Mitigation of Phosphorus Leaching from Agricultural Soils

Improved Fertilization and Soil Structure

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Mitigation of Phosphorus Leaching from Agricultural Soils. Improved Fertilization and Soil Structure

Abstract

Phosphorus (P) is an essential element in crop production, but P losses from agricultural soils are a major contributor to surface water eutrophication. This thesis examined the effects of chemical soil properties and soil structure, as governed by agricultural management practices, on P leaching from agricultural soils and how this leaching can be reduced. An initial investigation on the effect of plant-available P concentration in the soil (P-AL) on topsoil P leaching from five soils clearly showed that topsoil P leaching depends not only on P status, but also on other soil characteristics. In three of these soils, increased P leaching after manure application was further amplified by high P-AL, while manure application did not affect topsoil P leaching in the other two soils.

In a study assessing different management practices on a clay soil and the possible effect on P losses via tile drains, great spatial variation in P leaching was observed in the field, even though P-AL and discharge volume were relatively uniform across the field. Incorporation of quicklime (CaO) significantly reduced P leaching losses, primarily of particulate P, which was the dominant P form in drainage water. The other management options evaluated (conventional ploughing/shallow tillage; no P application/balanced P application; broadcasting/band spreading of fertilizer P) had no significant effects on P leaching. However, some effects of these management strategies could have been overshadowed by the large spatial variation in the data.

Stopping P application and removing soil P with harvested crops (phytomining) showed potential to reduce excessive P levels in soils. After 7-9 years of no P application to the four soils studied, topsoil P-AL was lowered but most soils still had excessive levels. Only one soil, a clay soil with the lowest P-AL value in the study, showed a significant downward trend in leaching of dissolved reactive P.

New knowledge outcomes were that: (i) the relationship between P-AL and topsoil P leaching clearly differs between soils, especially after manure application; (ii) incorporation of quicklime is a promising option for reducing P leaching from clay soils; and (iii) high P-AL values and P leaching may be reduced after phytomining, but this mitigation strategy takes a very long time.

Keywords: phosphorus leaching, soil test P, mitigation options, topsoil lysimeters, structure liming, animal manure, phytomining, soil structure

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Contents

List of Publications

This thesis is based on the work contained in the following papers, referred to by Roman numerals in the text:

I Svanbäck A., B. Ulén, A. Etana., L. Bergström, P.J.A. Kleinman & L. Mattsson (2013). Influence of soil phosphorus and manure on phosphorus leaching in Swedish topsoils. *Nutrient Cycling in Agroecosystems* 96, 133-147.

II Svanbäck A., B. Ulén & A. Etana (2014). Mitigation of phosphorus leaching losses via subsurface drains from a cracking marine clay soil. *Agriculture, Ecosystems and Environment* 184, 124-134.

III Svanbäck A., B. Ulén, L. Bergström & P.J.A. Kleinman (2014). Long-term trends in phosphorus leaching and changes in soil phosphorus with 'phytomining'. *Submitted manuscript*.

Papers I-II are reproduced with the permission of the publishers.

The contribution of Annika Svanbäck to the papers included in this thesis was as follows:

I Planned the study together with the second, third and fourth author. Performed the experimental work, data analyses, data interpretation and writing, with assistance from all co-authors.

II Planned the study together with the second author. Performed the data analyses, data interpretation and writing together with the second author.

III Planned the study together with the second author. Performed the experimental work, data analyses, data interpretation and writing, with assistance from all co-authors.

Abbreviations

P-AL	Ammonium lactate-extractable phosphorus, the common soil test for P in Swedish agriculture
DRP	Dissolved reactive phosphorus in water

1 Background

Phosphorus (P) is an essential element for all plants and animals, forming part of every cell. Phosphorus is a macronutrient and in agricultural crop production P needs to be applied in order to maintain production. However, if too much P is added to the soil, the risk of losses to rivers and lakes increases (Pautler & Sims, 2000; Sibbesen & Sharpley, 1997). Phosphorus is strongly bound in the soil and only a small proportion is lost to rivers and lakes, but this relatively small amount of P can be sufficient to cause detrimental effects on water quality (such as algal blooms and oxygen deficiency) and ecosystem changes in aquatic systems (Sharpley & Rekolainen, 1997). Phosphorus losses from agricultural soils are a concern in Northern European countries due to the accelerated eutrophication of the Baltic Sea and many inland surface waters. At least 45% of the total inputs of P to the Baltic Sea originate from diffuse anthropogenic sources, with agriculture estimated to contribute 60-80% of the total diffuse load (HELCOM, 2012). In the past there has been more research and progress in finding countermeasures to reduce the load of nitrogen (N) from agriculture to water. However, it is important to reduce both P and N levels in a balanced way (SEPA, 2006). If the P level in the water environment is high compared with the N level, N-fixing cyanobacteria can be favoured and this can lead to problems with toxic cyanobacterial blooms.

Besides eutrophication, another strong reason for not applying surplus P and for using available P sources efficiently is that phosphate rock, from which P fertilizers are manufactured, is a finite, non-renewable resource. The long-term availability of P for crop production will affect the possibility to feed the growing world population.

The availability of different sources of P for agricultural production and the economic possibilities to buy P fertilizers varies throughout the world. Between 1960 and 1980, large amounts of mineral fertilizer were used to increase soil fertility and crop yields in Sweden, as well as in many other developed countries (IFADATA, 2014). Manure was often applied at the same time, resulting in a rapid increase in the P content of many agricultural soils. This was especially true for southern Sweden, where animal density was higher and more P-demanding crops (*e.g.* potato and sugar beet) were grown. This built up a pool of soil P which is partly of benefit for today's farmers, since they do not have to apply as much fertilizer as they would otherwise need to. However, if soil P levels are maintained much above the agronomic optimum soil P value, P is used very inefficiently, since P application does not increase yield further (Syers *et al.*, 2008) and the risk of P losses to surface waters is high (Pautler & Sims, 2000; Heckrath *et al.*, 1995).

At present, the average P balance of Swedish agricultural soils is close to equilibrium (*i.e.* inputs = outputs) (SCB, 2013) (Figure 1). However, there is a considerable range in P balance across the country. For example, 5% of fields in Sweden received more than 60 kg P ha^{-1} in 2009 (Djodjic & Kyllmar, 2011) and manure is often added to soils already rich in P, especially on animal farms in southern Sweden. In the past, animal density was more uniform throughout the country and animal manure was more important for maintaining soil P and crop yields on the fields. However, the widespread use of mineral fertilizers allowed traditional crop production to be decoupled from livestock production. In Sweden, pig and poultry production are concentrated more in the south, while cereal production is concentrated more in central Sweden. The farm P balance increases with increasing animal density (SCB, 2013), with import of

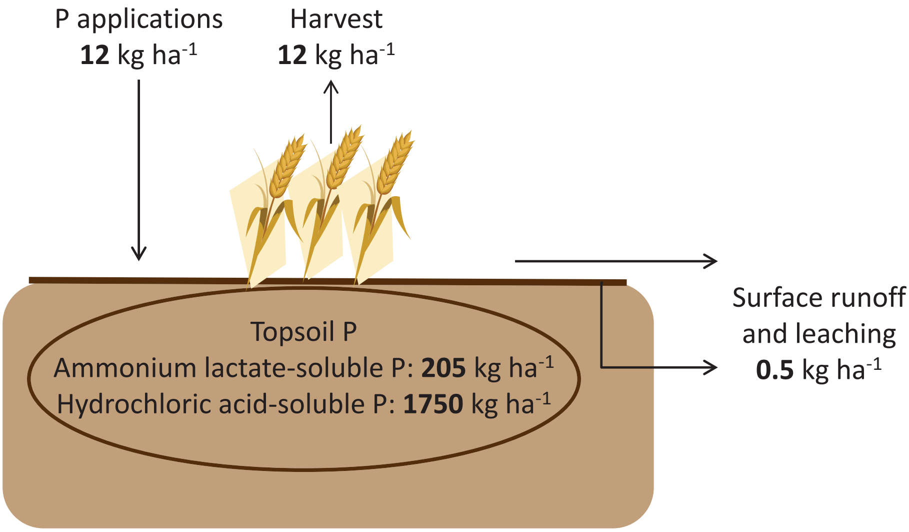

Figure 1. Some P pools and flows in Swedish agricultural soils (SCB, 2013; Blombäck *et al.*, 2011; Eriksson *et al.*, 2010). Average values are shown, although variation between regions and individual fields is large.

feed on animal farms contributing to the positive P balance. Soil test P levels are generally higher in the south of Sweden (Figure 2). High animal density often leads to high application rates of manure (*i.e.* P in excess of plant requirements) and, repeated over many years, the soil P content increases well above the agronomic optimum level (Kleinman *et al.*, 2011). Areas with high animal density and lack of sufficient land area for effective utilization of the manure produced are found in many places of the world, *e.g.* in the USA (Kellogg *et al.*, 2000), the Netherlands (Reijneveld *et al.*, 2010) and other parts of Europe (Csathó & Radimszky, 2012).

There is great variation in P losses from agricultural soils over time, both within and between years (Ulén *et al.*, 2007). Phosphorus losses and erosion are usually high during events with high water flow, such as intensive rainfall (Edwards & Owens, 1991) and snowmelt (Su *et al.*, 2011; Ulén, 2003).

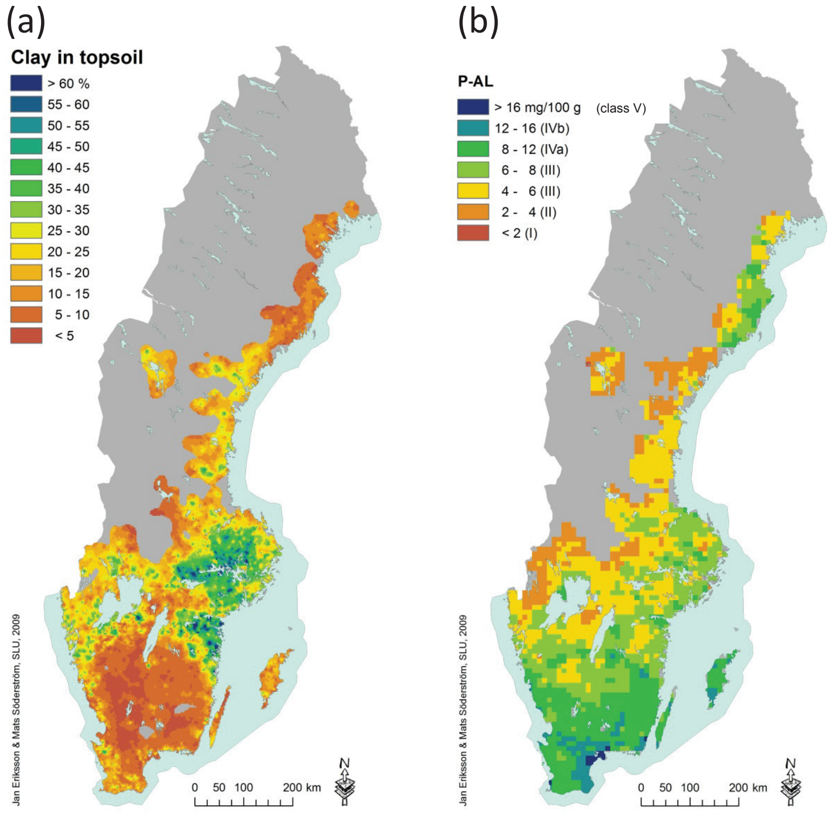

Figure 2. Maps of Sweden showing a) clay content and b) P-AL in agricultural topsoils (Eriksson *et al.*, 2010).

The majority of the annual P losses from a watershed can occur from a small proportion of the land area, and during only a few severe storm events (Sharpley *et al.* (1999).

Most research and mitigation efforts to combat P losses from agricultural soils have focused on surface runoff and erosion. However, during recent decades, the importance of P leaching and losses via agricultural drainage systems has received increasing attention. Some early studies of P losses in drainage water include Brink and Gustafson (1970) and Brink *et al.* (1978) in Sweden, Uhlen (1989) in Norway, Turtola and Paajanen (1995) in Finland, Bottcher *et al.* (1981) in the USA and Bolton *et al.* (1970) and Culley *et al.* (1983) in Canada.

Phosphorus leaching from agricultural land is of particular concern in the Baltic region, where leaching together with export via tile drains most likely represents a major transport pathway for P (*e.g.* Turtola & Jaakkola, 1995). A large proportion of the agricultural soils in Sweden and Finland are subsurface-drained and located in relatively flat landscapes (SCB, 2014; Yli-Halla & Mokma, 2002). Sources of P losses to drainage water range from P that has built up in the soil itself, generally due to historical application of fertilizers and manure (Beauchemin *et al.*, 1998), to P that is lost directly from recent amendments to soils with high soil P status (Kleinman *et al.*, 2009; Hart *et al.*, 2004; Sileika *et al.*, 2002; Preedy *et al.*, 2001). Phosphorus concentrations in water draining from soil vary widely, from almost undetectable levels to several milligrams per litre of drainage water from arable and grassland soils (Sims *et al.*, 1998; Brookes *et al.*, 1997).

1.1 Forms of P in the soil

The native P content in soils depends on the nature of the parent material and the degree of weathering. Except in cases of extreme build-up, the level of P in soil and in the soil solution is usually low compared with the levels of other nutrients such as N and potassium (K). During soil development, apatite P is weathered and gradually transformed into other inorganic or organic P forms. Secondary P minerals formed in acidic soils mainly comprise aluminium (Al) and iron (Fe) phosphates, while different types of secondary calcium (Ca) phosphates dominate in neutral to alkaline soils (Smeck, 1985). Adsorption of P occurs on the surface of soil particles (Figure 3), and this P is part of a labile inorganic pool. Phosphorus can be sorbed to positively charged edges of clay and, in calcareous soils, to $CaCO_3$. In acid soils, sorption by Al and Fe oxides and hydroxides is very common (Hemwall, 1957). Inorganic P is taken up by plants and microorganisms and is thereby transformed to different forms of organic P. Continuous turnover of P through mineralization and immobilization follows (Figure 3). Mineralization of organic P is influenced by many of the same factors as the general decomposition of soil organic matter, such as temperature, moisture and tillage.

Most of the P compounds formed are not available for plant uptake because they are highly insoluble in the soil solution. When soluble P is added, as fertilizer or manure, much is rapidly converted to forms not readily available for plant uptake and bound to particles in the soil. Since not all P may be taken up by the crop in the year of application, some farmers tended to apply more P than was removed with the crop (according to advice in the past). Repeated over several years, this leads to a higher degree of soil P saturation and decreased sorption capacity (Mozaffari & Sims, 1994), which may lead to enhanced P losses to water (Ulén, 2006).

Soils contain inorganic and organic P compounds, and the relative proportions of these P forms vary widely. Organic P often comprises between 20 and 65% of total P, although soils with a high organic matter content can contain up to 90% organic P (Harrison, 1987). Organic P can be hydrolyzed though enzymatic reactions and taken up by plants or microorganisms (Quiquampoix & Mousain, 2005).

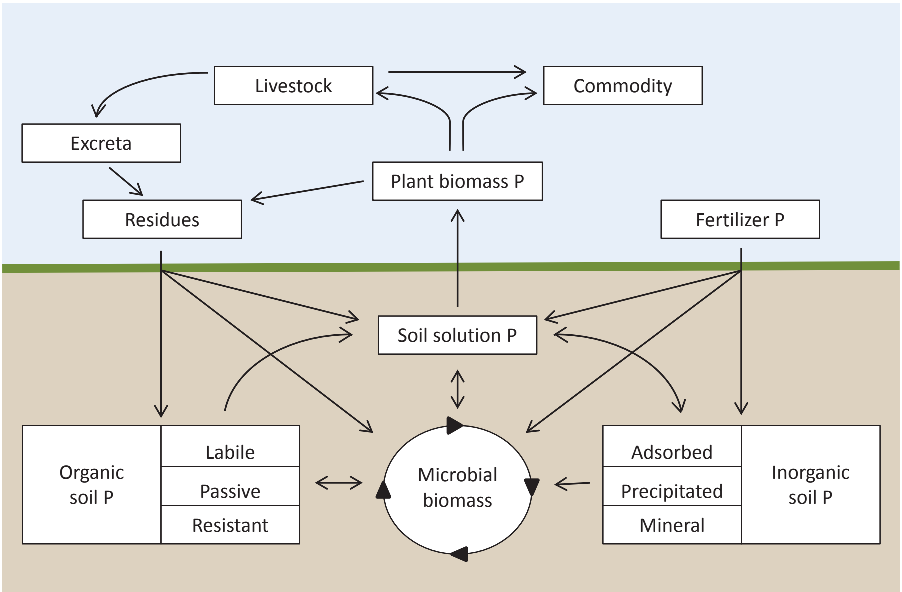

Figure 3. Conceptual diagram of the soil-plant P system, indicating major pathways for P transfer between different pools (adapted from Jakobsen *et al.*, 2005).

Plant roots absorb P dissolved in the soil solution, mainly as phosphate ions, but some soluble organic P compounds are also taken up. Mycorrhiza, a symbiotic association between a fungus and plant roots, may play an important role in the capture of nutrients in the soil (Smith & Read, 1997). The chemical form of P present in the soil solution is determined by the solution pH. In strongly acid soils $H_2PO_4^-$ dominates, while alkaline soils are characterized by HPO_4^{2-}. Both forms are readily available for plant uptake (Brady & Weil, 2002). Since dissolved P in the soil solution constitutes a very small part of total P in soils, the soil solution needs to be replenished with P from the labile pool several times during the growing season due to crop uptake (Frossard *et al.*, 2000).

1.2 Forms of P in leachate

The difference between dissolved P and particulate P in water is defined analytically by the pore diameter used in filtration before analysis of dissolved P. Filters with pore size 0.2 µm or 0.45 µm have been used in different studies. Dissolved reactive P (DRP) is usually measured as molybdate-reactive P, and total dissolved P is measured after digestion of the filtered sample (ISO, 2003). Dissolved organic P is often referred to as the difference between total dissolved P and DRP. However, clay particles are defined as < 2 µm and some fine clay particles and other fine colloids can pass through the filter and be analyzed as 'dissolved' P (Ulén, 2004). There is no simple routine analysis for measuring organic P forms in leachate, but nuclear magnetic resonance (NMR) spectroscopy has been used in a few studies (Fuentes *et al.*, 2012; Bourke *et al.*, 2009; Toor *et al.*, 2003). Particulate P is often calculated as the difference between total P and DRP.

1.3 Phosphorus losses to water

Phosphorus losses or P transfer from agricultural soils to receiving waters can be seen as a two-step process: mobilization, *i.e.* the transfer of a P-containing compound from the immobile phase (bulk soil) to the mobile phase (water) by desorption or detachment; followed by transport with the carrying water phase (Hens & Schoumans, 2002). In order to reduce the transport of P from arable land to waters, one can either control the sources or the transport itself (or both). In many countries the authorities have decided to control P fertilization, *i.e.* the main source of P to the soil. One approach is to fertilize with the same amount of P as will be removed with the following crop and according to soil P status. Efforts have also been made to reduce the causes of erosion and to prevent eroding material from reaching water by establishing buffer zones along waterways (reducing transport) (Stutter *et al.*, 2012). Improved soil structure and aggregate stability, through *e.g.* microbial activity, has been discussed as protecting against erosive water forces (Tebrügge & Düring, 1999). However, erosion is sometimes seen as a source of P and sometimes as a transport process. There are also other measures, *e.g.* sedimentation ponds and wetlands (Braskerud, 2001), aimed at capturing any P transported away from sources. The focus in this thesis was the systematic study of some potential field mitigation options aimed at reducing P leaching.

2 Aim

The main aim of this thesis was to gain a better understanding of how soil chemical and structural conditions, as governed by agricultural management practices, influence P leaching from agricultural soils to surface waters and how this leaching can be reduced. Specific objectives were to:

- Examine the role of soil test P and applied P sources on topsoil P leaching from main types of agricultural soils in Sweden, in particular: (i) relationships between ammonium lactate-soluble P (P-AL) and P leaching; (ii) changes in P leaching from soils with varying P-AL status following manure application; and (iii) effects on P leaching of two cropping systems representing farms with and without animals (Paper I)
- Quantify leaching losses of P from a tile-drained cracking clay soil in relation to topsoil management practices and investigate possible spatial variation in P leaching in the experimental field. The starting hypotheses were that: (i) P leaching losses are reduced for several years after structure liming (*i.e.* liming with CaO to improve soil structure and thereby reduce P leaching); (ii) shallow tillage does not reduce P leaching in comparison with conventional ploughing; and (iii) application of moderate amounts of mineral P fertilizer close to balance with crop needs does not increase P leaching compared with no fertilization. As an extension of hypothesis (iii), band spreading was compared with broadcasting of P fertilizer (Paper II)
- Evaluate the effects of P mining on a range of Swedish agricultural soils that had previously received high applications of manure and/or mineral fertilizer and therefore had elevated soil P status. In particular, to determine whether ceasing P application and phytomining P through crop removal reduced the concentration of plant-available P in soil (P-AL) over time, thereby significantly reducing P leaching losses (Paper III).

Three different methods were used to investigate these matters: topsoil columns to investigate the risk of P leaching (Paper I), tile-drained plots to test different mitigation options in the field (Paper II) and outdoor lysimeters to reduce high soil P levels and P leaching through crop removal of P (Paper III).

3 Materials and methods

Several methods were used in this thesis to study the effect of different soil factors and management options on P leaching, namely topsoil columns with simulated rainfall, long outdoor lysimeters (topsoil and subsoil), and an experimental field with separately drained plots.

3.1 Topsoil columns with simulated rainfall to estimate the risk of P leaching

Paper I used undisturbed topsoil columns (20 cm long and 20 cm in diameter), which were collected from five fields included in the long-term fertility trials in Sweden (Carlgren & Mattsson, 2001). The location of the fields (Bjertorp, Ekebo, Fjärdingslöv, Högåsa and Klostergården) is shown in Figure 4 and selected soil properties are shown in Table 1. The experiments were initiated between 1957 and 1969 and the experimental setup is similar at each site, with varying P fertilizer applications in different plots, which over time have resulted in plots with four P-AL levels at each site. There are also two cropping systems at each site, one which is intended to represent a farm without animals with mainly cereals in the crop rotation and no manure application. The other cropping system is intended to represent a farm with animals, and the crop rotation includes forage crops and moderate manure applications every fourth or sixth year.

Intact topsoil columns were collected from the four P levels in both the manured and unmanured cropping system at the five sites. In each field plot, four soil columns were collected, resulting in 160 columns in total (Paper I).

The leaching experiment was carried out in an indoor rainfall simulator. The rainfall intensity was 10 mm h^{-1} and the simulated rainfall was applied in three events lasting 2.5 h each, at 2-day intervals (76 mm in total). After each

Table 1. *Selected chemical and physical properties of soils used in Papers I-III*

Soil	Texture	Clay (%)	pH	PSC_{max} (mmol kg^{-1})
Bjertorp[a]	Silty clay loam	30	6.6	8.8
Bornsjön	Clay	60	6.4	n.d.
Ekebo[a]	Loam	17	6.5	10.2
Fjärdingslöv[a]	Sandy loam	19	7.5	6.0
Högåsa[a]	Loamy sand	7	5.8	10.0
Klostergården[a]	Silty clay loam	37	6.9	6.9
Kungsängen[a]	Clay	59	6.9	11.9
Mjällby[b]	Loamy sand	9	6.2	n.d.

[a]Börling *et al.* (2001) topsoil samples (0-20cm) from the unmanured cropping system (lowest P level).
[b]Ulén (1999) topsoil samples (0-20 cm)
PSC_{max}: maximum P sorption capacity

2.5 h simulated rainfall event, the leachate was collected and analyzed for total P and DRP. First, three simulated rainfall events (76 mm) were performed to measure leaching from only the soil. Then dairy cow manure was applied to the soil columns and another three simulated rainfall events (76 mm) were performed. The results were statistically evaluated using the Mixed model in the SAS software (Littell *et al.*, 2006).

3.2 Tile-drained plots to test different mitigation options in the field

An experimental field with 28 separately drained plots (20 m x 24 m) in a flat valley was used in Paper II. Selected soil properties for this site (Bornsjön, see Figure 4) are shown in Table 1. The P-AL concentration was moderate/low and the soil had a generally high ability to sorb P based on chemical soil properties. The P-AL concentration and the concentration of Fe and Al in ammonium lactate extract were similar for all plots. A previous study in a field close by reported high P leaching losses, with a large proportion of particulate P in leachate, and demonstrated a need for flow-proportional sampling at this site (Ulén & Persson, 1999).

Seven treatments (Table 2), with four replicates per treatment, were randomly assigned to 28 plots (Paper II). The treatments included three soil management practices: conventional autumn ploughing, incorporation of quicklime (CaO) in the first year (referred to as 'structure liming' in this text) and shallow autumn tillage. Band placement of fertilizer P was compared with broadcasting in the shallow-tilled plots, and no P application was compared with band placement of P in the conventionally ploughed plots. An unfertilized

Figure 4. Map of Sweden showing the experimental sites and locations where soil columns were collected.

fallow and a crop rotation including winter wheat (compared with only spring sown crops in the other plots) were also included in the treatments. All P fertilization doses were just slightly above the level expected to be removed by the following crop.

Drainage water from each plot was sampled flow proportionally and analyzed for total P, DRP, total nitrogen and nitrate nitrogen on a weekly basis. Annual losses were calculated and the results were statistically evaluated using the Mixed model in the SAS software (Littell *et al.*, 2006).

3.3 Reduce high soil P levels by crop P uptake in outdoor lysimeters

Paper III evaluated soil P changes and leachate P trends in undisturbed soil columns that were collected from fields where P had accumulated in the soil after long-term addition of fertilizers and/or manure. Results from two previous studies (Djodjic *et al.*, 2004; Ulén, 1999) were combined with additional measurements. The soils came from four sites: Fjärdingslöv, Klostergården, Kungsängen and Mjällby (see Figure 4). Selected soil properties are shown in Table 1. Soil columns were collected in 1991 (Mjällby) and 1999

(Fjärdingslöv, Klostergården and Kungsängen), and phytomining was then studied in the soil columns at a lysimeter station in Uppsala. The column sampling method employs a coring apparatus that allows a polyvinylchloride (PVC) cylinder to be installed around an intact soil column, without sidewall compaction. The gravity-drained soil columns were about 1.05 m long and the diameter was 0.295 m. After collection and preparation, the lysimeters were placed in belowground pipes in an outdoor lysimeter station described by Bergström and Johansson (1991).

Leachate volumes were measured and total P and DRP were analyzed in the leachate. Crops were grown in the soil columns and harvested over 7-16 years. Soil samples were collected and analyzed for P-AL at the start and end of the study (Paper III).

Seasonal Mann-Kendall tests (Libiseller & Grimvall, 2002; Kendall, 1975; Mann, 1945) were used to detect possible trends over time in concentration of total P and DRP, load of total P and DRP and leachate volume.

4 Factors affecting P leaching

Understanding how different factors affect P leaching processes was an important component of the work described in this thesis. An extensive body of work has documented P leaching through soils, emphasizing the soil-specific nature of P leaching potential and the varying influence of management variables on P leaching processes (*e.g*. Liu *et al.*, 2012; Kleinman *et al.*, 2009; Djodjic *et al.*, 2004; Sims *et al.*, 1998). In sections 4.1 to 4.3, important factors in Papers I-III relating to soil test P, P fertilizer and manure application, and transport pathways are discussed and results from Papers I and II are positioned in this context.

4.1 Soil test P and P leaching

Soil testing for P was primarily developed to assess the level of plant-available P in soils. The soil test P value is used (sometimes together with data on other chemical or physical properties of the soil and information about the crop) to evaluate whether, and how much, P needs to be applied to achieve good crop yields. During recent decades, soil P testing has also been used as an indicator of the risk of diffuse P losses to surface waters (*e.g*. Sims *et al.*, 2000; Sibbesen & Sharpley, 1997). Soil test P is extracted and analyzed in different ways, depending on the properties of the soil and on general regional practices. A common method in the Nordic and Eastern European countries is to extract plant-available P with an acid ammonium lactate solution (P-AL) (Egnér *et al.*, 1960). Other common methods include: double lactate (Riehm, 1943), which is similar to the P-AL method but the prediction of P availability in calcareous soils may be better; Olsen-P (Olsen *et al.*, 1954), which was developed in North America to be used on calcareous soils; Bray and Kurtz P-1 (Bray & Kurtz, 1945), which uses an acidic extractant (pH 2.6); Mehlich 1 (Mehlich, 1953; Nelson *et al.*, 1953), which is best suited for soils with acidic reaction;

and Mehlich 3 (Mehlich, 1984), which works well for a wide range of soils, both acidic and basic in reaction. Eriksson *et al.* (2013) compared some of these soil test P methods for a range of Baltic and Swedish soils and found that the amount of P extracted declined in the order: P-AL > Mehlich 3 > double lactate > Olsen P. Compared with the P-AL method, the other methods extracted 71% (Mehlich 3), 61% (double lactate) and 20% (Olsen P) of P, as means of absolute values. Eriksson *et al.* (2013) also concluded that for calcareous alkaline soils, the acid extracts overestimate the amount of soil P.

Research to date has yielded mixed findings on the relationship between soil test P and P leaching potential. A study by Heckrath *et al.* (1995), summarizing findings from shallow tile drains established in the Broadbalk (UK) cropping system trials, identified a threshold in Olsen-P of surface soils above which the potential for leaching significantly increased. This ‘change point’ analysis performed by Heckrath *et al.* (1995) sparked an array of studies investigating critical thresholds of soil P above which P solubility and/or mobility increase significantly (Figure 5). Significant change points in soil test P above which the P concentration in leachate in column leaching experiments increases have been reported, and the change point has also been related to other soil extractants, such as $CaCl_2$ (*e.g.* Maguire & Sims, 2002; McDowell & Sharpley, 2001). In Sweden, Börling *et al.* (2004) reported exponential relationships between 0.01 M $CaCl_2$-extractable P (used as an indicator of potentially leachable soil P) and P-AL. However, the increases differed markedly between soils, with soils with high P sorption capacity releasing less P than soils with low P sorption capacity at a particular P-AL value (Börling *et al.*, 2004). In another Swedish study, Ulén *et al*. (2011) found P-AL to be a reliable P risk index for soil profiles with a high clay content in a catchment with overall balanced soil P level. However, in an intact soil column leaching study in which a range of Swedish soils was assessed, no relationship between topsoil P-AL and leachate P was detected (Djodjic *et al.*, 2004).

In Paper I, clear relationships were found between P-AL and P leaching from topsoil columns taken from five different agricultural soils (Figure 6), although the relationship between P-AL and P leachate concentration varied between these soils. The P-AL values in the soil columns ranged from 15 to 236 mg kg^{-1}, thus covering poor to excessive P-AL values according to Swedish guidelines (Albertsson, 2013). The four different P-AL levels in each soil were the result of long-term P applications at different rates in different

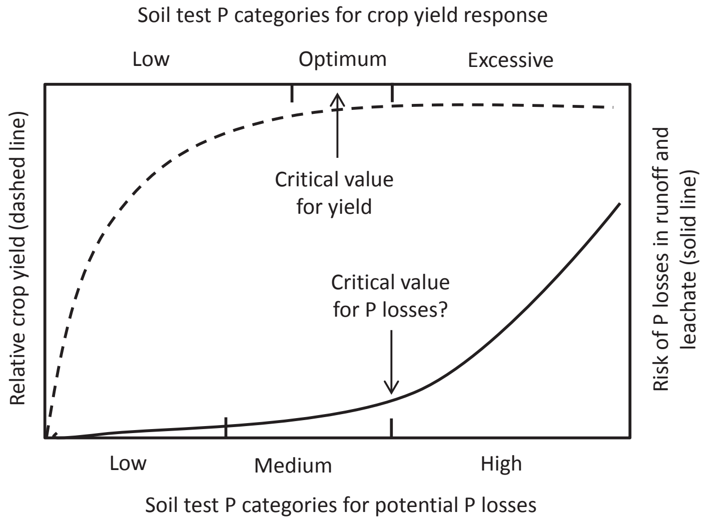

Figure 5. Conceptual model of the effects of soil test P on crop yield and P losses. Adapted from Wolf *et al.* (2000).

field plots. The results in Paper I confirm the controlling role of P-AL on P leaching from topsoil, in agreement with Börling *et al.* (2004), who observed clear relationships between P-AL and $CaCl_2$-extractable P (a surrogate for leachate P) for topsoils (0-20 cm) from the same long-term field experiments. However, both studies also show that the relationship between P-AL and potential P leaching varies between soils. The results obtained in Paper I for topsoil columns contrast with those reported for deeper soil cores (1 m) taken from the Swedish long-term field experiments, for which no relationships were observed between P-AL and P leaching (Djodjic *et al.*, 2004). This suggests that P-AL is an important explanatory variable for P leaching from topsoil and may indicate a risk of leaching, but that subsoil properties and water transport pathways can have a modifying effect on P leaching in deeper soil layers.

The concentrations in leachate following simulated rainfall events in Paper I were relatively low for soil columns from field experimental plots with long-term fertilization rates equivalent to P removal with harvested products. This stresses the importance of long-term P balance in limiting P leaching losses. The field experimental plots with long-term P balance used in Paper I had P-AL values at the agronomic optimum or lower.

When soil test P increases in a soil, the degree of P sorption saturation usually also increases (Börling, 2003), as more binding sites are occupied with P. The relationship between soil test P and the degree of P sorption saturation may be different between soils with different maximum P binding capacity.

4.2 Manure application

Application of manure to soils can temporarily elevate P concentrations in leachate from soils, primarily as a result of transfer of manure P to infiltrating water. Timing of manure applications is important (Aronsson *et al.*, 2014) and ‘rapid incidental transfers’ (Preedy *et al.*, 2001) of manure P to leachate are well documented (Kleinman *et al.*, 2009; 2005; Geohring *et al.*, 2001), with the greatest contributions of manure to leachate P typically occurring in the first leaching events after application (Withers *et al.*, 2003). However, little is known about the interactive effects of manure application and antecedent soil properties and soil P status. It was clear that the five soils studied in Paper I behaved differently regarding P leaching after recent manure application around current maximum permitted rates set by Swedish animal density regulations. In some soils, there was an increase in DRP concentration after dairy cow manure application and this increase was significantly correlated with soil test P. In other soils, there was no corresponding increase in P leaching after recent manure application. Identification of soils that are especially susceptible to P leaching when manure is applied is important in efforts to reduce P loads to water bodies. This identification cannot be made based on only a few soil properties, such as texture and P-AL, but is dependent on the interaction of many soil properties.

Animal manures contain both inorganic and organic forms of P, although the majority (60-90%) of P in animal manures is commonly in inorganic form (Mullins *et al.*, 2005). Sorption and retention in the soil vary for different forms of organic P (Turner, 2005). A large proportion of water-soluble P in organic amendments has been shown to increase P losses in runoff (Withers *et al.*, 2001) and leaching (Sharpley & Moyer, 2000). Increasing contact between the soil and applied P by incorporation or injection of manure can reduce P losses in surface runoff (Uusi-Kämppä & Heinonen-Tanski, 2008; Withers *et al.*, 2001) and leaching (Glaesner *et al.*, 2011), especially in fine-textured soils.

In Paper I, no consistent differences in topsoil P leaching were found between soil columns from long-term cropping systems intended to represent farms with or without animals. It should be noted that manure applications in the cropping system representing an animal farm were moderate and infrequent. A major issue with manure is often that livestock density is high in certain areas, which results in an excess of manure (Sims *et al.*, 2005). When excessive rates of manure are applied during several years, soil P builds up and the risk of P loss increases. Although disposal of manure is a problem in some regions with high animal densities, manure should be used efficiently, as it is a valuable resource of P and other nutrients and organic matter.

4.3 Transport pathways

Transport pathways through the soil were not measured directly in Papers I-III but are likely to have had an overall impact on the results, since transport pathway is always an important factor to consider as regards P leaching. Transport pathways, preferential flow in particular, were especially relevant in Paper II. There was large spatial variability in P leaching between plots, with a greater coefficient of variation even before the experiment started in total P leaching (64%) than in soil P status (20%) and drainage (26%), indicating the importance of local-scale transport pattern for P leaching in this clay soil. This spatial variation in P leaching was expressed as a gradient in P leaching over the field towards the middle of the flat valley in which it was situated. The results in Paper II cannot explain the gradient in P leaching, but one hypothesis is that there were more continuous macropores and permanent cracks towards the middle of the valley. It has also been shown that surface-applied herbicides leach in a similar pattern to particulate P at this site, suggesting that the topsoil is the major source of particulate P (Ulén *et al.*, 2014). Together with the large spatial variation in P leaching, this implies that preferential flow is an important transport pathway in this clay soil.

Depending on site-specific factors, such as sorption capacity, soil structure, infiltration and rain intensity, different transport pathways dominate P losses. These different pathways include: surface runoff, flow through the soil matrix and different forms of preferential flow. Once the dominant transport pathway from a field has been identified, the most appropriate countermeasure can be applied. Preferential macropore flow and transport is common in structured clay soils (Koestel & Jorda, 2014; Jarvis, 2007). Although varying extent and form of preferential flow appears to be the rule rather than the exception (Flury *et al.*, 1994), unstructured sandy soils often have a high proportion of matrix flow.

Downward movement of P in the soil profile was recognized early to occur in deep sandy soils (Bryan, 1933). In Sweden, sandy soil with low P sorption capacity in the soil profile is a soil type with a high risk of losing large amounts of P, especially if the soil has received high application rates of manure or P fertilizer for many years (Ulén & Jakobsson, 2005). Leaching water can be in good contact with the subsoil in sandy soils (Bergström & Shirmohammadi, 1999), and then the P sorption capacity of the whole profile controls the P concentration in the leachate (Andersson *et al.*, 2013; Djodjic *et al.*, 1999).

Macropores are large pores with equivalent diameter of 0.3-0.5 mm or more, which comprise structural cracks, packing voids between denser aggregates, faunal activity and root channels (Jarvis, 2007). Water with dissolved reactive P and P bound to particles can move rapidly through the soil profile in these large pores and sorption surfaces may be bypassed (de Jonge *et al.*, 2004; Akhtar *et al.*, 2003). However, if P is located in smaller pores in the soil and water transport in large pores bypasses this P, macropore flow may reduce P leaching. The soil surface and the plough layer have been suggested as the main source of P in drainage water (Djodjic *et al.*, 1999; Øygarden *et al.*, 1997). Tillage can break macropores but it does not always reduce P losses (Djodjic *et al.*, 2002; Ulén & Persson, 1999). Soils with a high clay content easily form macropores (cracks) through wetting/drying and freezing/thawing. These soils are usually drained and this can lead to fast transport of water, dissolved compounds and particles, first through macropores and then direct transport to a ditch or stream via the drainage system (Øygarden *et al.*, 1997). Considerable drainage losses of P have been recorded from this kind of soil (Turtola, 1999; Ulén & Persson, 1999). This type of preferential flow pathway has been shown to be most important following storm events after a dry period (Simard *et al.*, 2000).

Preferential flow occurs to varying degrees in different soils (Flury *et al.*, 1994), and may also vary within fields. In some soils there may be a relatively uniform network of rather large pores, which facilitates rapid transport of water, solutes and particles. In other soils, there may be fewer but very large pores, which may be unevenly distributed over the field. These pores can potentially have a major impact on total losses from that field, although the spatial variation within the field may be large. As mentioned above, variation in the degree of preferential flow is one possible explanation for the large spatial variation in P leaching in the field observed in Paper II. Continuity of macropores is an important factor for P losses, and if some of the large pores are continuous and lead to the tile drains or to the backfill above the tile drains where rapid transport can occur, the risk of rapid transport from the topsoil to the drainage system increases (Stamm *et al.*, 2002; Øygarden *et al.*, 1997).

Fine-textured soils with moderate P levels are commonly not considered high-risk soils for P leaching, mainly because they usually have a high P sorption capacity. However, the results in Paper II clearly contradict this perception, as leachate losses above 1 kg ha^{-1} $year^{-1}$ were observed in tile drainage water from plots in the experimental field on clay soil with moderate soil P status. Particulate P was on average 83% of total P in tile drainage water (Paper II), and preferential transport has been indicated at the site by simultaneous flows of P and pesticides with varying sorption characteristics (Ulén *et al.*, 2014).

4.3.1 Tile drains

Agricultural drainage systems are primarily installed to provide trafficable conditions so that management operations (such as seedbed preparation, planting and harvesting) can be performed in a timely manner, and to protect plants from excessively wet conditions. In arid and semi-arid areas, agricultural drainage systems are also used to control salinity (Smedema *et al.*, 2000). Drainage may be provided by surface modifications (such as a network of ditches and canals, land smoothing *etc.*) and by subsurface drainage systems. Surface drainage alone does not remove excess water from the soil profile as effectively as subsurface drainage. Buried drainage pipes are favoured in many locations, especially in areas where the growing season is short and trafficable conditions for timely planting and harvesting are critical (Skaggs *et al.*, 1994).

A large proportion of the agricultural soils in Sweden are located on relatively flat landscape, where artificial drainage is required for crop production (Wesström, 2002). It is estimated that 49% of Swedish agricultural land is systematically tile-drained (SCB, 2014). As leaching serves to connect P at the soil surface with subsurface drains, understanding the factors controlling P leaching through agricultural soils is key in assessing practices and strategies aimed at mitigating diffuse P loads from Swedish agriculture (Ulén *et al.*, 2007). Vertical leaching of P by macropore flow through the soil (Jarvis, 2007) may result in P reaching tile drains, and export via tile drains is a primary pathway of P transfer from agricultural fields to streams (Ulén *et al.*, 2007; Ulén, 1995). Heavy clay soils are common in eastern Sweden (Figure 2) and this soil type is usually tile-drained and often forms cracks. The soil in Paper II is one example of these clay soils in eastern Sweden.

One perception about particulate P losses to tile drainage systems is that particles move more or less slowly through pores in the soil in an episodic manner when water transport increases. Some particles accumulate around the tile drain and are washed into the drain and transported to *e.g.* an outlet ditch during a high flow event. At the experimental field described in Paper II, particulate transport appeared to be fast. Herbicides applied at the soil surface were detected in the first few rainfall/drainage events after application and these herbicides leached in a similar pattern to particulate P (Ulén *et al.*, 2014), suggesting that the topsoil was the major source of leached P and that particles could move quickly from the soil surface to the tile drains.

5 Mitigation options

In order to develop methods to reduce P leaching, it is critical to understand how different factors affect P leaching. Mitigation options can be divided into different types: preventative measures (such as binding P in manure with Al), measures in the field (*e.g.* fertilization, tillage) and measures beyond the field edge (*e.g.* sedimentation ponds, filters). This thesis focuses on field mitigation options aimed at reducing P leaching losses, more specifically balanced P application (Paper I), some management practices on a clay soil (Paper II) and phytomining to reduce soil test P (Paper III). Different aspects of these specific mitigation options are discussed below.

In a more general context, many mitigation options aimed at reducing P losses focus on surface runoff and erosion. Management practices aimed at reducing the speed of water flow during surface runoff events include contour farming and cover crops to protect the soil surface from erosion (Sims & Kleinman, 2005). Omitting tillage (no-till) or applying reduced tillage and leaving crop residues on the field can also reduce erosion and P losses through improved soil structure and increased infiltration, although losses of dissolved P may increase (Ulén *et al.*, 2010; Sharpley & Smith, 1994). When it comes to minimizing P losses, it is often better to carry out tillage during spring than autumn, but if the soil water content is high there is a risk of this damaging the soil structure, reducing the infiltration capacity and increasing surface runoff (Ulén *et al.*, 2010). Buffer zones along waterways can work as vegetation filters and reduce the transport of particles (Hoffmann *et al.*, 2009). The effect of buffer zones is strongly associated with their width (Uusi-Kämppä *et al.*, 2000). Efforts to reduce erosion can sometimes have undesired effects, *e.g.* crop residues and vegetation in buffer zones can be a source of P, especially during freezing and thawing events (Hoffmann *et al.*, 2009; Bechmann *et al.*, 2005; Miller *et al.*, 1994). Other efforts are aimed at managing the source of P, for example choosing an appropriate fertilizer and manure application method and calibrating the application equipment. In order to apply effective mitigation options, it is important to consider site-specific factors, identify sources and transport pathways of P and target these.

5.1 Balanced P application

Phosphorus fertilizers have been liberally used in the past to raise soil fertility and maximize crop production. However, economic and environmental incentives introduced since then have made farmers more aware of the need to use P efficiently. Several studies have found that the risk of P leaching increases with higher soil test P values (Maguire & Sims, 2002; McDowell & Sharpley, 2001; Heckrath *et al.*, 1995), which is in line with results in Paper I. In Paper I, strong relationships were found between P-AL and P leaching, although P leaching from different soils at a specific P-AL value varied (Figure 6). Avoiding a build-up of soil P by applying P according to soil test P and crop uptake is a common recommendation for limiting P losses (Albertsson, 2013; Kronvang *et al.*, 2009; Withers *et al.*, 2005). This is supported by the results in Paper I, since there was a significant increase in P leaching with increasing P-AL in all five soils, and also since topsoil columns from plots with long term P-balance had relatively low P leaching losses.

Values of P-AL are employed as input data in a model used for calculating losses of nutrients from Swedish agricultural soils (Johnsson *et al.*, 2008). These results are then used in Sweden's reports of nutrient loads to HELCOM and in the evaluation of the environmental goal "zero eutrophication" set by the Swedish parliament. The P-AL level is also often considered a risk indicator of P leaching by the farm advisory services in Sweden. This illustrates the importance of the results in Paper I, as no previous study has shown clear relationships between P-AL and P leaching for a number of different soils.

Timing of P application and application techniques are important factors for reducing incidental losses shortly after application (Withers *et al.*, 2003). However, Paper I showed that in soils where topsoil P leaching increased after manure application, the increase in P leaching was even larger at high P-AL (Figure 7). A possible explanation for this is higher degree of P sorption saturation at higher P-AL, and hence lower capacity to retain P (Börling, 2003). Although clear differences were found between soils, the results in Paper I show the importance of applying manure and fertilizer P according to soil test P and plant needs in order to avoid a build-up of soil P and to reduce the risk of P leaching.

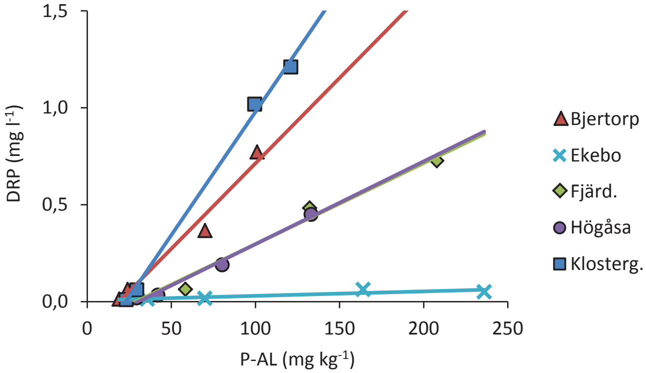

Figure 6. Leaching of dissolved reactive P (DRP) at varying P-AL values from topsoil (0-20 cm) lysimeters of the five soils used in Paper I. Results are for a cropping system including ley and moderate manure applications in the field, before manure application to soil columns in the laboratory. The statistical analysis was made with natural logarithm-transformed values.

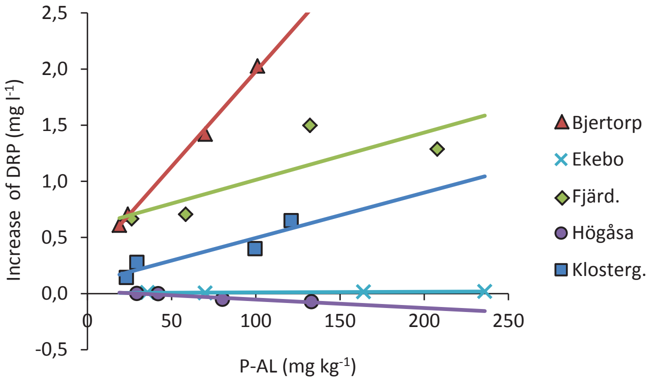

Figure 7. Increase in leaching of dissolved reactive P (DRP) at varying P-AL from topsoil (0-20 cm) lysimeters of the five soils used in Paper I. Results are for a cropping system including ley and moderate manure applications in the field, after manure application to soil columns in the laboratory.

5.2 Management practices on a cracking clay soil

In Paper II, some management options to reduce P leaching were tested on a flat experimental field with separately drained plots (Bornsjön) (Table 2). The soil has a high clay content (60%), moderate-low P-AL and low P saturation. Significant differences in P losses were found between some treatments, but losses of total P and particulate P from the plots were explained to a great extent by the spatial variation in the experimental field. There was a significant gradient in P leaching in the field during the experiment, and a greater coefficient of variation in total P leaching (64%) than in soil P status (20%)

and drainage (26%) in the spring before the experiment started. Seasonal patterns of P losses differed clearly between years, with peaks in transport occurring during snowmelt, in autumn and after intensive rainfall during summer. The unpredictability of occurrence of peaks in P leaching makes it more difficult to target these events and to develop effective mitigation options.

Bypass or preferential flow via soil macropores represents one of the major transport mechanisms of P leaching through well-structured soils (Simard *et al.*, 2000; Jensen *et al.*, 1998; Stamm *et al.*, 1998). As a result, cropping systems or practices that promote the maintenance of macropores (*e.g.* no-till and perennial forage systems) can be particularly susceptible to P leaching losses, although rapid flow through the soil may decrease surface runoff. Phosphorus leaching was once seen as a phenomenon restricted to coarse-textured soils, but has since been widely documented in finer-textured soils with extensive macropore networks (*e.g.* van Es *et al.*, 2004; Djodjic *et al.*, 1999). Djodjic *et al.* (2004) also found that a clay soil with low P saturation still had high leaching losses of P due to fast water transport through macropores, which meant that binding sites for P were bypassed. This confirms that water movement through soil is a very important factor regarding P losses and may override other factors such as soil P content and sorption capacity. However, both a source of P and a transport pathway are needed for P leaching to occur (Djodjic & Bergström, 2005).

Great efforts have been made to evaluate the effectiveness of measures to reduce P transport losses by water, which are often employed in combination with measures to reduce N losses (Newell Price *et al.*, 2011; Cherry *et al.*, 2008). Nevertheless, only a few field experiments have systematically tested management practices aimed at reducing P leaching with careful measurements of P transport in tile drains, and even fewer have found effective mitigation options for clay soils with fast water transport to tile drains.

5.2.1 Broadcasting, band placement or omission of P fertilizer

There are three general ways of applying fertilizer: broadcast placement, localized placement (band placement/drilling) and foliar application. When a fertilizer is broadcast, it is evenly spread over the entire field surface. It is then is mixed into the soil by tillage or left on the soil surface and allowed to be carried to the root zone by percolating rain. Broadcasting is effective when large amounts of fertilizer have to be spread over a wide area. For P, which tends to be strongly retained by the soil, broadcast application is sometimes

Table 2. *Phosphorus leaching (kg ha^{-1} year^{-1}) in the different treatments at the Bornsjön site in Paper II. Mean ±standard deviation of yearly transport from four plots and six years. Different letters within columns denote significant differences between treatments (based on log-transformed values). Fertilizer P was band spread unless otherwise specified*

Treatment	Total P	Particulate P	DRP
Conventional ploughing	0.79 ±0.53	0.68 ±0.49	0.13 ±0.09
Conventional ploughing, no P	0.97^{b} ±0.66	0.82^{b} ±0.55	0.15 ±0.11
Conventional ploughing, lime	0.59^{a} ±0.33	0.46^{a} ±0.29	0.13 ±0.06
Shallow tillage	0.96 ±0.56	0.85 ±0.51	0.11 ±0.07
Shallow tillage, broadcast P	1.13^{b} ±0.51	0.94^{b} ±0.38	0.20 ±0.16
Unfertilized fallow	0.77 ±0.42	0.60 ±0.31	0.17 ±0.16
Adapted crop rotation	0.84^{b} ±0.48	0.68 ±0.39	0.16 ±0.23

less efficient than localized placement (van der Eijk *et al.*, 2006; Randall & Hoeft, 1988). If the fertilizer is not incorporated into the soil, it is also easily washed away with runoff during heavy rain, especially during the first one or two heavy rainfall events after application. One example of localized placement is to drill the fertilizer in bands on either side of the seed when the crop is planted, a practice called band placement. Band placement of P can give higher yields than broadcasting, especially on soils with low soil P levels (Randall & Hoeft, 1988). When localized placement of fertilizer is more efficient than broadcasting, the total amount of fertilizer used can be reduced. If more of the smaller dose of band-placed P is taken up by the crop, less will remain in the soil and the likelihood of long-term P accumulation and P leaching losses may be lower than with broadcasting.

In Paper II, no significant differences in P leaching were found between band placement and broadcasting of fertilizers in the shallow-tilled plots. At the site used in Paper II, which had moderate soil P status (P-AL = 30-50 mg kg^{-1} soil), omitting P fertilization did not decrease P leaching, but crop yield decreased. The application rate was just slightly above expected crop uptake, and the results show that a balanced P application on a soil with moderate P-AL may increase crop yields while P-leaching is not increased. For other Swedish soils with similar moderate soil P status (P-AL <50 mg kg^{-1} soil), a positive yield response to P fertilization has been demonstrated (Ehde, 2012).

5.2.2 Conventional ploughing or shallow tillage

Agricultural soil management often involves disturbing the soil surface through tillage, which generally increases the amount of P carried away with particles via surface runoff (Ulén *et al.*, 2010; Lundekvam & Skoien, 1998). Tillage and tillage type can affect soil properties in many ways. Soil structure, aggregate strength and infiltration capacity are examples of factors which can be modified by different types of tillage and these factors are important for P leaching. In shallow tillage, usually referred to as reduced tillage, the soil is not inverted and is only tilled to a depth of 5-15 cm with a cultivator, disc harrow or rotovator. This leaves the soil surface covered with at least 15% of crop residues year-round, according to the US definition (ASABE, 2005). Reduced tillage has been shown to decrease erosion in both drainage flow and surface flow compared with ploughing (Koskiaho *et al.*, 2002). However, manure or fertilizer and crop residues left on the surface and not incorporated into the soil tend to increase the amount of dissolved P in surface runoff (Sharpley & Smith, 1994). Omission of tillage (no-till) can lead to stratification of soil P, with increased soil P close to the surface where P is applied (Cade-Menun *et al.*, 2010) and, as a consequence, higher losses of dissolved P in surface runoff (Koskiaho *et al.*, 2002; Sharpley & Smith, 1994) and also in tile drains (Gaynor & Findlay, 1995). On the other hand, conventional ploughing can counteract the stratification of soil P and may disrupt macropores and reduce hydraulic conductivity at tillage depth and consequently decrease losses of P from the topsoil. The shallow-tilled plots in Paper II had slightly higher (not statistically significant) P-AL in the upper topsoil than the conventionally ploughed plots, but there were no differences in DRP leaching.

The organic carbon content is usually higher in the upper soil layer in no-till or reduced tillage compared with mouldboard ploughing (Schjønning & Thomsen, 2013; Tebrügge & Düring, 1999). This is mainly due to the plant residue cover left on the surface of non-ploughed soils, which can be considered a key factor in promoting microbial activity, improving aggregate stability and protecting against erosive water forces (Tebrügge & Düring, 1999). The risk of particle losses has also been shown to be lower with shallow tillage than with mouldboard ploughing (Etana *et al.*, 2009).

A Norwegian study has shown that tillage has an effect on particle losses, both to the drainage system and with runoff (Øygarden *et al.*, 1997). After tillage, the concentration of suspended solids increased by a factor of 10 in that study, even with small runoff volumes. In the case of particle losses to the drainage system, these were attributed to particles being loosened from the plough layer by tillage and transported through large pores into the backfill. The backfill had an open structure and fine particles could pass through the envelope material surrounding the drain and enter the drain pipe. A dye tracer test demonstrated that rapid flows of water could be followed through cracks into a drain pipe (Øygarden *et al.*, 1997). This type of transport pathway through the backfill, together with cracks leading into the backfill, is possibly an important transport pathway at the site in Paper II. Omitting ploughing on sloping and erosion-prone soils generally reduces particulate P losses under Scandinavian conditions, while DRP losses may often increase (Ulén *et al.*, 2010).

In a Finnish study on a subsurface-drained clayey soil, conventional autumn ploughing (mouldboard ploughing) was compared with two forms of conservation tillage: no-till (stubble over winter) and shallow autumn cultivation. This site is similar to the Bornsjön site in Paper II in that both are subsurface-drained clay soils in a flat landscape. In the Finnish study, DRP losses were higher from plots under conservation tillage, due to a high proportion of surface runoff and higher concentrations of DRP in runoff than in the ploughed plots (Uusitalo *et al.*, 2007). Losses of particulate P were not reduced in treatments with conservation tillage (compared with ploughed plots), leading those authors to conclude that erosion rates were already quite low in the relatively flat agricultural landscape of southern Finland. Thus the potential for reducing agricultural P losses by reduced tillage in that region appears limited. In a different study at the same site, it was shown that erosion from the clay soil was lower when the soil was not tilled in autumn. However, reduced tillage in autumn (with crop residues left to cover the soil) produced as much erosion as autumn ploughing (Turtola *et al.*, 2007).

In a somewhat unexpected finding, the shallow-tilled plots in Paper II tended to have higher particulate P leaching than the conventionally ploughed plots (Table 2), although the differences were not statistically significant. The tendency for lower particulate P losses with conventional mouldboard ploughing could possibly be explained by disruption of macropores. Another possible explanatory factor could be shallow and uneven accumulation of crop residues in shallow-tilled plots, which might have resulted in uneven infiltration and preferential P transport along straw residues. However, this needs to be investigated further.

5.2.3 Incorporation of structure lime

The availability of P to crops is reduced by P complexation in soil with Ca at high pH, by Fe and Al at low pH and by high clay content. Liming can increase P availability in soils by stimulating mineralization of organic P or can decrease P availability by the formation of Ca phosphates at pH >6.5 (Sharpley & Rekolainen, 1997). However, the pH dependence of phosphate solubility can vary between different soil types (Gustafsson *et al.*, 2012). In Paper II, the soil pH before liming was 6.3, while five years after liming it was 6.6. Liming can also be used as a method to improve soil structure and aggregate stability, and these factors can influence water erosion on soil, *i.e.* the loss of colloids and particles from soil to water. Cations such as Ca stimulate the precipitation of compounds that act as bonding agents for primary particles. Cations also form bridges between clay and soil organic matter particles, resulting in aggregation (Bronick & Lal, 2005). In a long-term fertility experiment started in 1987 on a clay soil in central Sweden, plots were treated with lime at a high rate corresponding to 6.5 ton CaO per hectare. The results showed that the soil structure and aggregate stability improved in the limed plots (Ivarsson, 1996).

During major flow events and with water-saturated topsoil, the concentration of dispersed clay is known to be high in drainage water at the site in Paper II, while the concentration of dissolved P is low at this site, with its moderate-low soil P status (Ulén *et al.*, 2012; Ulén & Persson, 1999). There is an urgent need for improved technologies for long-term stabilization of this soil type and mitigation of accompanying preferential flows. Incorporation of quicklime (structure lime in the form of calcium oxide, CaO) into the topsoil is a measure which immediately improves the soil structure by flocculation and particle aggregation. In addition, pozzolanic reactions between lime, silica and alumina lead to the formation of cementing products and a long-term increase in soil strength (Locat *et al.*, 1990). At the site used in Paper II, a significant improvement in soil aggregate strength after structure liming, determined as a reduction in readily dispersed clay in a laboratory test, has been demonstrated (Ulén *et al.*, 2012).

In Paper II, mean annual losses of particulate P were significantly lower (0.36 kg ha^{-1} $year^{-1}$, a 44% reduction) from structure-limed plots than from conventionally ploughed plots without P fertilizer. A comparison between these treatments with yearly flow-weighted concentration of particulate P is shown in Figure 8. Particulate P was the dominant P form in leachate (Table 2). Total P and particulate P leaching losses were also significantly lower from plots with structure liming than from the other treatments grouped together.

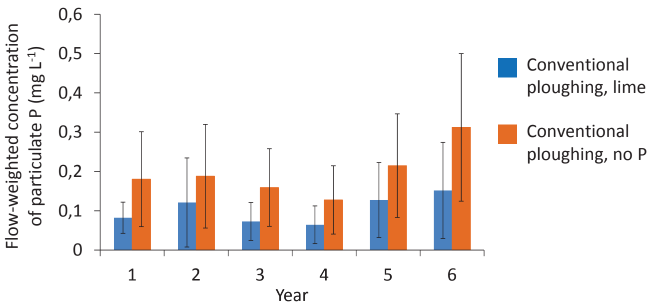

Figure 8. Yearly flow-weighted concentrations of particulate P in leachate from conventionally ploughed plots with application of structure lime in the first year and band-placed P fertilizer, compared with conventionally ploughed plots without any P application (Paper II). Error bars with standard deviations.

5.3 Phytomining to reduce soil test P

In areas with intensive livestock farming, soil P levels can be very high due to high application rates of manure for long periods. The risk of P losses to waters by erosion, runoff or leaching may increase when soil test P values increase and the soil becomes more saturated with P (Pautler & Sims, 2000). Once P concentrations in soil have risen over time, few effective mitigation strategies exist to reduce P leaching (Buda *et al.*, 2012). Depletion of soil P by ceasing further additions of P to soil and seasonally exporting P in harvested crop biomass (also referred to as 'mining' or 'phytomining') has been suggested as an effective remediation strategy to decrease the risk of P leaching from P-enriched soils (Koopmans *et al.*, 2004).

In a pot experiment in a greenhouse where ryegrass was grown with no P additions on a P-enriched non-calcareous sandy soil for 978 days, Koopmans *et al.* (2004) showed a fast and relatively large decrease in readily available soil P and P concentration in the soil solution. In a field experiment in the Netherlands, mining soil P by zero P application over a period of four years led to a strong reduction in readily available P forms in the soil solution in the upper soil layer (0-5 cm) (Van der Salm *et al.*, 2007). The rate of decline in extractable soil P was shown to be greater when soil P was higher and to decrease with decreasing soil P level in a study in which maize was grown for four years without any P addition (Eghball *et al.*, 2003). As the level of soluble P decreases, it becomes more difficult for plants to take up P. However, plants have developed a number of mechanisms to increase the availability of soil P. These include the development of highly branched root systems, the release of root exudates and secretion of root phosphatases (Raghothama, 1999). Mycorrhiza can also increase the availability of P for plants living in symbiosis with this fungus (Smith & Read, 1997). This may provide opportunities to develop cropping systems that use soil (and fertilizer) P efficiently and to identify plant species which have a high P acquisition efficiency even at low soil P levels, in order to achieve cropping systems with optimum utilization of P (Frossard *et al.*, 2000).

The literature on soil P decreases with phytomining is quite variable. For example, Kleinman *et al.* (2011) found that soil test P was not significantly reduced after 10 years of no P application in a phytomining experiment on soils in Maryland, USA, with a history with poultry litter additions and that yearly Mehlich 3 P values showed quite large variation. Elsewhere, McCollum (1991) found that phytomining of a soil with P levels well above yield-limiting levels resulted in declines in Mechlich-1 P that were faster at very high soil P levels than at lower soil P levels. Barber (1979) also found a greater rate of decline in Bray P1 at high levels compared with low following cessation of P application.

Dodd *et al.* (2012) found exponential decreases in Olsen P and water-extractable P concentration over time in three out of four long-term grassland field trials with no P fertilizer application in New Zealand. Application of N, as well as applying P at half the rate designed to maintain soil P concentration, also reduced leaching of dissolved P in a lysimeter study with regular cutting and removal of pasture biomass (Dodd *et al.*, 2014). Schulte *et al.* (2010) found that the relative rate of decline in Morgan's P was to a large extent explained by the relative P balance, expressed as P balance/total P. The rate of decline is also likely to be dependent on the strength of the soil extract. A weak extract is only able to extract a smaller amount of P and is more sensitive to changes in easily soluble P, *e.g.* van der Salm *et al.* (2009) found a larger decline in weakly bound P pools (water-extractable P and P-AL) than in more strongly bound P forms after 5 years of phytomining. However, the soil's ability to replenish easily soluble P from less soluble P pools would also influence the decline in soil test P values. In the exhaustion land experiment at Rothamsted, which involves 70 years of phytomining, it took nine years for the amount of Olsen P to halve as a result of P removal in the harvested crop (Syers *et al.*, 2008). Some of the soil P pools not extracted by Olsen P at the beginning of the exhaustion experiment were released for plant uptake during the 70 years, which supports the claim that soil P is not irreversibly fixed in the soil. However, results from the Swedish long-term fertility experiments indicate that decreasing P-AL by phytomining is a slower process than increasing P-AL by fertilizer application, as a decrease in P-AL of 10 mg kg^{-1} took about 17 years, while an increase of 10 mg kg^{-1} was achieved within 7 years (Bergström *et al.*, 2014). Contradictory to van der Salm *et al.* (2009), Bergström *et al.* (2014) also found larger changes in strongly bound P forms (P extracted with HCl) compared with changes in P-AL, as a result of long-term negative P balances.

In the lysimeter experiment in Paper III, the crops were grown and harvested without any P applications for 7-9 years on four soils with topsoil P-AL values ranging from 77 to 431 mg kg^{-1} at the start of the experiment. The P-AL concentrations in the topsoil were consistently lower at the end of the experiment, although in most soils P-AL remained at excessive levels. Lowering soil test P by phytoextraction appeared to be a slow method in Paper III. Rate of decline in soil test P concentration has been quite variable in previous studies (Dodd *et al.*, 2012; Schulte *et al.*, 2010; McCollum, 1991), although most studies indicate that it will take many years to go from very high soil test P to agronomic optimum levels. Soil testing indicated downward movement of soil P from the topsoil to deeper layers between the start and end of the study in three out of the four soils tested in Paper III. Only one soil, a clay soil with the lowest P-AL value, showed a significant decreasing trend in

DRP leaching losses. To the best of our knowledge, no other long-term studies have provided direct measurements of P leaching in connection with phytomining. The slow response in P concentration to halted P applications should be noted by policymakers setting environmental targets.

6 Leachate studies – evaluation of methods

All methods used to determine leaching in soils have different advantages and disadvantages. More controlled methods often have the benefit of allowing the researcher to focus on a few parameters and evaluate their effects. However, these methods may involve simplifications, they may be partly artificial systems and they may represent reality to different extents. Measurements in the field under more 'natural' conditions are often thought to represent real conditions quite well, but may be more difficult to interpret because of many varying factors. Choice of measurement techniques is an important factor.

6.1 Lysimeters

Intact soil columns were used in Papers I and III to preserve soil structure. Free drainage systems were used in both studies, in which a water-saturated zone must form at the bottom of the soil column before water can drain out (Bergström, 1990). For the soil columns used in Paper I, which were 20 cm long, this would represent conditions with a high groundwater level. The soil columns in Paper III were approximately 1 m long, which is close to the common tile drainage depth in Sweden. However, upward flow of groundwater and/or lateral flow are not possible in lysimeters. Sidewall flow along the lysimeter wall has been discussed by *e.g*. Bergström (1990), and in some studies a sealant has been applied between the soil and column wall (*e.g*. Wildenschild *et al*., 1994; Weber & Whitacre, 1982). However, intrusion of the sealant into the pore system has been observed, which may block transport pathways (Vanderborght *et al*., 2002). Soil column diameter was 20 cm in Paper I and 29.5 cm in Paper III. An illustration of the lysimeter type used in Paper III is given in Figure 9.

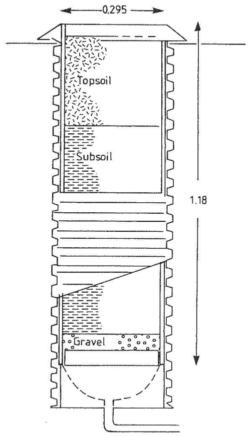

Figure 9. Lysimeter of the type used in Paper III, placed in a belowground pipe. From Bergström and Johansson (1991).

As mentioned in Paper I, the topsoil columns had varying initial soil moisture (based on varying field conditions for different soils) and this may have affected P leaching results in the first of the three simulated rainfall events. None of the soils was extremely dry, but dry initial conditions are known to promote preferential flow, *e.g.* through unstable infiltration fronts and water repellence in dry soils leading to finger flow (Hardie *et al.*, 2011; Ritsema *et al.*, 1998), and through less antecedent water in the soil needing to be displaced when the soil is dry. The simulated rainfall events in Paper I, with high rain intensities, represented very wet 'worst case' conditions, close to saturation. Ponding was observed in a few soil columns. Conditions close to saturation and high rainfall intensities promote macropore flow (Jarvis, 2007; Bergström & Shirmohammadi, 1999). Another factor which may affect studies investigating transport pathways is entrapped air in lysimeters. In some studies the soil columns have been pre-treated by slowly saturating them from the bottom to avoid this (*e.g.* Kjaergaard *et al.*, 2004).

Leaching from the topsoil columns can be seen as 'potential P leaching', but subsoil properties and water transport pathways can have a modifying effect on P leaching in deeper soil layers.

It was very valuable to have access to the Swedish long-term fertility experiments, where long-term treatments with varying P applications in different parts of the fields resulted in four P-AL levels in separate plots in each field. This allowed us to evaluate the effect of P-AL alone for different soil types. The five soils used in Paper I represent common Swedish agricultural soil types and include loamy sand, sandy loam, loam and silty clay loam.

6.2 Experimental field with separately drained plots

Experimental fields are needed in order to study the effects of management practices where real farm machinery is used. Field plots also integrate a larger area than soil columns. There are risks of lateral flow between plots, upward flow of groundwater which dilutes the drainage water, and bypass of drainage pipes (*i.e*. leachate going to the groundwater instead of the drainage pipes).

In Paper II, losses in tile drains were studied in an experimental field with separately tile-drained plots. The experimental field is flat, with efficient drainage, and surface runoff has not been indicated. Some of the transport through the soil, to the drainage pipes, probably occurs in the drain backfill (Øygarden *et al.*, 1997). The proportion of the transport which moves through the backfill (gravel with soil on top at this site) is not affected by the chemical and physical properties of the soil in other parts of the field (although the properties of the soil affect the transport to the backfill). The proportion of the transport going through the backfill has not yet been investigated or quantified at this site.

Drainage water was sampled flow-proportionally and analyzed on a weekly basis. This provided good values for calculating transport but the peaks in concentration and transport became flatter and broader, which is not ideal if different processes are being studied. Hence, it is better to focus on yearly or seasonal values from this type of measurement.

7 Summary and conclusions

7.1 Topsoil P leaching (Paper I)

A long-term perspective is needed in P management. Long-term fertilization rates resulting in varying soil P status had clear effects on P leaching from the topsoil in Paper I. No clear differences in topsoil P leaching were found between the cropping systems representing farms with or without animals, but in some soils the short-term effect of manure application on topsoil P leaching was further amplified by high P-AL values. Interactive effects between manure P and soil P need to be further evaluated. It was also clear that topsoil P leaching depends not only on soil P status, but also on other soil characteristics. It is important to identify soils which are especially susceptible to P leaching losses, and on these soils it is particularly important to apply manure and/or fertilizer P according to soil test P values and plant requirements. Topsoil P leaching losses were generally low from soils with a long-term balance between harvested and applied P (Paper I). These soils were in the agronomic optimum P-AL class (III) or below the optimum (class II) according to Swedish recommendations. Besides the concentration of soil P readily available for plant uptake (measured as P-AL), other chemical factors such as P sorption capacity and P sorption saturation are important for P leaching potential. However, one must always consider the transport pathways through the soil. For example, in the case of dissolved P transport via preferential flow, binding sites in the soil matrix are to a large extent bypassed.

7.2 Management practices on a clay soil (Paper II)

The spatial variation in P leaching was large for the experimental field on clay soil used in Paper II, even though P-AL and discharge volumes were relatively uniform across the field. Incorporation of structure lime significantly reduced P leaching losses from this clay soil, by increasing aggregate strength and possibly causing more homogeneous infiltration through the soil (reducing the risk of critical fast flows). Incorporation of structure lime appears to be a promising option for reducing P leaching from this type of soil with a high clay content. However, the precise effects on soil structure and flow pathways need to be further investigated and the effect on P losses needs to be evaluated for a number of soils with varying clay content, soil P status and other properties.

In this thesis it was not possible to identify significant effects on P leaching of the other management options in the study (conventional ploughing/shallow tillage; no P application/balanced P application; broadcasting/band spreading of fertilizer P). However, less pronounced effects on P leaching of the different management options may have been overshadowed by the large spatial variation observed in the data. It would be interesting to conduct further studies comparing the effects of mouldboard ploughing and shallow tillage on P leaching.

7.3 Phytomining (Paper III)

Lowering soil test P by phytomining, *i.e.* by removal of P with the harvested crop from soil with no P fertilization, takes a long time. Soil test P was consistently lower at the end of the phytomining experiment, although in most soils P-AL remained at excessive levels. Only one soil showed a significant decreasing trend in DRP leaching. Going from excessive to optimum soil test P (in the topsoil) may take decades in many cases and visible effects on P leaching may take even longer. It would be valuable if the rate of decline in soil test P could be increased by different forms of management, *e.g.* N fertilization and other methods of maximizing crop uptake and harvest of P. Investigating how different soil properties affect the rate of soil P decline would also be interesting. However, efforts should first of all be made to avoid soil P levels reaching values well above the agronomic optimum.

7.4 New knowledge outcomes

The results presented in this thesis show that: (i) there are clear differences between soils as regards the relationship between P-AL and topsoil P leaching, and in some soils the increase in topsoil P leaching after manure application is even larger at high P-AL; (ii) incorporation of quicklime is a promising mitigation option for reducing P leaching from clay soils; and (iii) P leaching may be reduced after phytomining, but this mitigation strategy takes a very long time.

7.5 Management recommendations

Applying manure and fertilizer P according to soil P status and plant requirements and avoiding soil P levels above the agronomic optimum are elements of a sound basic strategy. Stabilizing the soil aggregates by incorporation of amendments such as quicklime on clay soils is also a promising measure to reduce P leaching. A long-term perspective is needed in soil P management, and soil-specific properties need to be considered when choosing appropriate mitigation strategies to reduce P leaching.

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