Phosphorus Sorption, Accumulation and Leaching

Effects of long-term inorganic fertilization of cultivated soils

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Abstract

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Arable land is a major diffuse source of P loads to surface waters. The main processes for P losses from agricultural fields are erosion, surface runoff and subsurface leaching. To identify agricultural soils vulnerable to P losses, it is necessary to understand the processes behind these losses. This thesis mainly concerns processes influencing subsurface leaching. Phosphorus sorption and accumulation were studied in the laboratory to evaluate how these processes affect the release of P, which potentially can be leached. Furthermore, P leaching from undisturbed soil cores exposed to natural conditions was studied. All studies were performed on soils from the Swedish long-term fertility experiment, which includes soil types common in southern and central Sweden, each with four soil P levels.

P sorption capacity in the soils studied ranged from 6.0 to 12.2 mmol kg^{-1} soil and was correlated with the amounts of oxalate extractable Fe and Al in the soils. Phosphorus release was correlated with soil test P values (STP) for individual soils, but STP could not explain P release when soils with different P sorption capacities were considered. Instead, estimates of P sorption saturation using a ratio of STP and P sorption capacity proved to be useful for assessing P release. Long-term inorganic P fertilization of 42 to 49 kg P $ha^{-1}yr^{-1}$ for more than 30 years caused P accumulation down to 40 cm depth in the soil profiles. Below this depth no differences in P properties were found between fertilized and non-fertilized soils. Total P losses from the lysimeters ranged from 0.03 to 1.09 kg $ha^{-1}yr^{-1}$ and were not correlated with either STP or P sorption saturation. Total P leaching was greatest from a soil in which macropore flow dominated water transport, irrespective of STP. In another soil, with low P sorption capacity, P sorption saturation and P leaching were high from the highest fertilized treatment. In the remaining soils, P sorption and release processes in the subsoils influenced P losses. The subsoils seemed to act either as a source or a sink of P and reduced the differences between treatments.

Key words: batch experiment, long-term field experiment, lysimeter, phosphorus, P release, P sorption saturation, soil test P, Swedish

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Abbreviations used in this thesis

P-AL – P extractable in ammonium lactate/acetic acid

Olsen-P – P extractable in sodium bicarbonate

$CaCl_2$-TP – Total P extractable in $CaCl_2$

$CaCl_2$-RP - Reactive P extractable in $CaCl_2$

$CaCl_2$-UP – Unreactive P extractable in $CaCl_2$

P_w – P extractable in water

P_{ox}, Fe_{ox}, Al_{ox} – Ammonium oxalate extractable P, Fe and Al, respectively

X_m – Maximum P sorption capacity determined from sorption isotherms using the Langmuir equation (referred to as PSC_{max} in Paper II)

PSI_1 – Single point P sorption index using an addition of 19.4 mmol P kg^{-1} soil

PSI_2 - Single point P sorption index using an addition of 50 mmol P kg^{-1} soil

PSC_{ox} – P sorption capacity determined from Fe_{ox} and Al_{ox} using the equation from Paper I

EPC – Equilibrium P concentration

DPS – Degree of P saturation (in %)

STP – Soil test P determined from P-AL or Olsen-P

Contents

Appendix

Paper I-IV

The present thesis is based on the following papers, which are referred to in the text by their Roman numerals:

I.　　Börling, K., Otabbong, E. & Barberis, E. 2001. Phosphorus sorption in relation to soil properties in some cultivated Swedish soils. Nutrient Cycling in Agroecosystems, 59, 39-46.

II.　　Börling, K., Otabbong, E. & Barberis, E. 2004. Soil variables for prediction of potential phosphorus release in Swedish non-calcareous soils. Journal of Environmental Quality. Volume 33. (In press).

III.　　Börling, K., Barberis, E. & Otabbong, E. Impact of long-term inorganic phosphorus fertilization on accumulation, sorption and release of phosphorus in five Swedish soil profiles. (Submitted to Nutrient Cycling in Agroecosystems).

IV.　　Djodjic, F., Börling, K. & Bergström, L. Phosphorus leaching in relation to soil type and soil phosphorus content. Journal of Environmental Quality. (In press).

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Introduction

Phosphorus (P) is one of the essential elements for plant growth and the amount of plant-available P in the soil is often inadequate to meet plant requirements. Phosphorus is therefore applied to agricultural fields in inorganic and/or organic fertilizers. However, the amount of fertilizer applied often exceeds the uptake by plants and this result in a build-up of P in the soil. Most of the excess P is bound to the soil and some of it is transformed to less available forms but there is also a risk of some of the excess P being transported from agricultural fields to surface waters. About one third of the total P load to surface waters in Sweden comes from agricultural land (SCB, 2003). Phosphorus is often the limiting nutrient in surface water systems, and even small additions of P can have a great influence on primary production in these waters (Correll, 1998). So even if losses of P from agriculture are small from an agronomic viewpoint, they constitute a serious environmental problem.

The main processes for P losses from agricultural fields to surface waters are erosion, surface runoff and subsurface transfer. For a long time, the first two processes were thought to be the most important. Since P is usually strongly bound by the soil, subsurface transfer of P was thought not to be a problem. Today it is well known that subsurface transfer from agricultural fields cannot be ignored (Sims *et al*., 1998). Phosphorus subsurface transfer can occur both in dissolved form or bound to particles that are transported with the water (Heckrath *et al*., 1995). Dissolved P is directly bio-available and can therefore affect eutrophication in a short time scale. However, P bound to particles can also cause eutrophication since desorption or mineralization of P can occur when the particles enter a stream or lake with other chemical conditions, *e.g.* a difference in pH or redox potential. In this thesis, the term leaching is used in a general sense, describing P subsurface transfer of both particulate and dissolved P forms.

Agricultural soils are very different in their susceptibility to P leaching and it is therefore necessary to identify the most vulnerable soils in this respect as well as identifying the main properties of the soils that make them vulnerable for P leaching (Sims *et al*., 1998). A significant proportion of P lost from agricultural fields through leaching is transported in dissolved form (Turner & Haygarth, 2000). Since the concentration of P in the soil solution is critical for losses of dissolved P, processes such as P sorption and release are crucial. The main focus in this thesis was on these two processes and on studying the impact of them for losses of P through leaching. This was done by sorption/release experiments in the laboratory and by studying losses of P from lysimeters in a variety of soil types representative for Swedish agricultural fields, with a range of soil P levels.

Background

Phosphorus in agriculture and eutrophication

Phosphorus, together with nitrogen, is often the limiting nutrient for primary production in lakes and streams. This means that an increased P level in a lake increases primary production and oxygen demand and the lake becomes more eutrophic (Correll, 1998). Eutrophication is a very slow, natural ageing process for lakes with increasing productivity and nutrient status, which can be accelerated by nutrient inputs. About 15% of the lakes in Sweden have total P concentrations of 0.025 mg l^{-1} or more, which classifies them as eutrophic (Naturvårdsverket, 2003). Most of the eutrophic lakes are situated in southern and central Sweden. The anthropogenic input of P to freshwaters is 3000 tonnes per year in Sweden (Larsson, 1997). Since point-sources of P have been reduced due to an improved P removal from wastewater, the percentage of total P loads that comes from arable land has increased and has now reached about 35% (SCB, 2003).

Sweden, as well as many other countries, experienced a major increase in fertilization of arable land in the middle of the last century. The high inputs of fertilizer P caused a build-up of P in the soil. The average P accumulation in Swedish arable soils since the 1950s has been estimated at 600-700 kg P ha^{-1} in the topsoil, measured as P extractable in 2.0 M HCl (Andersson $et\ al.$, 1998). During the past 20 years, P applications have decreased, but the P status of many cultivated soils is still high. About 65% of arable Swedish soils are fertilized with P and on these soils, average P application is about 24 kg $ha^{-1}yr^{-1}$. About 40% of the amount of P applied comes from mineral fertilizers and the remainder from manure (SCB, 2003). Although fertilizer loads in total have been considerably reduced in Sweden during the last 20 years, the application is not evenly distributed between fields. Even with reduced P application, some soils still have a surplus of P that may cause environmental effects over many years and there is a general concern about P transport from agricultural fields to freshwater. The losses of P from cultivated fields are very low in proportion to P application and P uptake by the crops grown (average 0.3 kg total P $ha^{-1}\ yr^{-1}$; Ulén $et\ al.$, 2001). However, this amount is still enough to cause increased eutrophication in many rivers and lakes in Sweden. Ulén $et\ al.$ (2001) found in 15 agricultural fields that despite reduction in P inputs and finally a negative P balance in most of the fields, output of P was more or less constant over a period of 21 years. The authors also found that two of the 15 fields contributed about half of the total P transported from all fields. This indicates the importance of identifying fields vulnerable to P losses, which requires knowledge of the soil properties that cause this propensity for P losses.

Phosphorus in soil

The ultimate source of soil P is the primary mineral apatite (Smeck, 1985). Apatite is a complex compound with the empirical formula $3[Ca_3(PO_4)_2] \times CaX_2$, where X can be F^-, Cl^-, OH^- or CO_3^{2-}. The native P content in soils depends on the nature of

the parent material and the degree of weathering. The normal range of total P in soils is 100 to 3000 mg kg^{-1} (Frossard *et al*., 2000). During soil development, apatite P is weathered and gradually transformed to other inorganic and organic P forms through precipitation to other secondary minerals or through plant or microbial uptake (Figure 1). Secondary P minerals formed in acidic soils are mainly Al and Fe phosphates such as variscite, $AlPO_4 \times 2H_2O$, and strengite, $FePO_4 \times 2H_2O$, (Smeck, 1985). In neutral to alkaline soils, different types of secondary Ca-phosphates predominate. Adsorption of P can occur on the surfaces of soil particles. Phosphorus can be sorbed to positive edges of kaolinite clay and in calcareous soils to $CaCO_3$. In acid soils, sorption by Al and Fe oxides and hydroxides, such as gibbsite, haematite, goethite and ferrihydrite, is very common. Phosphorus sorbed on the surfaces of Al and Fe oxides and hydroxides can then be physically encapsulated or occluded by the minerals at which it is sorbed and thereby rendered much less available (Smeck, 1985). This process whereby P becomes less available is also known as ageing. When P is taken up by plants or microorganisms, different forms of organic P are formed, and then a continuous turnover occurs through mineralization and immobilization (Figure 1). There is usually a close relationship between the amount of organic P and the amount of organic matter in the soil and 20-80% of total P in soils can be in organic forms. Many forms of organic P present in the soil are still unknown even though studies using chemical fractionation and ^{31}P-NMR spectroscopy to identify organic P components in soils have considerably increased the knowledge of soil organic P (*e.g.* Turner *et al*., 2003). Organic P forms identified in soils are mainly mono- and diesters of orthophosphate. The three most common esters are inositol phosphates, phospholipids and nucleic acids.
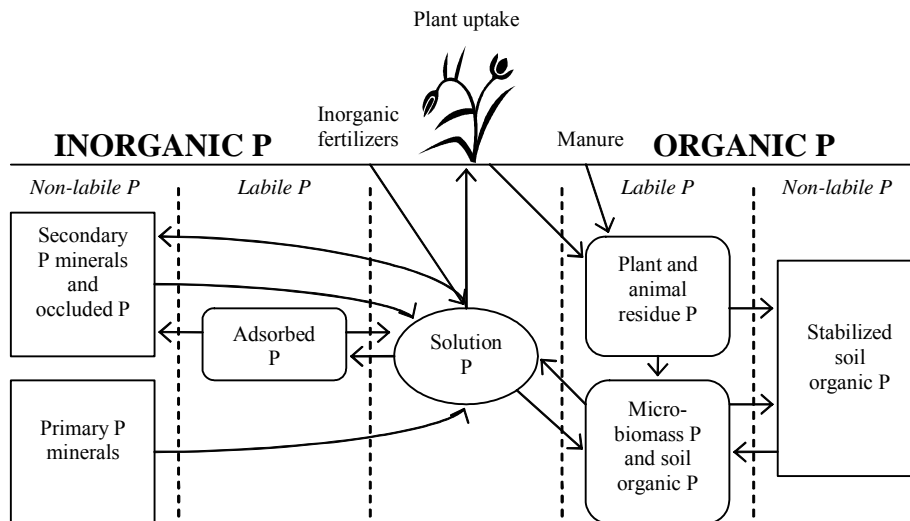

Figure 1. Phosphorus cycle in soil (Adapted from Ivarsson, 1989 and Chauhan *et al*., 1981).

The main proportion of soil P occurs in non-labile forms, such as primary and secondary minerals, occluded P and stabilized soil organic P (Figure 1). These forms of P are only available through dissolution or mineralization. Phosphorus sorbed to surfaces of oxides, hydroxides and clay particles and some of the organic P constitutes a labile pool of P which is much smaller than the non-labile pool. Furthermore, dissolved P in soil solution constitutes an even smaller pool, less than 1 kg P ha^{-1}, and occurs mainly as HPO_4^{2-} and $H_2PO_4^-$ in the pH range 4 to 10 (Jansson, 1977). Since crops can take up 10-20 kg P ha^{-1}yr^{-1}, the soil solution needs to be replenished with P several times during one season. This is achieved through the dynamic relationship between labile P and solution P.

Phosphorus sorption and release

As mentioned above, sorption of P in acid soils occurs mainly on surfaces of Fe and Al oxides and hydroxides. Sorption of P occurs through ligand exchange on variable charge surfaces by the exchange of OH$^-$ on the surface for the phosphate ion (Figure 2). There is a covalent bond between the metal ion and the phosphate ion. Phosphate is considered to sorb mainly as an inner-sphere complex which means that the sorption takes place at specific coordination sites on the oxides or hydroxides and no water molecules are present between the surface and the phosphate ion.
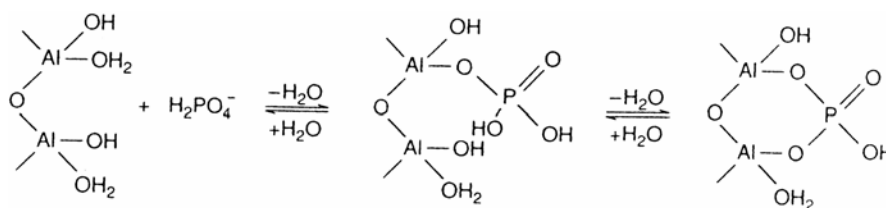

Figure 2. Mechanism of P adsorption on Al oxide surface.

In the first step in Figure 2, P is bound to one Al ion through an Al-O-P bond, and at this stage P is still labile. In the second step, a ring structure is formed with two Al ions and in this case P is much less easily desorbed from the surface. This is also a part of the process called ageing of P, which renders P less available. The process described above is a chemisorption, *i.e.* adsorption of P to the surface of the soil components which is a two-dimensional surface process. It should be borne in mind that under high P concentrations or longer periods of time, sorption can also include some precipitation processes where a new solid phase is formed (van der Zee & van Riemsdijk, 1988). Phosphorus sorption is a continuous sequence of adsorption and precipitation and consists of two processes, one relatively fast, reversible adsorption process and a relatively slow, practically irreversible precipitation-like process (van der Zee & van Riemsdijk, 1988) and it is very difficult to distinguish between the two. In the present study the word sorption, which can include both adsorption and precipitation, is used. In calcareous soils,

10

phosphate can be sorbed to the surfaces of $CaCO_3$, but precipitation of different Ca-P minerals on the $CaCO_3$ surface is also common.

The relationship between labile P sorbed to the soil surface and solution P can be described by a quantity-intensity relationship or Q/I plot, which shows P sorption or desorption as a function of P in the equilibrium solution (Figure 3). The shape of the curve reflects the P sorption capacity and the slope of the curve reflects the buffering capacity for freshly added P (Bache & Williams, 1971). The shape and placement of the Q/I plot depend both on soil properties and P fertilization history. Previous fertilization with P can reduce the ability of the soil to sorb P by blocking sorption sites and thus change the placement and decrease the slope of the Q/I plot (Barrow, 1974; Hartikainen, 1991). A common way to measure P sorption capacity in a soil is by construction of a sorption isotherm, which is the same as the soil Q/I plot (Figure 3). Sorption isotherms are normally made by equilibration of soil with a solution containing a known amount of P (batch process). After equilibration, soil and solution are separated by centrifugation and/or filtration. Phosphorus in the solution is measured and the difference between initial P concentration and P in the equilibrium solution is assumed to be a measure of P sorbed or desorbed by the soil. This is repeated with increasing initial P concentrations. However, this procedure does not give any information about the sorption processes or the kind of surfaces to which the ions are bound.

Phosphorus sorption is often described by empirical equations such as the Langmuir or Freundlich equations. The Langmuir equation has the form:

$$X = \frac{K\,X_m\,C}{1 + K\,C} \qquad\qquad [1]$$

where C (in mmol l^{-1}) is the P concentration in the solution, X (in mmol kg^{-1} soil) is P sorbed by the soil and K and X_m are empirical parameters. From the linear form of the Langmuir equation, it is possible to calculate K and X_m:

$$\frac{C}{X} = \frac{1}{K\,X_m} + \frac{C}{X_m} \qquad\qquad [2]$$

The plot of C/X versus C gives a nearly straight line, with the slope $1/X_m$ and the intercept $1/(K\,X_m)$. K (in l $mmol^{-1}$) is a constant related to the bonding energy and X_m (in mmol kg^{-1} soil) is defined as the maximum P sorption capacity of the soil. The Langmuir equation implies that sorption occurs in a monolayer on the soil surface and that a further increase in P concentration above P sorption maximum would not result in an increased sorption. Even if this is not true in most cases, the sorption maximum derived from the Langmuir equation is useful for estimating P sorption capacity and for comparing different soils.
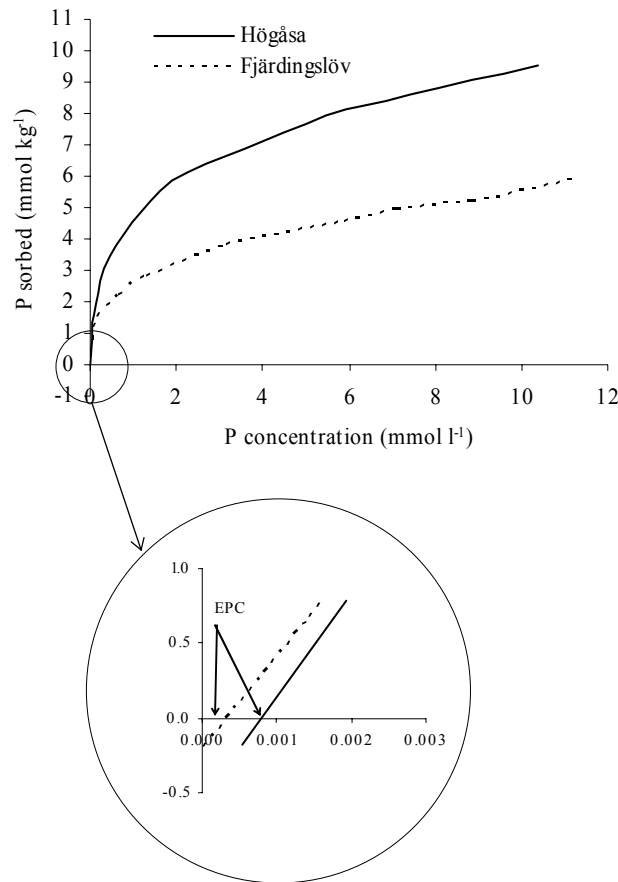
Figure 3. Example of two sorption isotherms and detailed picture of intercepts with the x-axis (EPC).

The Freundlich equation has the form:

$$X = a_F \, C^{b_F} \qquad\qquad [3]$$

where X and C have the same meaning as in the Langmuir equation and a_F and b_F are empirical parameters. The Freundlich equation is often used in its logarithmic form:

$$\log X = \log a_F + b_F \log C \qquad\qquad [4]$$

In this case no value of maximum P sorption capacity can be derived, nevertheless a_F and b_F can be calculated and different soils can be compared for sorption characteristics and a_F represents the amount of P sorbed (in mmol kg^{-1} soil) when C is 1 mmol l^{-1}.

12

Release of P from the soil can occur through desorption of P sorbed to soil surfaces but also through dissolution of phosphate minerals and through mineralization of organic P. Similarly to sorption, desorption occurs through ligand exchange with OH^-. However, desorption of P from soil surfaces is a much slower process than sorption. As mentioned above, P sorption is a combination of adsorption and precipitation. This means that some of the P sorbed by the soil is not readily desorbable, particularly if a ring structure has been formed (Figure 2). Occlusion of P in Fe and Al oxides or hydroxide structures also prevents desorption.

Different methods have been used to estimate potential P release from soils. Equilibration in the presence of a sink for P, *i.e.* resin (Sibbesen, 1978) or iron-impregnated strips (van der Zee *et al.*, 1987) which subsequently bind and remove P that is released, has been used. In this case, the removal of P from the solution is supposed to mimic plant uptake or P transported from the soil solution. Another method that has been shown to give a good estimate of potential P release from soils is extraction with water or a dilute salt solution (McDowell and Sharpley, 2001). During extraction, P concentration in the solution increases until equilibrium between P in solution and P sorbed by the soil is reached. In the present study, extraction with water and/or a dilute salt solution was used to estimate potential P release from the soils.

Using the lowest part of the sorption isotherm ($C \leq 0.1$ mg P l^{-1}), which is normally linear, the slope and the intercept with the x-axis can be calculated (Hartikainen, 1991). The intercept with the x-axis where $X=0$ (Figure 3), corresponds to the P concentration in solution at which no net sorption or desorption occurs and is called equilibrium P concentration (EPC). This is an estimate of the intensity of P in the soil. EPC depends on soil properties but is also affected by fertilization, usually increasing with increasing fertilization (Hartikainen, 1991).

Phosphorus subsurface leaching

In addition to erosion and surface runoff, subsurface leaching has been identified as one of the dominating processes for P losses from agricultural fields (Ulén, 1997; Turner & Haygarth, 2000). Subsurface leaching was previously thought to be insignificant in comparison to the other pathways since the subsoil is expected to bind P transported down the soil profile. However, subsurface leaching has gained increased attention during the past decade. There are two situations in particular in which an increased risk of P leaching has been noticed. The first is in soils where preferential flow dominates water transport through the soil profile, *i.e.* water transport occurs rapidly through cracks and biopores and only a small part of the subsoil is in contact with the solute. In this case, the water bypasses most of the sorbing area of the subsoil and P transported with the water can be leached (Djodjic, 2001). The second situation is in highly fertilized sandy soils or organic soils with low P sorption capacity and a shallow watertable. In this case, P in the soil can exceed the P sorption capacity of the soil and the soil has a lower capacity

to retain P within the profile (Breeuwsma & Silva, 1992). However, it has been found that even in other soil types, P concentration in subsurface drainage water can be high enough to cause environmental problems (Turner & Haygarth, 2000).

Soil testing and phosphorus leaching

There is a need to evaluate the vulnerability of soils for subsurface P leaching. The most common tool used to evaluate the risk for P leaching is soil P testing (Maguire & Sims, 2002). The soil testing is usually carried out on samples from the topsoil layer with tests developed for agronomic purposes, *i.e.* with the aim of describing P available for plant uptake. These P tests are very valuable since they are relatively inexpensive and reference values are available for many agricultural soils. However, they are not developed for evaluation of P leaching risks. Nevertheless, some researchers have found good relationships between soil test P (STP) and P leaching. Heckrath *et al.* (1995) found that P leaching losses were low when P extractable in 0.5 M sodium bicarbonate (Olsen-P) was less than 60 mg kg^{-1} and then increased rapidly when Olsen-P exceeded 60 mg kg^{-1}. They called this value a change-point, above which the risk for P leaching increased significantly. Theoretically, P is sorbed only at high energy sites below the change-point value, and hence desorption is low. Above the change-point value, P release increases significantly, since P is sorbed not only at high energy sites but also at low energy sites and thus P desorption is promoted. The change-point obtained by Heckrath *et al.* (1995) at the Broadbalk Continuous Wheat Experiment at Rothamsted has been intensively discussed and many researchers have tried to find corresponding change-points in other studies (*e.g.* Hesketh & Brookes, 2000; Kleinman *et al.*, 2000; Mc Dowell *et al.*, 2001). To find a change-point would be very attractive in practical environmental monitoring, since a value can be given that should not be exceeded. However, the change-point value seems to be sensitive to experimental conditions, such as the range of STP values tested and the soil to solution ratio for the P desorption parameter (Koopmans *et al.*, 2002). Furthermore, there is evidence indicating that even if a change-point can be identified, it would be individual for each soil. Hesketh & Brookes (2000) determined change-points in seven soils and found that they varied from 10 to 119 mg kg^{-1} Olsen-P.

Another approach, first developed in the Netherlands, is the use of degree of P saturation (DPS) to evaluate the risk of P leaching from soils (van der Zee *et al.*, 1990):

$$\text{DPS} = \frac{\text{Sorbed P}}{\text{P sorption capacity}} \times 100 \qquad [5]$$

DPS estimates how close the soil is to saturation and provides possibilities to compare soils with varying P sorption capacities. Different methods of estimating sorbed P and P sorption capacity can be combined to determine DPS. In the Netherlands and several other countries, P extracted with ammonium oxalate has

14

been used to estimate sorbed P, while Fe and Al in the same extract are used to estimate P sorption capacity:

$$DPS = \frac{P_{ox}}{(Fe_{ox} + Al_{ox})\alpha} \times 100 \qquad [6]$$

where α is a value between 0 and 1 which is derived from the relationship

$$\text{P sorption capacity} = (Fe_{ox} + Al_{ox})\alpha \qquad [7]$$

In the Netherlands, $\alpha = 0.5$ was recommended by van der Zee *et al.* (1990). DPS has been used to evaluate the risk for P leaching in sandy soils and a critical value for DPS was set at 25% which should not be exceeded and would correspond to a P concentration of 0.1 mg l^{-1} in the soil solution at the mean highest water level (Breeuwsma & Silva, 1992). In a summary by Beauchemin & Simard (1999) of studies that determined DPS, it was found that P_{ox}, Al_{ox} and Fe_{ox} were commonly used. However, for determination of DPS both standard agronomic methods, such as Olsen-P and Melich-3 P, and other methods, such as iron-impregnated strip P, have been used for estimation of sorbed P. For estimation of P sorption capacity, P sorption isotherms and Melich-3 extractable Al and Fe have been used (*e.g.* Kuo *et al.*, 1988; Sharpley, 1995, 1996; Maguire & Sims, 2002). The methods used to estimate sorbed P and P sorption capacity for determination of DPS in a region or a country need to be tested on representative soil types (Beauchemin & Simard, 1999). Furthermore, they need to be correlated with measures of potential P release or P in leachate water.

Objectives

The overall objective of this thesis was to determine the influence of soil P level and P sorption saturation on potential P release and P leaching in a range of soil types common in southern and central Sweden.

The specific objectives were:

- To determine the main soil properties influencing P sorption capacity and to evaluate some empirical methods for estimation of P sorption capacity (Paper I).
- To identify soil variables that can be used for prediction of potential P release from topsoils (Paper II).
- To study the impact of long-term inorganic P fertilization on P accumulation, P sorption saturation and potential P release in the soil profile (Paper III).
- To study the influence of soil properties such as soil P level, P sorption capacity and water transport mechanisms on P leaching from lysimeters (Paper IV).

Materials and Methods

Sites and soil sampling

All experiments were carried out using soils from the Swedish long-term fertility experiment initiated during the period 1957-1966 (Figure 4). These soils were primarily chosen since they include a range of four P levels built up during long-term fertilization with inorganic P (Table 1). They are also well documented and represent a range of texture, organic matter, pH and climatic conditions representative for Swedish agricultural soils (Table 2; Figure 4).

Table 1. *Fertilizer treatments in field experiment (kg ha^{-1} yr^{-1})*

PK level	PK addition	
	Southern Sweden	Central Sweden
A	0	0
B	R[a]	R[a]
C	R[a]+15 kg P+40 kg K	R[a]+20 kg P+50 kg K
D	R[a]+30 kg P+80 kg K	R[a]+30 kg P+80 kg K

[a]Replacement of P and K removed by harvesting. Replacement of P ranged from 9 to 19 kg ha^{-1} yr^{-1}.

Soils were sampled in a crop rotation with inorganic fertilization and crop residues incorporated into the soil. Crop rotations are four or six years and include cereals and oilseeds and, at sites in southern Sweden, also sugar beet. Phosphorus fertilizers are applied as superphosphate twice during each crop rotation, *i.e.* every second or third year. Fertilizers are incorporated into the soils immediately after application either at sowing or ploughing. The P and K treatments are coupled (Table 1), which limits the possibility of distinguishing between the effects of P and K (Carlgren & Mattsson, 2001). In each PK treatment there are four nitrogen (N) levels. In this study, soil samples and lysimeters were collected in treatments with N application rates of 82-125 kg N ha^{-1}yr^{-1}.

Topsoil samples (0-20 cm layer) were collected in autumn 1997 at five sites in southern Sweden (Fjärdingslöv, Ekebo, Orup, Örja and S. Ugglarp) and five sites in central Sweden (Kungsängen, Fors, Högåsa, Klostergården and Bjertorp). Soils were collected from all four P levels (Papers I and II). In Paper II, the calcareous Fors soil was omitted because it contains residue of Thomas phosphate applied before the start of the field experiment, which still affects the P properties in this soil.

Undisturbed soil cores (0.295 m diameter and 1.18 m length) were collected for the lysimeter experiment at five sites in autumn 1999 (Paper IV). Two sites in southern Sweden (Fjärdinglöv and Ekebo) and three sites in central Sweden (Högåsa, Klostergården and Kungsängen) were sampled. Soil cores were collected from all four P levels. However, due to the presence of large stones in the profile at Ekebo, no core was collected in treatment B at this site. On the same occasion as

the lysimeter sampling, topsoil samples (0-20 cm) were collected from all soils, and subsoil samples were collected at three depths in treatment A (20-40, 40-60 and 60-100 cm) and at eight depths in treatment D (10 cm intervals from 20 to 100 cm) at all five sites (Paper III).
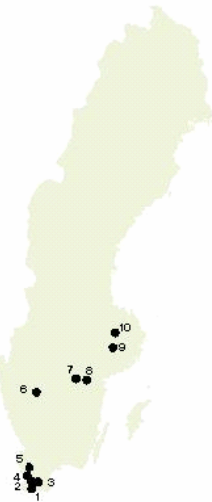

Figure 4. Map of Sweden showing the experimental sites. 1. Fjärdingslöv (54°24' N, 13°14' E), 2. S. Ugglarp, 3. Orup, 4. Örja, 5. Ekebo, 6. Bjertorp, 7. Högåsa, 8. Klostergården, 9. Kungsängen, 10. Fors (60°20' N, 17°29' E).

The applications of PK fertilizers in the experiments are not synchronized between the sites. At all sites in southern Sweden the last PK fertilization before sampling was in spring 1997. In central Sweden, at Bjertorp, Högåsa and Klostergården, PK was applied in spring 1996 while at Fors and Kungsängen fertilization took place in autumn 1996. At Högåsa and Klostergården, PK was also applied in autumn 1998, between the two samplings. This means that the time between fertilization and sampling was different for different sites and also between the sampling occasions. However there was always at least one cropping season between fertilization and sampling and the length of the experiments (more than 30 years) probably makes the differences less important. Nevertheless, as a result of these differences, results of the P analyses of samples from the same soils taken in 1997 and 1999 are not always comparable.

Table 2. *Classification according to Soil Taxonomy, some general properties and P sorption capacity (X_m; Paper I) of the soils (0-20 cm)*

Site	Classification	Texture	Clay	pH	Org. C	X_m
			%	(H_2O)	%	mmol kg^{-1}
Högåsa	Humic Dystrocryept[a]	Loamy sand	7	5.8	1.5	10.0
Orup	Aquic Haploboroll[b]	Sandy loam	10	5.9	1.9	12.2
S. Ugglarp	Typic Hapludoll[c]	Sandy loam	11	6.0	1.5	6.2
Fors	Udic Haploboroll[d]	Silty loam	17	8.0	1.1	6.6
Ekebo	Oxyaquic Hapludoll[e]	Loam	17	6.5	2.2	10.2
Fjärdingslöv	Oxyaquic Hapludoll[e]	Sandy loam	19	7.5	1.1	6.0
Örja	Typic Eutrocrept[b]	Loam	23	7.1	1.1	6.3
Bjertorp	Not determined	Silty clay loam	30	6.6	2.0	8.8
Klostergården	Oxyaquic Haplocryoll[a]	Silty clay loam	37	6.9	1.9	6.9
Kungsängen	Typic Haplaquept[d]	Clay	59	6.9	2.3	11.9

[a]Kirchmann, unpublished data; [b]Kirchmann & Eriksson (1993); [c]Kirchmann *et al.* (1996); [d]Kirchmann (1991); [e]Kirchmann *et al.* (1999)

Methods

Three of the experiments were carried out in the laboratory (Papers I, II and III; Table 3). All soil samples used in these experiments were air-dried and sieved through a 2-mm mesh prior to analyses. The fourth experiment (Paper IV) was carried out on undisturbed soil cores under natural conditions at an outdoor lysimeter station.

Table 3. *Sampling and experimental set-up for the four papers*

Paper	Type of study	Depth (cm)	P-levels	Number of sites	Sampling year
I	Laboratory	0-20	A	10	1997
II	Laboratory	0-20	A, B, C, D	9	1997
III	Laboratory	0-100	A, D	5	1999
IV	Lysimeters	0-100	A, B, C, D	5	1999

General soil properties

Texture was determined by the pipette sedimentation procedure as described by Ljung (1987). Soil pH was measured in water at a soil:water ratio of 1:5. Organic carbon was determined by dry combustion with an E-12 LECO CNS 2000 carbon analyzer. Iron and aluminium were extracted with 0.2 M ammonium oxalate (Fe_{ox} and Al_{ox}) at pH 3 for 2 hours (Schwertmann, 1964), 0.1 M sodium pyrophosphate (Fe_p and Al_p) at pH 10 for 16 hours (Loeppert & Inskeep, 1996), and dithionite-citrate-bicarbonate (Fe_{dcb} and Al_{dcb}) at near neutral pH for 16 hours (Mehra & Jackson, 1960). Fe and Al in the extracts were analyzed by atomic-absorption spectroscopy.

Soil phosphorus analyses

P in the soils was analysed using two agronomic methods, P-AL and Olsen-P. P-AL is the standard method used for agricultural fields in Sweden. This method includes extraction using a soil/solution ratio of 1:20 (w/v) with ammonium lactate/acetic acid for 90 min at pH 3.75 (Egnér *et al.*, 1960). Since Olsen-P is widely used, especially in Europe, Olsen-P was measured for comparison with other studies. Furthermore P-AL, which has a low pH, is less suitable on calcareous and alkaline soils since Ca-P compounds can be dissolved and plant-available P can thus be overestimated. Therefore, Olsen-P has been discussed to complement P-AL on these kinds of soils in Sweden. Olsen-P involves extraction using a soil/solution ratio of 1:20 (w/v) with 0.5 M sodium bicarbonate for 30 min at pH 8.5 (Olsen & Sommers, 1982). Phosphorus was also extracted with 0.2 M ammonium oxalate (P_{ox}) at pH 3.0 for 2 hours according to Schwertmann (1964) and P in the extract was analyzed according to Wolf and Baker (1990) (Paper II). To estimate potential P release, P was extracted in 0.01 M $CaCl_2$ (Papers II and III) and in distilled water (Paper III) using a soil/solution ratio of 1:3 (w/v) and an extraction time of 1 hour. Following centrifugation at 1500 rpm for 10 min, extracts were filtered through Millipore filter paper (<0.45μm) and reactive P ($CaCl_2$-RP and P_w, respectively) was determined. In Paper II, total P in the filtered $CaCl_2$ extract ($CaCl_2$-TP) was also determined after digestion in sulphuric-perchloric acid (Martin *et al.*, 1999). Phosphorus in $CaCl_2$- and water extracts was determined according to the green malachite method which is suitable at low P concentrations (Ohno & Zibilske, 1991).

Phosphorus sorption capacity

To determine P sorption capacity, sorption isotherms were constructed for the non-fertilized soils in treatment A (Paper I). Two grams of air-dried soil (≤2 mm) were equilibrated with 20 ml 0.01 M $CaCl_2$ containing increasing amounts of KH_2PO_4 in centrifuge tubes. Two drops of toluene were added to inhibit microbial activity. The tubes were shaken for 20 h. Following centrifugation at 3000 rpm for 10 min, the P concentration in the solution (C) was analyzed colorimetrically according to Murphy & Riley (1962). The amount of P sorbed by the soil (X) was calculated by subtracting the amount of P in the equilibrium solution from the amount added. Maximum P sorption capacity (X_m) was calculated from the isotherms according to the Langmuir equation (Paper I). Equilibrium P concentration (EPC) of the soils from treatment A was also calculated using the lowest part of the sorption isotherms (Paper II). Two indices of P sorption capacity (PSI) were determined using a single-point addition of 19.4 and 50 mmol P kg^{-1} soil (PSI_1 and PSI_2, respectively) as suggested by Bache & Williams (1971). The samples were treated in the same way as described for sorption isotherms. PSI indices were calculated as sorbed P (X) divided by the logarithm of P concentration (log C) at the single-point P addition (X/log C; Bache & Williams, 1971).

Lysimeter study

In the lysimeter study, the undisturbed soil cores (Figure 5) were placed in belowground pipes permanently installed at a lysimeter station in Uppsala, Sweden (59°49'N, 17°39'E). They were exposed to natural climatic conditions from October 1999 to September 2002. All lysimeters were fertilized with NH_4NO_3 and K_2SO_4 in spring every year at rates of 100 kg N ha^{-1} and 30 kg K ha^{-1}, respectively, whereas no P fertilizer was applied. Spring barley was grown in all soil cores in 2000 and 2001, while oats were grown in 2002. Water samples were collected after each major drain flow event. The concentration of total P was measured in unfiltered samples (TP) and dissolved reactive P (DRP) was measured after filtration through membranes with a 0.2 μm pore size according to the methods of the European Committee for Standardisation (1996). Unreactive P (UP) was calculated as the difference between TP and DRP.
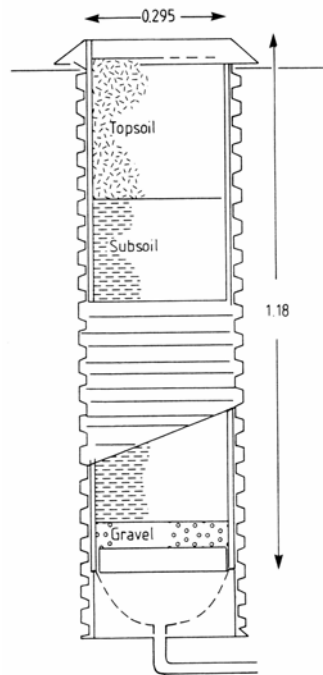

*Figure 5.*Lysimeter placed in a belowground pipe (From Bergström & Johansson, 1991).

Results and Discussion

Phosphorus sorption capacity

The maximum P sorption capacity of a soil is determined by soil properties and not by the P content in the soil. However, soils usually contain some sorbed P, and when P sorption capacity is determined using *e.g.* sorption isotherms, it is affected by P already sorbed by the soil (Bache & Williams, 1971; Barrow, 1974). In the present study, P sorption capacity was determined in soils from treatment A, using P sorption isotherms (Paper I). Examples of sorption isotherms for two of the soils (Högåsa and Fjärdingslöv) are shown in Figure 3. Since the soils in treatment A had been continuously cropped without P fertilization for more than 30 years, the soils were depleted in P and the influence of P already sorbed by the soil was thereby reduced. The P sorption capacity (X_m) was calculated from the sorption isotherms using the Langmuir equation and X_m ranged from 6.0 to 12.2 mmol kg^{-1} in the ten soils studied (Table 2). The a_F values determined from the Freundlich equation ranged from 8.2 to 18.2 mmol kg^{-1} and were highly correlated with X_m (r=0.99***; Paper I).

The two single-point P sorption indices, PSI_1 and PSI_2, ranged from 2.6 to 4.6 and from 3.0 to 5.4 mmol kg^{-1}, respectively, in the topsoils in treatment A (Paper I). However, it should be noted that these values are indices and not absolute values of P sorption capacity. The indices were found to be well correlated with X_m (r≥0.98***) with PSI_1 giving the highest correlation. The amount of P added should be high enough to exceed the sorption maximum but not too high, since the accuracy of the value of the difference between initial and final P concentrations decreases if the difference is very low. X_m measured for the topsoils was less than 12.2 mmol kg^{-1} for all the sites and thus addition of 19.4 mmol kg^{-1} would be sufficiently high for single-point addition in topsoils. Hence, PSI_1 was used in the topsoils in the following studies. In the subsoils, however, some soils sorbed more than 90% of the P when 19.4 mmol kg^{-1} soil was added and therefore PSI_2 was used for the subsoils. The variation in P sorption capacity was greater in the subsoils than in the topsoils. PSI_2 in the subsoils ranged from 2.0 to 16.8 mmol kg^{-1} and thus both higher and lower values of PSI_2 were obtained in the subsoils than in the topsoils. The higher PSI_2 addition of 50 mmol kg^{-1} is suggested both for topsoils and subsoils in future studies, to have one general index and to ensure that P sorption maximum is exceeded.

P sorption index (PSI) is presumed to be affected by previous fertilization in the same way as the sorption isotherm, *i.e.* P sorption is decreased as P previously added blocks parts of the sorption sites (Barrow, 1974). When PSI_1 was determined in treatments A to D for nine of the soils, there was a tendency for PSI_1 to decrease with increasing fertilization for most of the soils, indicating that P already sorbed had affected PSI_1 (Paper II). PSI_2 measured in the whole soil profile in treatments A and D also differed between treatments in some of the soils, but the differences were not consistent and in some cases treatment D had higher PSI_2 than treatment A, which was unexpected. In a clay loam soil, Sharpley *et al.* (1984)

found a significant decrease in PSI with increasing addition of inorganic or organic P fertilizers. However in the present study, there were no significant differences between P treatments in either PSI_1 in the topsoils (Paper II) or PSI_2 in the soil profiles (Paper III) when all soils were considered and thus PSI can probably also be used to estimate P sorption capacity in fertilized soils.

The variation in PSI_2 with depth did not show any consistent pattern between soils (Paper III). PSI_2 was more or less constant down the profile in one soil while it decreased in another and increased in the remaining three soils. Other studies have also shown varying results with respect to P sorption capacity in the soil profile. Lookman *et al*. (1995) reported a significant decrease in P sorption capacity, based on Fe_{ox} and Al_{ox}, in 301 sandy to sandy loamy soils in northern Belgium. They had no clear explanation for the decrease in P sorption capacity with depth, but they assumed that higher rates of weathering and higher content of organic matter in the shallow layers could have promoted formation and stability of oxalate extractable Fe and Al. On the other hand, both Sharpley *et al*. (1984) and Mozaffari & Sims (1994) found that P sorption maxima measured from sorption isotherms were consistently higher in the subsoils than in the topsoils and Mozaffari & Sims (1994) attributed this to higher clay content in the subsoils than in the topsoils. In the present study, clay content also increased with depth in the soils where PSI_2 increased with depth, even though the increase in clay content was very small in some of the soils.

To determine the main soil properties affecting P sorption capacity in Swedish soils, the correlation between X_m and soil properties in the topsoil (10 soils; Paper I) and the correlation between PSI_2 and soil properties in the entire soil profile (5 soils; Paper III) were studied for treatment A. Since P is commonly sorbed to Fe and Al oxides and hydroxides, the correlations between different fractions of Fe and Al (Fe_{ox}, Fe_{dcb}, Fe_p, Al_{ox}, Al_{dcb} and Al_p) and P sorption capacity were studied in the topsoils (Paper I). The exact forms of Fe and Al extracted by the different solutions are not known but it is generally assumed that Fe_p is an estimate of Fe bound to organic matter (Bascomb, 1968), Fe_{ox} estimates poorly crystalline Fe oxides Fe bound to organic matter, whereas Fe_{dcb} estimates the total amount of Fe oxides including well crystallized forms (Cornell & Schwertmann, 1996). The same forms of Al are often assumed to be extracted, although some differences may occur (Kaiser & Zech, 1996).

The fractions of Fe and Al most strongly correlated with X_m in the topsoils (n=10) were (Fe_{ox}+Al_{ox}) (r=0.83**), Al_{ox} (r=0.73*), Al_{dcb} (r=0.73*), Fe_{ox} (r=0.69*) and Fe_p (r=0.63*). Thus, poorly crystalline Fe oxides and Fe bound to organic matter seemed to be the forms of Fe that mainly affected P sorption capacity. This was expected since they have large specific areas with a high proportion of reactive sites (Parfitt & Childs, 1988). However for Al, Al_{dcb} seemed to be as important for sorption capacity as Al_{ox}. Al was usually better correlated to X_m than Fe even though the differences were small. Similarly, other authors have also found that Al was generally a more important factor for P sorption capacity than Fe (*e.g.* Willams *et al.*, 1958; Niskanen, 1990). Niskanen (1990) suggested that the difference was due to the appearance of the metals in the soil, while Fe oxides and

22

hydroxides occur as discrete mineral particles in the soil, Al oxides and hydroxides tend to form a film on clay particles, which results in a greater surface of Al than Fe oxides and hydroxides.

Multiple regressions were also used to find a way to predict X_m in the topsoils (n=10) using a combination of the different forms of Fe and Al (Paper I). The best predictions were found using Fe_{ox} and Al_{dcb} (Equation 8; $R^2=0.85**$) and Fe_{ox} and Al_{ox} (Equation 9; $R^2=0.72**$).

$$X_m = 2.12 + 0.0421\ Fe_{ox} + 0.0954\ Al_{dcb} \qquad [8]$$

$$X_m = 1.29 + 0.0369\ Fe_{ox} + 0.109\ Al_{ox} \qquad [9]$$

Here it is also evident that Al_{dcb} is important to P sorption capacity since Al_{ox} gave a lower coefficient of determination. Since two extractions are needed when using Fe_{ox} together with Al_{dcb} for predicting X_m, it would anyway be preferable for routine analyses to use Fe_{ox} and Al_{ox} which only requires one extraction, despite the slightly lower coefficient of determination.

In the subsoils Fe and Al was only extracted with ammonium oxalate (Fe_{ox} and Al_{ox}). PSI_2 was weakly but significantly correlated to ($Fe_{ox}+Al_{ox}$) when all soils and depths were included (r=0.65**, n=20) (Paper III). However, the correlation was markedly increased when only 0-60 cm depths were included (r=0.90***, n=15). Below 60 cm depth ($Fe_{ox}+Al_{ox}$) seemed to sorb more P per mol of oxide or hydroxide in relation to the more shallow layers. This could suggest that in the deeper horizons, Fe and Al oxides and hydroxides have a lower degree of crystallization and thus a larger surface area. Nevertheless, Fe_{ox} and Al_{ox} seemed to be main soil parameters influencing P sorption capacity in both topsoil and subsoil.

Correlations between X_m in the topsoils (10 soils) and PSI_2 in the whole profile (5 soils) and some general properties such as pH, organic carbon and clay were also studied (Papers I and III). No correlation was found between P sorption capacity and pH either in the topsoils or in the subsoils. Organic carbon was positively correlated with X_m (r=0.74*) in the topsoils but as expected, no correlation was found between PSI_2 and organic carbon in the subsoils. Organic matter might compete with P for sorption sites on Fe and Al oxides and hydroxides and clay. On the other hand, a positive correlation between organic carbon and P sorption is often found and is probably due to organic matter associated with Fe and Al oxides and hydroxides and organic matter inhibiting crystallization of Fe and Al oxides and hydroxides and thereby promoting sorption capacity (Borggaard *et al.*, 1990). Indeed, organic carbon in the topsoils was significantly correlated with Al_{ox} and ($Fe_{ox}+Al_{ox}$) (r≥0.75*) in this study. No correlation was found between clay and X_m in the topsoils. In contrast, a weak but significant correlation between PSI_2 and clay was found when the five soils and all depths were considered (r=0.69***, n=20). Similarly, Beauchemin & Simard (2000) found that clay content had a greater effect on P sorption capacity in the subsoil than in the topsoil. The difference between topsoils and subsoils in this respect could be due to

a higher content and greater influence of organic matter in the topsoil which can bind to clay and inhibit sorption of P to the clay surface (Sample *et al.*, 1980).

Phosphorus accumulation in the soils

In order to study P accumulation in the soils following long-term P application with inorganic fertilizers, two methods were used; P-AL and Olsen-P. P-AL is the standard method used for agricultural purposes in Swedish soils. Olsen-P was chosen as it is a possible alternative to P-AL and for comparison reasons since it is a well-known method and it is used as a routine analysis in many countries in Europe. There is also a difference in pH in the extraction solutions (pH 3.75 for P-AL and 8.5 for Olsen-P) which makes Olsen-P a better option in soils with high pH.

Total fertilizer P applied since the start of the experiment, including replacement, ranged from 290 to 704 kg ha^{-1} for treatment B, 1001 to 1343 kg ha^{-1} for treatment C and 1317 to 1970 kg ha^{-1} for treatment D. As expected, P-AL increased significantly from treatment A to D in all nine topsoils studied (Figure 6). Compared with P-AL values in the initial samples, taken at the beginning of the field experiment, P-AL decreased in all soils by 1.9 to 5.5 mg P 100 g^{-1} soil in treatment A, which indicates a depletion of P in the topsoil as a result of cropping (Paper II). Treatment B received replacement fertilization, *i.e.* the same amount of P that was removed with harvest was then applied to the soils. In treatment B, P-AL increased slightly in Fjärdinglöv compared to the initial samples while it was equal in two soils and decreased in the others (Paper II). This implies that replacement fertilization was not sufficient to maintain the P level in six out of nine soils. This is probably due to the retention of P in soils, caused by adsorption and precipitation reactions, which renders P less available (Sample *et al.*, 1980). In treatments C and D, the soils are enriched in P and P-AL increased in all soils by up to 15.3 mg P 100 g^{-1} soil compared with the initial samples (Paper II). The increases in P-AL were highest at Fjärdinglöv and lowest at Bjertorp

Phosphorus accumulation in response to long-term inorganic P fertilization was also studied in the whole soil profile for five of the soils. P-AL and Olsen-P were compared at different depths in treatments A and D (Paper III). The annual total P application in treatment D was 42-49 kg P ha^{-1}yr^{-1}. The differences in P-AL and Olsen-P between the treatments were statistically significant down to 40 cm depth, considering the five sites as replicates (Figure 7). The differences between treatments were due to both depletion in the non-fertilized treatment A and fertilization exceeding crop uptake in treatment D. Below 40 cm depth, the differences in P content were not significant. When only studying the fertilized profiles it is evident that the main accumulation of P occurred in the 0-30 cm layer (Figure 7). This implies that P applied as inorganic fertilizers stayed in the plough layer or in the nearest 10 cm of the plough layer.
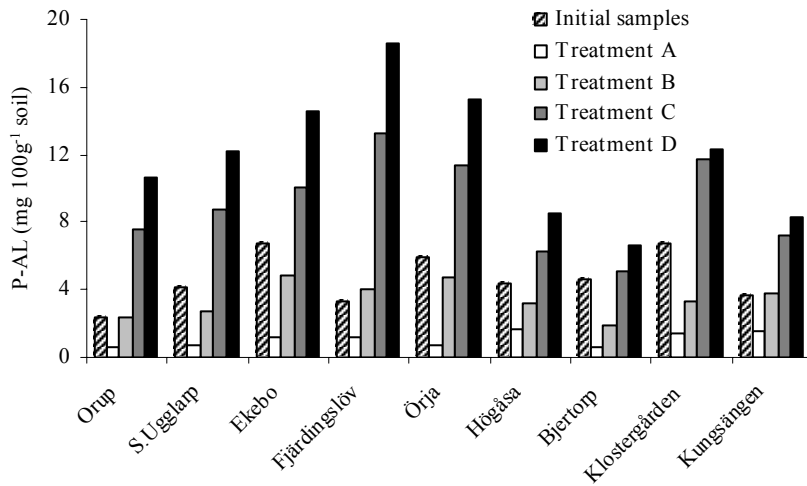
Figure 6. Values of P-AL in the initial samples taken at the start of the field experiment and the four P treatments sampled in 1997 (0-20 cm).
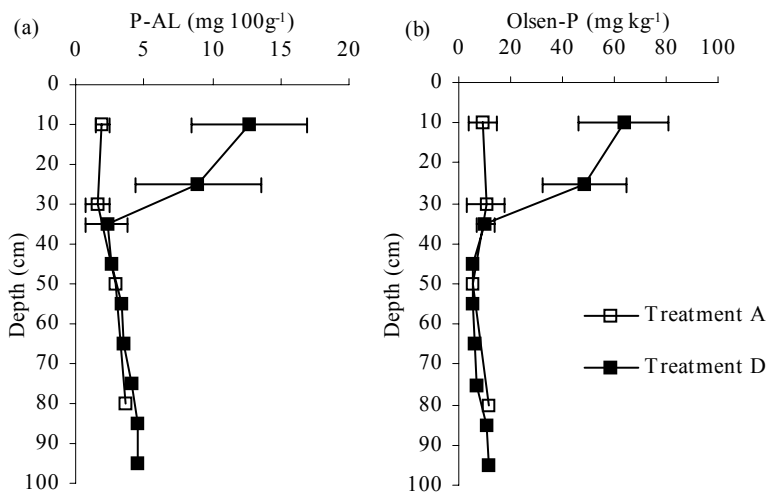

Figure 7. Mean of (a) P-AL and (b) Olsen-P in the five soil profiles. Error bars show SD for each treatment where significant differences between treatments occurred.

For the five soils sampled in 1999, P-AL in treatment D was compared with P-AL in the initial soil samples taken at the start of the field experiment. In treatment D, a total of 930-1200 kg P ha^{-1} in excess of plant uptake had been applied since the start of the experiment. The increases in P extractable with AL-solution compared to initial soil samples in the top 20 cm corresponded to 104 to 409 kg ha^{-1}, which means that 10 to 34% of excess fertilizer P applied was found in the AL-fraction in the 0-20 cm layer. Assuming the same P-AL for the 20-30 cm layer as for the 0-20 cm layer in the initial soil samples, 0-158 kg P ha^{-1} (0-15%) of excess

fertilizer P was found as P-AL in the 20-30 cm layer. Since differences in P content between treatments A and D were not significant below 30 cm, the main accumulation of excess P was expected to be in the 0-30 cm layer. This means that a total of 10-49% (average 24%) excess fertilizer P was found as P-AL in the 0-30 cm layer. This suggests that the main proportion of excess P was transformed to less available forms which were not extractable by the AL-solution. Another possibility would be that excess P could have been leached or lost through surface runoff or erosion. However, according to previous studies (*e.g.* Ulén *et al.*, 2001) and measurements of leaching from the lysimeters in the present study (Paper IV), P losses would only constitute a minor proportion (<5 %) of excess P applied.

To study the effects of soil accumulation or depletion of P on crop growth was beyond the scope of this thesis. However, results from 35-40 years of cultivation were summarized by Carlgren & Mattsson (2001). In brief, the effects of PK fertilization were minor compared to the effects of N fertilization. In the treatments with N application of 82-100 kg $ha^{-1}yr^{-1}$, the average grain yields for cereals increased by 2-17% (average 12%) in treatment C compared with treatment A. However, for oilseeds the average grain yield increased by 32% and for sugar beet, which is a highly nutrient-demanding crop, the average root yield increased by 58% in treatment C compared with treatment A (Carlgren & Mattsson, 2001).

Phosphorus release

As mentioned above, the most common tool used to evaluate the risk for P leaching is soil P testing (Maguire & Sims, 2002). To evaluate the relationship between STP values and P release in the soils studied, values of P-AL and Olsen-P were related to potential P release (Paper II). Potential P release was determined by extraction with 0.01 M $CaCl_2$. Both total P and reactive P in the $CaCl_2$ extract were determined ($CaCl_2$-TP and $CaCl_2$-RP, respectively). An exponential increase in potential P release was found in response to increasing P-AL or Olsen-P and the logarithmic value of $CaCl_2$-TP was fairly well related to Olsen-P and P-AL (0.74 $\leq R^2 \leq$ 0.99) for each soil (Paper II). However, those relationships differed between soils and potential P release was very different between soils with similar STP values if the soils had different P sorption capacities (Paper II). Thus, a method which could be used for different types of soils would be desirable.

In order to study the approach of using degree of P saturation (DPS) as a tool to predict P release, a number of methods were tested for estimating sorbed P and P sorption capacity in the non-calcareous soils according to Equation 5 (Table 4; Paper II). Two indices of P sorption capacity (PSI_1 and PSI_2) were also tested in this approach, not giving DPS as a percentage, but rather P sorption saturation as a ratio between sorbed P and PSI. This is a simple, empirical alternative to obtain an estimate of P sorption saturation which could be useful in practice.

First, P_{ox}, Fe_{ox} and Al_{ox} were tested for determination of degree of P saturation (DPS-1) according to Equation 6 in the non-calcareous soils. However, there are some uncertainties about using this method in Swedish soils: Firstly, Swedish soils

are relatively young and have a high percentage of acid soluble P such as apatite and other Ca-phosphates (Fredriksson & Haak, 1995). Ca-phosphates can be dissolved by the acid ammonium oxalate solution (Hartikainen, 1979). Indeed, high values of P_{ox} were obtained especially in treatment A (Paper II) and hence, P_{ox} probably overestimated sorbed P in these soils. Similarly, Uusitalo & Tuhkanen (2000) and Peltovuori *et al.* (2002) noticed this problem in Finnish soils, which are also rich in Ca-phosphate. They suggested sequential extraction with ammonium chloride (NH_4Cl), ammonium fluoride (NH_4F) and sodium hydroxide (NaOH) instead of P_{ox} to estimate sorbed P. However this is a laborious method which is not suitable for routine analyses. Secondly, if Fe_{ox} and Al_{ox} are to be used for estimation of P sorption capacity, the α-value determined according to Equation 7 needs to be checked for Swedish soils. In the Netherlands, and also in many other countries, $\alpha=0.5$ is used (van der Zee *et al.*, 1990; Lookman *et al.*, 1995; De Smet *et al.*, 1996; Turtola & Yli-Halla, 1999). $\alpha=0.5$ was recommended by van der Zee *et al.* (1990) since $\alpha=0.5\pm0.1$ was obtained for acid sandy soils and peat soils in central Europe. However, α strongly depends on the laboratory conditions under which P sorption capacity is determined, and it also depends on the degree of crystallinity of iron and aluminium oxides in the soils (van der Zee *et al.*, 1990). Since Swedish soils are younger and less weathered than those in Central Europe, it cannot be assumed without further studies that the properties of iron and aluminium oxides are equal (Beauchemin & Simard, 1999; Uusitalo & Tuhkanen, 2000). Therefore, P_{ox}, Fe_{ox} and Al_{ox} were not used for determination of DPS in this study.

Owing to uncertainty in the P_{ox} and the α-value, other methods to estimate sorbed P and P sorption capacity were combined to estimate P sorption saturation (Table 4; Paper II). The routine methods, P-AL and Olsen-P, were used as estimates of sorbed P. Three different methods were used to estimate P sorption capacity: X_m was calculated from P sorption isotherms using the Langmuir equation, P sorption capacity determined from Fe_{ox} and Al_{ox} using Equation 9 (hereafter referred to as PSC_{ox}) and the two single-point P sorption indices (PSI_1 and PSI_2, respectively). When using X_m and PSC_{ox} to estimate P sorption capacity, DPS was calculated according to Equation 5 (DPS-2 to DPS-5), while P sorption saturation was expressed as a ratio of sorbed P and P sorption indices, when PSI_1 and PSI_2 were used. Values of the different P sorption saturation indices were evaluated as predictors of potential P release (measured as $CaCl_2$-TP or $CaCl_2$-RP or P_w).

In the topsoil, all combinations studied gave good relationships with potential P release ($R^2 \geq 0.79$; Table 4), indicating that there are several possible methods that can be used to predict P release. When X_m or PSC_{ox} were used for P sorption capacity, the relationships with potential P release were exponential. This implies that P release increases more per unit increase in DPS as the saturation degree increases. This was expected since at low saturation degree, high affinity sites are used while at higher saturation degree low affinity sites are also used. In addition, sorption of negative phosphate ions increases the negative charge on the surface which decreases the surface affinity for P sorption at higher degree of saturation (Barrow, 1978). In contrast, when P sorption saturation was expressed as the ratio

27

between P-AL or Olsen-P and PSI_1, the relationships with potential P release were linear (Table 4). This could probably be due to the slightly decreasing PSI_1 values in the fertilized soils (Paper II), which compensate for the above mentioned mechanisms. In all cases, slightly higher coefficients of determination were obtained when Olsen-P was used than when P-AL was used for estimating sorbed P (Table 4). P sorption capacity derived from a sorption isotherm (X_m) is laborious to obtain and not suitable for routine analyses. Even though differences were small, using PSI_1 as an estimate of P sorption capacity gave slightly higher coefficients of determination than when PSC_{ox} was used ($R^2 \geq 0.86$ and $R^2 \geq 0.79$, respectively) and thus PSI_1 seemed to be the most suitable parameter for estimation of P sorption capacity when predicting P sorption saturation in the topsoil.

Table 4. *Combinations of sorbed P and P sorption capacity to determine P sorption saturation*

Saturation index	Sorbed P	P sorption capacity	Depth (cm)	Estimate of P release	Relationship	R^2
DPS-1	P_{ox}	$(Fe_{ox}+Al_{ox}) \times 0.5$	0-20	-	-	-
DPS-2	Olsen-P	X_m	0-20	$CaCl_2$-TP	exponential	0.85
DPS-3	P-AL	X_m	0-20	$CaCl_2$-TP	exponential	0.83
DPS-4	Olsen-P	PSC_{ox}	0-20	$CaCl_2$-TP	exponential	0.83
DPS-5	P-AL	PSC_{ox}	0-20	$CaCl_2$-TP	exponential	0.79
Olsen-P/PSI_1	Olsen-P	PSI_1	0-20	$CaCl_2$-TP/ $CaCl_2$-RP	linear	≥ 0.88
P-AL/PSI_1	P-AL	PSI_1	0-20	$CaCl_2$-TP/ $CaCl_2$-RP	linear	≥ 0.86
Olsen-P/PSI_2	Olsen-P	PSI_2	0-100	$CaCl_2$-RP/ P_w	linear	≥ 0.88
P-AL/PSI_2	P-AL	PSI_2	0-100	$CaCl_2$-RP/ P_w	linear	≥ 0.61

Since it was not possible to use PSI_1 in subsoils, PSI_2 was used for estimation of P sorption capacity in the profiles (Table 4). The ratios of P-AL/PSI_2 and Olsen-P/PSI_2 were determined down to 100 cm depth in treatments A and D for five of the soils (Paper III). P_w was used in addition to $CaCl_2$-RP as an estimate of potential P release in the subsoils. The main reason for using the two different extractants was to simulate two different situations, one with low ionic strength, which could occur at heavy rainfall or snowmelt and during macropore flow (Jensen *et al.*, 1998) and one with higher ionic strength, more similar to soil solution in equilibrium with the soil (Wiklander & Andersson, 1974). Another reason for using the two extractants was that $CaCl_2$-RP was very low in the deeper layers and since P_w is normally higher than $CaCl_2$-RP it was easier to distinguish between soils. $CaCl_2$-RP and P_w were weakly but significantly related to P-AL/PSI_2

($R^2 \geq 0.61$***, n=65) when all soils and horizons were included. However, coefficients of determination were markedly increased if only 0-40 cm horizons were included ($R^2 \geq 0.88$***, n=25). Both $CaCl_2$-RP and P_w were highly related to Olsen-P/PSI_2 ($R^2 \geq 0.88$***, n=65) when all depths were included and no increase in coefficients of determination was obtained when subsoils below 40 cm were excluded. Hence, P-AL/PSI_2 proved to be a good tool for predicting potential P release at least for 0-40 cm depth while Olsen-P/PSI_2 could be used for all depths down to 100 cm.

Phosphorus leaching from lysimeters

Total P losses from the lysimeters ranged from 0.03 to 1.09 kg ha^{-1}yr^{-1} with an average of 0.29 kg ha^{-1}yr^{-1} during the three years studied (Paper IV). Mean values for the three years are shown in Figure 8. Using the mean values of total P leaching during the three years, total P leaching since the start of the field experiment (33 to 42 years) was calculated to be 3-25 kg ha^{-1} total P, with an average of 11 kg ha^{-1}.
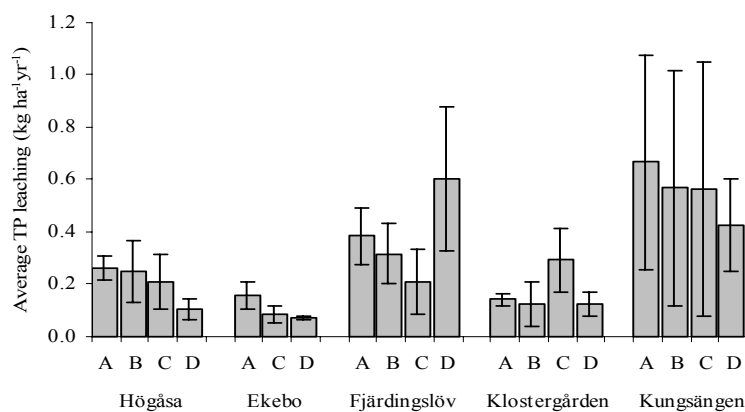

Figure 8. Average TP leaching during three years. Error bars show SD for the three years.

The leaching of total P from the lysimeters did not show any clear or consistent pattern when comparing different treatments in each soil (Figure 8; Paper IV). In some of the soils, the highest fertilized treatment even had the lowest losses of P. No significant differences were obtained between treatments when the five sites were considered as replicates. Neither STP (P-AL and Olsen-P) nor P sorption saturation (ratios of P-AL/PSI and Olsen-P/PSI) measured in the topsoils could explain the losses of P. Rather there was a difference between soil types. Total P losses from Kungsängen were significantly higher than the losses from all other soil, independent of P level. These differences are probably due to the differences in P transport pathways through the soil profile. Total P losses from the remaining four soils were not significantly different.

Kungsängen is a clay soil and is the only soil that showed clear evidence of macropore flow (Kirchmann, 1991). Even though Klostergården also is a clay soil, there was a lack of continuous macropores in the profile (Kirchmann, unpublished data). Hence, when comparing these five soils, macropore flow seemed to be a crucial factor governing P losses. Fjärdingslöv was the only soil where the highest P level (Treatment D) resulted in clearly higher P leaching losses. This soil had the lowest P sorption capacity (X_m) in the topsoil of all ten soils studied (Paper I). Furthermore, in the topsoil of treatment D, both potential P release measured as $CaCl_2$-RP, and P_w and P sorption saturation measured as P-AL/PSI_1 and Olsen-P/PSI_1 were the highest of the five soils in the study. Phosphorus sorption capacity increased with depth in Fjärdingslöv and P-AL/PSI_2 and Olsen-P/PSI_2 were very low below 50 cm in treatment D (Paper III). Nevertheless, the low P sorption capacity of the topsoil seemed to have caused a high P release and P was transported down the profile and leached. In this case the subsoil was not able to readsorb P even though there was no clear evidence of macropore flow. However, the clay in Fjärdingslöv contains smectite-like minerals which can give some swelling and shrinking properties and cause cracks (Kirchmann *et al.*, 1999) and thereby allow the soil solution to bypass the subsoil without interaction. For the other three soils, Högåsa, Ekebo and Klostergården, P sorption and desorption processes in the subsoil seemed to be decisive for P leaching. Treatment D in Ekebo and Klostergården had higher values than Högåsa of both P-AL and Olsen-P, P sorption saturation and potential P release (measured as $CaCl_2$-RP and P_w) in the topsoil (Paper III). Nevertheless, mean total P leaching from Högåsa (0.206 kg ha^{-1}yr^{-1}) was higher than from Ekebo and Klostergården (0.105 and 0.170 kg ha^{-1}yr^{-1}, respectively). Högåsa had a decreasing P sorption capacity with depth and a high potential P release, ($P_w \geq 0.18$ mg l^{-1}) below 60 cm in both treatments A and D. Ekebo and Klostergården, on the other hand, had constant or increasing P sorption capacity with depth and very low potential P release ($P_w \leq 0.02$ mg l^{-1}) below 60 cm depth (Paper III). It seems that P released in the topsoil of Ekebo and Klostergården was readsorbed in the subsoil and the lower horizons acted as a buffer zone and also levelled out the differences between treatments. In Högåsa, there was a high potential P release throughout the profile, and the subsoil in all treatments may have acted as a P source. This implies that sorption and desorption processes in the subsoils were decisive for P leaching in these soils where water transport was slow.

Importance of phosphorus source and transport mechanisms for leaching

Phosphorus losses are dependent both on P source factors and transport mechanisms. If there is a P source, there is a high *potential* for P losses. However, increased risk for P losses occurs if there is a P source in combination with a high potential for transport (Gburek *et al.*, 2000). The P source is influenced by soil P characteristics, fertilization, management *etc.* and transport factors are influenced by the dominating water transport mechanisms such as surface runoff, erosion or macropore flow. The importance of the interplay between P source and transport mechanisms for P leaching was evident in this study. Phosphorus sorption and

release processes studied in the laboratory in Paper II and Paper III gave very clear results on the P source with a clearly increasing potential P release with increased P level and the ratios P-AL/PSI and Olsen-P/PSI seemed to be good indicators of P release and hence potential for P losses. However, when transport mechanisms were added in Paper IV, the results were very different and much more complex. In this case, both P sorption and release processes in the profile and the water transport mechanism were taken into account. In four of the soils included in the lysimeter study, water was mainly transported slowly down the profile through piston flow. In these cases, P sorption and release processes can occur throughout the profile. The P released in the topsoil was buffered by the P sorption capacity in the subsoil. The buffering capacity of the subsoil was high enough to level out the differences between the P treatments except for treatment D of Fjärdingslöv. So in these cases, the slow water transport seemed to permit processes of P sorption and release throughout the profile that were decisive for P leaching. In Kungsängen, which was the only soil in the lysimeter study with evidence of macropore flow, P sorption and release in the topsoil would be more important than in the subsoil since the subsoil is bypassed quickly by most of the soil water. However the results showed no difference in TP losses between treatments, which was unexpected. Nevertheless, potential P release measured as $CaCl_2$-TP (Paper II) also showed small differences between treatments in Kungsängen, and concentrations of $CaCl_2$-TP (0.21-0.27 mg l^{-1}) were very similar to total P concentrations in the leachate from the lysimeters (0.22-0.27 mg l^{-1}). Although these values are not directly comparable, they may indicate small changes in solution P concentration as water is transported through the soil profile. In summary, the transport factor seemed to be crucial for P leaching from the lysimeters. When water transport was slow and dominated by piston flow, it seemed to be necessary to consider P sorption and release in the entire soil profile. The higher P leaching from Kungsängen compared to the other soils indicated that the presence of macropores can be important for the risk of P leaching.

Scaling aspects and limitations

When conducting research, experiments can be carried out at different scales. In studying P losses from agriculture, experiments can be performed in the laboratory under controlled conditions or in lysimeters and up to plot, field and catchment scale. In this thesis, three experiments were carried out in the laboratory and one at a lysimeter scale, *i.e.* all experiments were carried out under relatively controlled conditions. Experiments at a smaller scale, such as laboratory and lysimeter experiments, are necessary to separate different processes from each other and to evaluate the importance of the different processes when they are put together in a system. When trying to scale up results from laboratory or lysimeter experiments to field or catchments, the limitations must be borne in mind. In particular quantitative values cannot be directly applied on the larger scale.

In the laboratory experiments, soils were air dried and sieved to <2mm. Thereby only the fine part of the soils was included and the largest aggregates and the structure of the soils were destroyed. The contact area in the soils was probably

larger than naturally as larger aggregates were broken down. Furthermore, experiments were conducted at a constant temperature (approx. 21 ^{o}C) which was higher than the mean temperature under natural conditions and this could probably increase the rate of the reactions. The larger contact area and the higher temperature may have resulted in *e.g.* higher P sorption capacity than would have been found in a natural system. Drying and then rewetting the soil could also influence the results to some extent, especially for the biological processes. For example, rapid rewetting can cause an osmotic shock and lysis of microbial cells which in turn can cause increased release of P (Turner & Haygarth, 2001). However in this thesis, the main focus was on the chemical processes, which are not affected to the same extent by air drying.

In the lysimeter study, the structure and aggregates were intact and water transport was more similar to natural conditions. However there are also limitations in lysimeters compared with natural conditions. In the lysimeters, no lateral surface or subsurface water flow is possible, which could have influenced the transport of P. Furthermore, lateral crop root growth is restricted, which could influence P uptake by the crop and thus P removal from the soil profile. In addition, there is always a risk of side-wall flow in lysimeters. However, no side wall flow was detected in an experiment using lysimeters similar to those in this thesis (Bergström *et al.*, 1994).

The spatial variability within and between field plots can be high and the sampling of the soils and the lysimeters is, of course, another factor affecting the results. Furthermore, Sibbesen *et al.* (2000) found that in field experiments without boundaries, soil particles and P bound to them can be moved from one plot to another through tillage, affecting treatment effects.

Practical implications of the results

P leaching is a very complex process with many factors involved such as water transport, soil properties, fertilization, soil management *etc*. For practical use, it would have been desirable to find a critical value of P-AL or Olsen-P for all soils that could be used as a limit value to minimize the risk of P leaching losses. However, these studies have shown that this was difficult to achieve because each soil behaved differently and many factors need to be taken into account. In this study, P-AL and Olsen-P were not even correlated with P leaching from lysimeters for each individual soil. Instead, the results showed the effects of inherent soil properties for P leaching since there was rather a difference between soil types than between different P levels. The soil where macropore flow was evident had the highest P leaching losses, which implies that macropores can be a major factor increasing P leaching losses and thus an indicator of the presence of macropores would be necessary for risk assessment. In the soils where water transport through the profile was slow, P sorption and release processes in the subsoil proved to be as important as topsoil properties, since the subsoil can act either as a source or a sink of P transported down the profile. This would suggest that in these soils, analyses

of the subsoil in addition to topsoil analyses are necessary when assessing the risk for P leaching.

Including P sorption capacity improved estimates of the ability of the soil to release P, and thus an estimate of the P source can be obtained. However, in this study there was no direct correlation between P sorption saturation in the topsoil and P leaching losses. Nevertheless, P sorption saturation in the topsoil is probably one factor that can be useful to include in a risk assessment system. In addition, even though it was not tested in this thesis, P sorption saturation measured in the 0-5 cm could probably be useful for estimation of the risk for P losses through surface runoff.

In summary, the results from this study were obtained from a limited number of soils and the different soils showed very divergent patterns of P leaching. Further research would be necessary to draw more general conclusions on how to evaluate the risk for subsurface P leaching in different soil types.

Conclusions

• The contents of different Fe and Al forms were the main soil variables determining P sorption capacity in the soils investigated. Fe and Al extractable in ammonium oxalate proved to be useful for indirect estimation of P sorption capacity.

• One single P addition could be used to obtain an index of P sorption capacity (PSI). Addition of 50 mmol kg^{-1} is suggested, to ensure that the P sorption maximum is exceeded.

• P-AL and Olsen-P were not effective for prediction of P release in soils possessing different P sorption capacities. However, several estimates of P sorption saturation were well correlated to potential P release in a range of soil types and P levels.

• Effects of long-term inorganic P application were limited to the 0-40 cm layer of the soil profiles.

• P leaching from the lysimeters was not correlated with STP or P sorption saturation in the topsoils. Phosphorus leaching seemed to depend more on inherent soil characteristics, such as water transport mechanisms and P sorption capacity in the profile.

• Macropore flow seemed to increase P leaching, and hence an indicator of the presence and continuity of macropores in the soil profile should be included in risk assessments of P leaching losses.

• When piston flow dominates water transport, information on P sorption capacity and P sorption saturation of the subsoil is necessary when evaluating the risk for P leaching.

Sammanfattning (Swedish Summary)

Fosfor är det begränsande näringsämnet i många sjöar och vattendrag och tillförsel av fosfor medför en ökad eutrofiering. Cirka 1/3 av den fosfor som tillförs sjöar och vattendrag i Sverige kommer från jordbruksmark. De viktigaste förlustvägarna för fosfor från åkermark är erosion, ytavrinning och utlakning. I denna avhandling studerades främst processer som påverkar utlakning. Accumulering, bindning och frigörelse av fosfor studerades i tre olika försök i laboratoriemiljö. Utlakning av fosfor från lysimeterar (ostörda jordkolonner) som placerats utomhus, studerades i ett försök. I alla försök har jordar från de långliggande svenska bördighetförsöken använts eftersom de representerar olika jordtyper som är vanligt förekommande i Sverige och varje jord har fyra olika fosfornivåer.

Jordarnas kapacitet att binda fosfor undersöktes och relaterades till andra egenskaper hos jordarna. Fosforbindningskapaciteten i matjordslagret (0-20 cm) varierade mellan 6 och 12 mmol kg^{-1} jord och var korrelerat till förekomsten av olika järn och aluminiumföreningar. Gödsling med oorganisk fosfor, 42-49 kg ha^{-1} år^{-1}, under *ca* 30-40 års tid medförde ackumulering av fosfor, ökad fosformättnadsgrad och fosforfrigörelse ner till 40 cm djup. Under 40 cm djup syntes inga skillnader mellan gödslat och ogödslat led. Jordarnas förmåga att frigöra fosfor var korrelerat till fosforhalten i marken (*t. ex.* P-AL) för varje enskild jord, men eftersom jordarnas kapacitet att binda fosfor varierade kunde inte ett generellt samband erhållas för alla jordtyper. Istället testades ett antal olika metoder för att bestämma fosformättnadsgrad i jorden, dvs jordens innehåll av fosfor i förhållande till jordens kapacitet att binda fosfor. Flera olika metoder gav bra samband med fosforfrigörelse och ett mått på jordens fosformättnadsgrad skulle kunna vara en användbar variabel vid riskbedömning av fosforförluster.

Fosforförluster från lysimeterförsöket uppmättes till mellan 0.03 och 1.09 kg ha^{-1} år^{-1}. Fosforförlusterna var inte relaterade till fosforhalten i marken och inte heller till fosformättnadsgraden. De största fosforförlusterna, oavsett fosforhalt i marken, uppmättes från den jord där makroporflöde dominerade, *dvs* vatten (och fosfor) transporteras snabbt genom *t. ex.* sprickor och maskgångar i profilen utan kontakt med alvjorden. Den jord som hade lägst kapacitet att binda fosfor hade en hög fosformättnadsgrad och stor utlakning från det högst gödslade ledet. I de övriga jordarna var bindning/frigörelse av fosfor i alven betydelsefullt för utlakning och alven visade sig i vissa fall fungera som ett filter för vidare fosfortransport nedåt i profilen och i andra fall som källa för ytterligare fosforfrigörelse.

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