fosfaatbelasting van het oppervlaktewater vanuit landbouwgronden in kaart te brengen en

(d) een overzicht van maatregelen te genereren om de fosfaatuitspoeling uit landbouwgronden terug te dringen en opties aan te geven om de fosfaatbalans beter te sluiten.

Gedrag van fosfaat in de bodem

De kinetiek van fosfaatsorptie en –desorptie van laagveengronden kan worden beschreven met een snelle reversibele adsorptiereactie en een tijdsafhankelijke langzame fosfaatreactie die zeer beperkt reversibel is. Zowel de maximale fosfaatsorptie als de maximale hoeveelheid reversibel gebonden fosfaat is gerelateerd aan de som van het gehalte aan oxalaatextraheerbaar aluminium en ijzer van de bodem. De maximale fosfaatsorptiecapaciteit van de bodemlagen neemt af met de diepte terwijl in de ondergrond het aandeel reversibel gebonden fosfaat toeneemt. Het in laagveengronden opgehoopte fosfaat kan gemakkelijk uitspoelen naar het oppervlaktewater als gevolg van de hoge grondwaterstanden die in laagveengebieden voorkomen en het grote aandeel makkelijk desorbeerbaar fosfaat dat in laagveengronden aanwezig is.

Ook in kalkrijke zandgronden kan de fosfaatsorptie beschreven worden met een snelle reversibele reactie en een tijdsafhankelijke langzame reactie. De maximale fosfaatsorptie is relatief laag vergeleken met andere Nederlandse grondsoorten. Een klein deel van het gesorbeerde fosfaat is reversibel gebonden (5-15%). Echter, deze kleine fractie reversibel gebonden fosfaat komt makkelijk in oplossing door de geringe bindingssterkte waardoor hoge P concentraties in de bodemoplossing al kunnen ontstaan bij een laag fosfaatgehalte in de bodem.

Door het grote aandeel reversibel gebonden fosfaat in laagveengronden en de lage affiniteit om fosfaat te binden in kalkrijke zandgronden, zijn beide grondsoorten kwetsbaar voor fosfaatuitspoeling.

Risicoschatting voor fosfaatuitspoeling

In het begin van de jaren negentig is in Nederland een protocol ontwikkeld voor het vaststellen van de kritische fosfaatverzadigingsgraad (FVG) van kalkarme zandgronden als maat voor het potentiële risico van verhoogde P concentraties die op termijn in het bovenste grondwater kunnen ontstaan en die boven de natuurlijke achtergrond-concentraties liggen. De kritische FVG voor kalkarme zandgronden werd vastgesteld op 25%. Dit betekent in de praktijk dat het actuele fosfaatgehalte in de bodem in het traject tussen maaiveld en de gemiddelde hoogste grondwaterstand (GHG) beneden de 25% van de maximale fosfaatbindingscapaciteit van deze bodemlaag moet blijven.

In deze thesis is dezelfde methodiek gehanteerd om de kritische FVG van andere grondsoorten af te leiden, op basis van de karakteristieke fosfaatbindings-eigenschappen en de natuurlijke achtergrondconcentraties van de verschillende grondsoorten. Voor de belangrijkste grondsoorten neemt de kritieke FVG toe in de volgorde: laagveengronden (5%), kalkrijke zandgronden (23%), kalkarme zandgronden (25%), kalkarme kleigronden (31%) en kalkrijke kleigronden (78%). De relatief lage kritieke FVG van laagveengronden en kalkrijke zandgronden benadrukt hun kwetsbaarheid voor fosfaatuitspoeling. Op basis van de chemische kenmerken van grondmonsters die zijn genomen in het kader van een landelijke steekproef van de bodem, is het areaal landbouwgronden berekend dat aangemerkt moet worden als fosfaatverzadigde grond omdat de kritieke FVG is overschreden. Op basis hiervan kan ongeveer 43% van het landbouwareaal in Nederland aangeduid worden als fosfaatverzadigd. Geconcludeerd wordt dat een aanzienlijk areaal landbouwgrond nu al bijdraagt, of op termijn zal gaan bijdragen, aan de fosfaatbelasting van het oppervlaktewater.

Het actuele risico van P verliezen vanuit landbouwgronden naar het oppervlaktewater kan bepaald worden met proces-georiënteerde dynamische modellen die rekening houden met het gedrag van fosfaat in de bodem en het watertransport. In Nederland wordt het bodem- en waterkwaliteitsmodel ANIMO gebruikt, als onderdeel van het STONE modelinstrumentarium, voor beleidsevaluaties van de Mestwetgeving en de Kaderrichtlijn Water (KRW). Procesgeoriënteerde modellen hebben een groot aantal voordelen voor het uitvoeren van scenario-analyses, maar zijn over het algemeen tijdrovend (qua data verzameling en invoer van gegevens) en daardoor relatief duur, waardoor dergelijke modellen beperkt op regionale schaal worden toegepast. Er zijn daarom twee nieuwe, vereenvoudigde P risk assessment benaderingen ontwikkeld om het actuele risico van P belasting van het oppervlaktewater te voorspellen, namelijk één voor toepassing op lokaal niveau (perceel) en een voor toepassing op regionaal niveau. De eerste methode is gebaseerd op de relatie tussen gemeten bodemvruchtbaarheidsparameters en de P sorptie- en desorptieparameters van de bodem in combinatie met hydrologische kenmerken van het perceel. Deze

modelbenadering wordt de PLEASE-methodiek genoemd, wat een afkorting is van de Engelse benaming *P*hosphorus *LEA*ching from *S*oils to the *E*nvironment. Het PLEASE-model is een veelbelovende methode om de verschillen in P uitspoeling van percelen in een stroomgebied te duiden. Het belangrijkste voordeel van deze methode is dat actuele gegevens van het perceel worden gebruikt om de lokale P verliezen naar het oppervlaktewater te kwantificeren. De tweede methode wordt SIMPLE genoemd, wat is afgeleid van de Engelse benaming *S*mart prediction of the *I*mpact of *M*anagement strategies (nutrient and water) on *P*hosphorus losses by *LE*aching. Deze methodiek is een statistisch model voor schatting van de P uitspoeling naar het oppervlaktewater, gebaseerd op de relatie tussen de P-uitspoeling die is berekend met behulp van het procesgeoriënteerde dynamisch model ANIMO (STONE instrumentarium) en de daarbij behorende belangrijke geografische kenmerken die als invoer voor het model zijn gehanteerd en die veelal beschikbaar zijn of eenvoudig gekarteerd kunnen worden. Dit eenvoudige metamodel is een krachtige benadering om snel P verliezen door uitspoeling en maaiveldafvoer vanuit landbouwgronden naar het oppervlaktewater regionaal in kaart te brengen, voor combinaties van gebiedskenmerken die in het stroomgebied voorkomen. De fosfaatuitspoeling wordt gekarakteriseerd door: historisch cumulatief P overschot, huidige P bemesting, grondsoort, gewas, grondwaterklasse, neerslagoverschot, en bijdrage van kwel/wegzijging. De meest gevoelige variabelen voor de P uitspoeling zijn: historisch cumulatief P overschot, huidige P bemesting en grondwaterklasse.

Het is evident dat alle methoden hun voor- en nadelen hebben en dat niet altijd dezelfde gebieden als kwetsbaar voor P uitspoeling zullen worden aangewezen. Desalniettemin maken de eenvoud van de PLEASE en SIMPLE methoden, de relatief goede beschikbaarheid van invoergegevens, en de lage operationele kosten het mogelijk om snel dergelijke methoden toe te passen en onderling te vergelijken. Uit de verschillen in uitkomsten tussen de modellen kan relatief eenvoudig inzicht worden verkregen in mogelijke oorzaken van de verschillend (een "ensemble model approach"). Toepassen van verschillende modellen kan helpen om eenvoudig gebieden te onderscheiden waar zeker problemen zijn te verwachten. Daarnaast wordt ook duidelijk welke gebieden aanvullende aandacht vragen, wanneer verschillende methoden een andere indicatie van kwetsbaarheid aangeven. Door de transparantie van deze eenvoudige modellen kan vrij snel achterhaald worden waardoor verschillen in geschatte P belasting van het oppervlaktewater binnen het stroomgebied veroorzaakt worden en welke invoergegevens verbeterd dienen te worden.

Verminderen van fosfaatverliezen

In het kader van COST[14] action 869 getiteld "Mitigation options for nutrient reduction in surface water and groundwaters" zijn maatregelen geïnventariseerd om de P belasting van het oppervlaktewater uit het landelijk gebied te verminderen en die kunnen bijdragen aan het realiseren van de doelstellingen van de Kaderrichtlijn Water. In totaal zijn 83 maatregelen beoordeeld op geschiktheid en kosteneffectiviteit om de nutriëntenuitspoeling naar het oppervlaktewater vanuit het landelijke gebied te verminderen. Een onderscheid is gemaakt in maatregelen gericht op het niveau van een bedrijf, het perceel, het landschap, of het oppervlaktewatersysteem zelf. De onderliggende mechanismen van de managementmaatregelen konden over het algemeen goed beschreven worden, echter de beschikbaarheid van data om de effectiviteit aan te geven onder verschillende omstandigheden is vaak beperkt en vraagt nadere aandacht. Aan de andere kant, veel maatregelen zijn no-regret maatregelen en behoren onderdeel te zijn van Goede Landbouwkundige Praktijk (GLP). Managementmaatregelen die zich op het landschap richten of rechtstreeks op het oppervlaktewater doen de waterkwaliteit over het algemeen snel verbeteren. De meer brongerichte maatregelen op bedrijfs- of perceelsniveau, zoals verlagen van de bemesting of het verlagen van het fosfaatgehalte in de bodem, leveren vaak pas op langere termijn een verbetering van de waterkwaliteit op. Een landbouw-milieukundige benadering is dan ook nodig voor P management van landbouwgronden, waarbij niet alleen op agronomische en economische factoren wordt gestuurd maar ook op het risico op P-verliezen naar het milieu. Toepassing van de eenvoudige methoden om de actuele P belasting van het oppervlaktewater te schatten, die zijn ontwikkeld en in dit proefschrift zijn beschreven, biedt hiervoor aanknopingspunten.

Sluiten van de P balans

Het fosfaatmanagement binnen Europa dient te veranderen omdat (1) de wereldwijde fosfaatvoorraden op termijn opraken, (2) Europa's voedselproductie zeer afhankelijk is van de import van P en (3) klimaatveranderingen de waterkwaliteit negatief zullen beïnvloeden. De import van P kan eenvoudig teruggedrongen worden door kunstmest alleen nog toe te passen waar dat landbouwkundig gezien nog echt nodig is, waarbij goed rekening wordt gehouden met de fosfaatvoorraad in de bodem. Daarnaast kan de P die via veevoer wordt geïmporteerd verminderd worden door het P-gehalte in

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[14] COST staat voor **CO**operation in **S**cience and **T**echnology en COST-acties worden gesubsidieerd vanuit de EU RTD Framework Programme

veevoer te verlagen en af te stemmen op de P-behoefte van de landbouwhuisdieren. De grootste reductie in P import kan bereikt worden door de P uit afvalstromen en mest op een economisch haalbare manier terug te winnen, en de geproduceerde secondaire ruwe minerale P-grondstof te hergebruiken in de voedselketen. Er zijn verschillende opties om P terug te winnen, maar veel technieken dienen nog op praktijkschaal getest en gedemonstreerd te worden, alvorens ze op brede schaal geïmplementeerd kunnen worden. Dit geldt zeker voor technieken om (een deel van de) P te verwijderen uit dierlijke mest, als een van de belangrijkste bronnen van fosfaatophoping in landbouwsystemen. Hierdoor wordt het mogelijk om meer organische mest (met een verlaagd P gehalte) toch als bodemverbeteraar toe te dienen. Dergelijke strategieën zullen een bijdrage leveren aan het efficiënt gebruik van P en dientengevolge de verliezen naar het milieu terugdringen, zeker als ook de bemesting beter afgestemd wordt op de beschikbare fosfaatvoorraden in de bodem. Deze aanpak zal ook bijdragen aan het verminderen van de verhoging van de fosfaatconcentratie die in het oppervlaktewater verwacht wordt. Ondanks dat er veel maatregelen beschikbaar zijn om de P uitspoeling vanuit landbouwgronden te verminderen, zullen ook deze opnieuw geëvalueerd moeten worden op de vraag of ze ook qua effectiviteit klimaatbestendig zijn om de doelstellingen van de Kaderrichtlijn Water ook op langere termijn te realiseren.

Conclusies en aanbevelingen

Op basis van de uitkomsten van de in dit proefschrift beschreven studies kunnen de volgende aanbevelingen worden geformuleerd:

- Om de fosfaatbelasting van het oppervlaktewater vanuit landbouwgronden terug te dringen zal niet alleen aandacht moeten worden besteed aan gronden in de gebieden met hoge mestoverschotten, zoals de kalkarme zandgronden, maar ook aan gronden die kwetsbaar zijn voor fosfaatuitspoeling als gevolg van hun lage fosfaatbindingscapaciteit of door de sterke mate van fosfaatnalevering bij een lage fosfaatverzadigingsgraad; voorbeelden hiervan zijn laagveengronden en kalkrijke zandgronden.

- Om de juiste maatregel op de juiste plaats in een stroomgebied te kunnen nemen, is het van belang inzicht te hebben in de ruimtelijke verdeling van de actuele fosforbelasting van het oppervlaktewater vanuit landbouwgronden. Als aanvulling op de mogelijke toepassing van procesgeoriënteerde dynamische modellen, kunnen ook de vereenvoudigde methoden PLEASE (perceelniveau) en SIMPLE (regionaal niveau), die hiervoor ontwikkeld zijn, een uitkomst bieden.

- Hoewel er veel maatregelen beschikbaar zijn om de fosfaatuitspoeling naar het oppervlaktewater te verminderen of om de effecten in het oppervlaktewater te beperken, is het noodzakelijk om het gebruik van fosfaat (via de fosfaat-gebruiksnormen) meer te enten op het actuele risico van P belasting van het oppervlaktewater, teneinde een duurzame landbouwkundige praktijk te ontwikkelen die beter aansluit bij het realiseren van de doelstellingen van de Kaderrichtlijn Water.

- Naast de noodzaak om de uitspoeling van P te verminderen is het ook noodzakelijk om de P-balans op regionaal, nationaal of Europees niveau beter te sluiten. Door grootschalig terugwinnen en valorisatie van (een deel van de) P in dierlijke mest als secundaire ruwe minerale grondstof voor de kunstmest- en veevoederindustrie, wordt de landbouw beduidend minder afhankelijk van de import van fosfor.

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In de afgelopen jaren heb ik naast mijn werkzaamheden bij Alterra veel tijd en energie gestoken in het schrijven van dit proefschrift, vaak juist in die schaarse vrije uurtjes van de week. Allereerst, Ans, wil ik jou bedanken voor je enorme morele steun en al het geduld dat je met me hebt gehad in deze periode.

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Two chapters of this thesis (chapter 6 and 9) are the synthesis of the outcome of two European projects, EUROHARP en COST-action 869 and I would like to thank all the co-authors for their contribution in those projects, the discussions we had and the publication of the results. Christian, Fayçal, Oene and Kimo many thanks for your contribution to the opinion paper on the options to overcome the phosphorus challenges in our changing world in the nearby future. Furthermore, I would like to thank Joy Burrough-Boenisch as language editor of many articles.

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Oscar Schoumans
April 2015

Levensloop

Oscar Frédéric Schoumans werd geboren op 26 augustus 1958 te Amsterdam. Na het behalen van zijn VWO diploma aan het Sweelinck College in Amsterdam begon hij in 1978 zijn studie aan de Landbouwuniversiteit te Wageningen en studeerde af op de doctoraalvakken bodemchemie, bodemvruchtbaarheid en informatica. Sedert 1985 is hij werkzaam bij Dienst Landbouwkundig Onderzoek (DLO-Wageningen) en begon hij bij het voormalige Stiboka met onderzoek naar de fosfaatophoping in de mestoverschotgebieden in opdracht van het toenmalige ministerie van VROM. In deze periode was hij intensief betrokken bij het laboratorium- en veldonderzoek, dat de basis heeft gevormd voor de onderbouwing van de modellering van de fosfaatophoping in de bodem. In de periode daarna heeft hij bij het voormalige Staring Centrum (afdeling Water en Milieu) veel projecten uitgevoerd op het gebied van modellering van de fosfaatuitspoeling vanuit de bodem naar het oppervlaktewater, en projecten waarin maatregelen werden getest om deze fosfaatuitspoeling te verminderen. In de periode eind jaren negentig – 2010 werd hij voor Wageningen UR programmaleider en later clusterleider van een aantal beleidsondersteunende onderzoeksprogramma's en -clusters voor het ministerie van LNV (thans Economische Zaken). In deze periode was hij betrokken bij een aantal beleidsevaluaties die zijn uitgevoerd op het gebied van de mestwetgeving, Nitraatrichtlijn en Kaderrichtlijn Water. Sinds 2008 heeft hij op verzoek van de Minister van LNV een WUR-breed onderzoek gecoördineerd en uitgevoerd naar de mogelijkheden om het fosfaatoverschot in de vorm van dierlijke mest te verminderen (programma 'Mest van Bedreiging naar Kans'). Dit heeft onder andere geleid tot zijn huidige activiteiten op het gebied van valorisatie van waardevolle componenten in dierlijke mest (topsectorproject 'Meerwaarde Mest en Mineralen'). Hij is sinds 1980 zeer gelukkig getrouwd met Ans Wijde en is een trotse vader van twee dochters Marianne en Brenda.

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