Phosphorus Leaching as Influenced by Animal Manure and Catch Crops

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Cover: Pig slurry and catch crops, and the methods used for studying their influences on phosphorus losses in this thesis including lysimeters, field measurements, model simulations and greenhouse study.
(photo: Jian Liu)

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Abstract

Leaching of phosphorus (P) constitutes an important part of P losses from Swedish agricultural soils. Phosphorus leaching is complex and is influenced by many factors, from source and mobilisation to transport pathways, as well as agricultural management practices. In order to design appropriate mitigation strategies to reduce P leaching, it is urgent to understand how different factors influence P leaching and to understand the methods for assessing P leaching.

This thesis investigated the influence of two management practices, application of animal manure and use of catch crops, on P leaching under Swedish conditions and devised corresponding mitigation strategies. In the case of manure application, lysimeters were used to study P leaching from topsoil as influenced by soil type, manure application method and long-term manure application. In addition, P leaching from a field associated with long-term manure application was simulated with the ICECREAM model to clarify the processes dominating P leaching. In the case of catch crops, uptake of P by potential species and leaching of P from them after freezing and thawing were examined in a greenhouse and in a topsoil lysimeter study.

Conclusions are: (1) Recent manure application to clay soils with macropore flow pathways generates a high risk of P leaching and thus such application of P during wet periods must be followed by incorporation of manure into the soil or avoided; (2) application of moderate rates of pig slurry to sandy soils with sufficient P sorption capacity does not increase the risk of P leaching, and P can be applied at a rate in balance with crop removal; (3) given the same P rate, pig slurry does not constitute a larger risk of P leaching than mineral P fertilisers; (4) descriptions of P sorption/desorption processes dominated by Fe and Al oxides must be included in P models such as ICECREAM; and (5) catch crops can become a source of P losses after exposure to freezing-thawing, which should be considered when using a catch crop.

In future, more research is needed to investigate mitigation strategies to minimise P leaching from clay soils, to select or modify catch crop species to be efficient for P, and to develop methods for accurately assessing risk of P leaching.

Keywords: catch crop, degree of phosphorus saturation, freezing-thawing, ICECREAM model, lysimeter, manure application, phosphorus leaching, soil type, sorption-desorption processes

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Dedication

To my daughter Nora (暖蕙) and my wife Anan (安安)

When one drinks water, one shall think of where it comes from.
Yu, Xin
饮水思源 – 庾信

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 Liu, J., Aronsson, H., Ulén, B. & Bergström, L. (2012) Potential phosphorus leaching from sandy topsoils with different fertiliser histories before and after application of pig slurry. *Soil Use and Management* 28(4), 457-467.

II Liu, J., Aronsson, H., Bergström, L. & Sharpley, A. (2012) Phosphorus leaching from loamy sand and clay loam topsoils after application of pig slurry. *SpringerPlus* 1: Paper 53 (10 pp) http://www.springerplus.com/content/1/1/53.

III Liu, J., Aronsson, H., Blombäck, K., Persson, K. & Bergström, L. (2012) Long-term measurements and model simulations of phosphorus leaching from a manured sandy soil. *Journal of Soil and Water Conservation* 67(2), 101-110.

IV Liu, J., Khalaf, R., Ulén, B. & Bergkvist, G. (2013) Potential phosphorus release from catch crop shoots and roots after freezing-thawing. *Plant and Soil* DOI 10.1007/s11104-013-1716-y (in press).

The contribution of Jian Liu to the papers included in this thesis was as follows:

I Took part in planning the study together with the second author. Performed the experimental work, data analyses, data interpretation and writing, with assistance from all co-authors.

II Took part in planning the study together with the second author. Performed the experimental work, data analyses, data interpretation and writing, with assistance from all co-authors.

III Model simulation after data collection by the second author based on an original idea by the third author. Performed data analyses, data interpretation and writing, with assistance from all co-authors.

IV Planned the study. Supervised and assisted the second author in the experimental work. Performed data analyses, data interpretation and writing, with assistance from all co-authors.

Abbreviations

AL	Soil extraction method with ammonium lactate
DOP	Dissolved organic phosphorus
DPS	Degree of phosphorus saturation
DRP	Dissolved reactive phosphorus
FTC	Freezing-thawing cycle
GLM	General Linear Model
P_A	Active inorganic phosphorus pool
P_{FO}	Fresh organic matter phosphorus pool
P_L	Labile inorganic phosphorus pool
P_{MAN}	Manure phosphorus pool
PP	Particulate phosphorus
P_S	Stable inorganic phosphorus pool
PSC	Phosphorus sorption capacity
PSI	Phosphorus sorption index
P_{SO}	Slowly mineralisable humus phosphorus pool
SSA	Specific root surface area

1 Background

Eutrophication of water bodies caused by phosphorus (P) is a severe environmental problem in many parts of the world. Agriculture is frequently considered to be the major source of P loads to water. In Sweden, agriculture is estimated to contribute roughly 40% of the P loading to fresh waters and the Baltic Sea (Brandt *et al*., 2008). Phosphorus transfer from soil to water is a result of a combination of source, mobilisation and transport factors before P causes eutrophication in P limited waters (Haygarth *et al*., 2005; Sharpley *et al*., 2001). These factors are often influenced by one or several physical, chemical and biological processes. Consequently, a considerable number of mitigation options aiming at altering these factors and/or processes have been identified or proposed by, for instance, the EU COST Action 869 in Europe (www.cost869.alterra.nl) and SERA-17 in the United States (www.sera17.ext.vt.edu), to reduce losses of P from agricultural soils.

Phosphorus in the soil may be lost to water via surface runoff and erosion and/or leaching. The pathway that dominates in terms of total amount of P lost is often dependent on factors such as weather conditions, topography and soil properties. In the past, surface runoff and erosion were generally regarded by many as the dominant pathways for P losses, whereas leaching of P was often considered relatively small due to P sorption to *e.g.*, iron (Fe) and aluminium (Al) oxides in the soil (Sharpley *et al.*, 2001). However, leaching losses can be similar or even greater than those in surface runoff when the soil has a low P sorption capacity (PSC) or has been saturated with P, and when hydrological conditions are suitable for leaching (Dils & Heathwaite, 1999; Djodjic *et al.*, 1999; Sims *et al*., 1998). Similarly, leaching losses of particulate P (PP) in tile drains can be very high (Ulén & Persson, 1999; Ulén, 1995).

In Sweden, leaching of P constitutes an important part of P losses because most agricultural fields are relatively flat, which implies that erosion is often relatively small. Moreover, according to Wesström (2002), around 85% of

Swedish fields have more or less good drainage conditions, either naturally or through artificial tile-drainage systems. The clay soils prone to erosion are usually drained, which decreases the risk of losses of P in surface runoff (Ulén *et al.*, 2007). Many agricultural management practices influence P leaching. The work presented in this thesis mainly focused on investigating two practices, application of animal manure and use of catch crops, which are of high relevance for Swedish conditions; more P is added in the form of manure than as mineral fertilisers in Sweden today and catch crops are subsidized and frequently used in the south of Sweden.

1.1 Why study P leaching from use of animal manure?

Manure, an essential by-product of animal production, is a valuable nutrient source for crop growth, in particular in organic farming systems where manure is often the major or only source of P. Besides nitrogen (N) fixation, it is also the main source of N in organic farming. A worldwide inventory has shown that the manure P produced by domestic animals is equivalent to the total consumption of commercial P fertilisers each year, and that 60-90% of the P in the manures is in inorganic form (Mullins *et al*., 2005). In 2011, there were 1.5 million cattle, 0.6 million sheep and lambs, 1.5 million pigs, 8.2 million poultry and 0.4 million horses in Sweden (SCB, 2012). These animals excreted approximately 20 thousand tons of P annually with manure, constituting a major part of the P input to the soil.

Meanwhile, large P applications to the soil in the period 1950-1990 caused major environmental concerns, including P losses to surface waters. Recently applied manure P becomes instantly available for losses to waters via runoff or leaching, but the surplus P also constitutes a long-term risk of P losses due to build-up of soil P pools over time. Particularly, large amounts of P may be lost as ‘incidental’ P losses, when rainfall interacts directly with manure and fertiliser recently spread or excreted on the soil surface (Withers *et al*., 2003; Haygarth, 1997).

There has been much discussion about regulating animal density or rate and/or method of manure P application with the aim of reducing P losses in many countries during recent decades. For instance, farmers in Sweden are not allowed to apply more than 110 kg P ha^{-1} with animal manure during a 5-year period (average 22 kg ha^{-1} yr^{-1}) on an entire farm basis to ensure that good water quality is not jeopardised (SBA, 2010), but they can choose how to allocate the 110 kg ha^{-1} yr^{-1} between these 5 years. For example, in the 2008/2009 season, Swedish fertilised arable land (56% of total arable land) received on average 25 kg P ha^{-1} with manures and mineral fertilisers. Despite this average rate of P application being slightly higher than the average amount of P removed by crops, around 40% of the total P-fertilised Swedish arable land received >25 kg P ha^{-1} (Figure 1). The highest rates of P application were mainly seen in some counties in the south of Sweden with intensive animal production. Extremely large amounts of P (>60 kg P ha^{-1}) are still being applied on individual farms and the soil P pool is increasing.

Mineral fertilisers are generally applied in amounts meeting crop needs, and overloading of P happens mostly with manures on farms with animal production. This is partly because of practical problems, such as difficulties in applying small amounts of manure, and partly because of extra costs for dealing with manures remaining on the farm. This is a particular concern in regions with more intensive and specialized livestock production systems, where application of manure exceeding crop requirements for P often occurs continuously and creates a soil P surplus (Bergström *et al*., 2005). Additional applications of manure, even at moderate rates, to soil with a high P content and P saturation, may create a great risk of P losses. Therefore, P application needs to be reduced on such soils.

To minimise short-term P losses when using manures, it is recommended to carefully consider application rate (not exceeding crop needs), time of application (*e.g.*, avoiding wet seasons) and placement. Manure placement is to a large extent dependent on the application method used. It has been reported that injection of slurry into the soil instead of applying it to the soil surface efficiently reduces potential P losses in surface runoff (Uusi-Kämppä & Heinonen-Tanski, 2008; Kleinman *et al*., 2002) and by leaching (Glæsner *et al*., 2011).

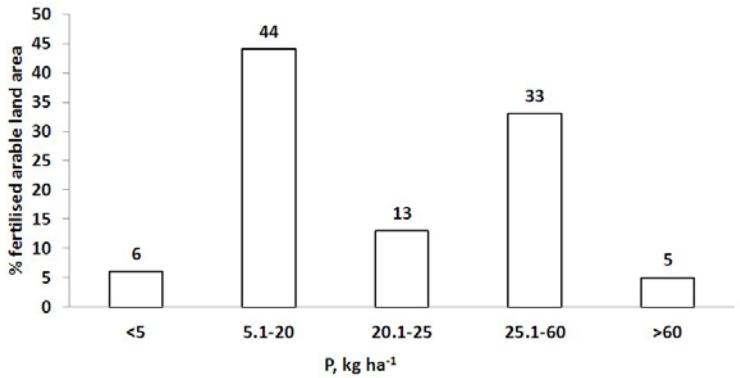

Figure 1. Percentage of total fertilised Swedish arable land area applied with different amounts of P in mineral fertilisers and animal manures in 2008/2009 (adapted from Djodjic & Kyllmar, 2011). Note that about 40% of the total P-fertilised Swedish arable land received >22 kg P ha^{-1}, the average amount of P allowed for one year during a 5-year period.

1.2 Why study P leaching from use of catch crops?

Growing an intercrop between two main crops is an important component in many cropping systems. For example, green manure crops with N-fixing capacity may provide N for the following crop. So-called catch crops are mainly grown to capture soil mineral N and to reduce N losses in the period between two main crops, when the soil is otherwise bare (Figure 2). Such crops are also widely referred to as cover crops when they are grown to protect the soil from erosion (Morgan, 2005; Bechmann *et al.*, 2005). Catch/cover crops can be either under-sown in the previous main crop in spring, or sown after the main crop is harvested in autumn. Under-sown crops are often perennial species that need a long growing period to become well established, such as grasses, clovers and chicory (*Cichorium intybus* L.). In contrast, the crops sown after harvest of main crops are often annual species that grow relatively quickly, such as members of the Brassicaceae (*e.g.*, radishes and mustards) and phacelia (*Phacelia tanacetifolia* L.). They are generally incorporated into the soil before sowing of the following crop.

A great number of studies world-wide have investigated the efficiency of catch crops in reducing N leaching (see *e.g.*, review by Dabney *et al.*, 2010). It has been well demonstrated that catch crops can commonly reduce N leaching by 20-80% depending on the species (Dabney *et al.*, 2010; Meisinger & Randall, 1991). Catch crops are frequently grown in southern Sweden and Denmark, with government subsidies available to promote the practice (Ulén *et al.*, 2007; Ulén, 1997). In some parts of southern Sweden, catch crops were grown on two-thirds of arable land with cereals in 2011 (SBA, 2012). Perennial ryegrass (*Lolium perenne* L.) under-sown in cereal crops is an efficient and frequently used N catch crop in Sweden (Aronsson & Torstensson, 1998). Among farmers, there is great interest in cultivating catch crops which provide other benefits for the crop rotation than reduced leaching, such as fertiliser effects, reduction of pathogens or structural effects (Thorup-Kristensen *et al.*, 2003). Brassica catch crops, *e.g.*, oilseed radish (*Raphanus sativus* L.) and white mustard (*Sinapis alba* L.), are commonly grown on farms that do not grow oilseed rape (*Brassica napus* L.) or other related main crops (SBA, 2012).

Figure 2. Catch/cover crops are grown in the period between two main crops (adapted from Aronsson *et al*., 2012).

In terms of P, catch crops have been shown to be able to reduce potential P losses in surface runoff by preventing soil erosion (De Baets *et al*., 2011). Catch crops can also take up considerable amounts of P, depending on species. For instance, Eichler-Löbermann *et al*. (2008) observed that oilseed radish, phacelia and ryegrass (*Lolium westerwoldicum*) took up 5.2-5.5 kg P ha^{-1} while buckwheat (*Fagopyrum esculentum*) and serradella (*Ornithopus sativus*) took up 2.7-3.1 kg P ha^{-1} in above-ground parts, all measured 8 weeks after sowing. In addition, roots can account for approximately 5-25% of the total biomass production in phacelia, mustard, oats, rye and radish (MESAM, 2007) and as much as 60-90% of the total biomass in grasses (Reicosky & Forcella, 1998). However, little is known about the efficiency of catch crops in reducing P leaching losses.

In fact, a great concern in northern European conditions with cold winters is that catch crops may become sources of P losses after they are exposed to freezing-thawing events. In winter-time, plant cells may burst due to formation of ice crystal and frost damage (Jones 1992), which can lead to the release of inter/intra-cellular P from catch crops. Bechmann *et al*. (2005) observed that 40% of the P in Italian ryegrass (*Lolium multiflorum* L.) was released after one freezing-thawing cycle (FTC) and all the plant P was released after eight FTCs. Losses of P from catch crops is a particular concern in the context of climate change, as increasing numbers of soil FTCs of greater intensity are predicted to occur in Scandinavia during the next 50 to 100 years (Mellander *et al*., 2007). Water transport can also be very fast through clay soils, which facilitates losses of P leached from catch crop tissues (Riddle & Bergström, 2013). Therefore, appropriate catch crop species with extensive nutrient uptake, but the smallest possible release of P after frost damage, should be selected.

2 Aims

The overall aims of this thesis were to study how application of animal manure, in the short- and long-term, and use of catch crops influence P leaching from Swedish soils and, based on this, to propose corresponding mitigation strategies. Specific objectives were to:

1. Investigate the risk of P leaching from different types of soils associated with long-term manure P application and examine how the risk correlated to soil P properties (Papers I and II).
2. Investigate the risk of P leaching from different types of soils after a single application of pig slurry and determine the extent to which the risk can be reduced by incorporation of the applied slurry (Papers I and II).
3. Evaluate sources of P for leaching, *i.e.*, slurry P and mineral P (Papers I, II and III).
4. Evaluate long-term P leaching from a sandy soil associated with application of pig slurry by applying the ICECREAM P model to field data (Paper III).
5. Examine potential uptake and release of P from catch crops after freezing and thawing, and identify differences in terms of species, plant parts and root morphology (Paper IV).

3 Overview - factors influencing P leaching

Phosphorus leaching from soil to water often involves complex processes, but all these processes are determined by three main factors:

- ❖ Source (mainly soil P and added P in manures and mineral fertilisers)
- ❖ Mobilisation (chemical or biological solubilisation to dissolved form, detachment of particle- or colloid-bound P, plant-driven mobilisation)
- ❖ Transport pathways (matrix and preferential flow).

Any of these factors may be the dominant cause of P leaching, but they all must be present simultaneously for high P leaching to occur. The different factors and relevant processes affecting P leaching are presented in Figure 3.

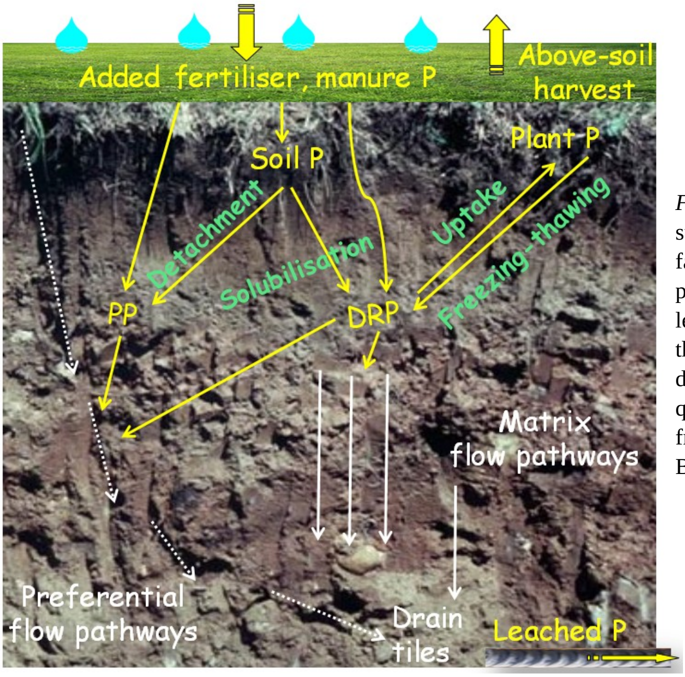

Figure 3. Simplified summary of the main factors and relevant processes affecting P leaching in soil. The thickness of the lines does not reflect quantity (adapted from Djodjic & Bergström, 2005).

3.1 Sources of P for leaching

Sources of P for leaching in soil can be categorised as indigenous P (not affected by humans) and anthropogenic (deliberately added P). While high loads of P due to indigenous soil P have been observed in some Swedish clay soil areas (Ulén *et al*., 2007), natural background P losses in dissolved form from non-fertilised arable land are generally low. Consequently, the P that is added to soil in the form of animal manures and mineral fertilisers is the main concern, especially under conditions where the P is added in amounts exceeding crop needs, as is the case in many parts of the world (OECD, 2008). Crop residues which may contain substantial amounts of P can also contribute to high P concentrations in runoff or drainage. This source includes catch crops after freezing-thawing in winter.

The added P contributes to the risk of P leaching in two ways. First, the short-term risk of P leaching is connected to recent P applications if high mobility of P in soil is combined with active transport pathways (Sharpley *et al*., 2003). This kind of risk can be reduced by rational management of the added P, *e.g.*, reduced application rate of P, incorporation of P into the soil and avoided application of P during wet seasons. Second, surplus P in soil can become a constituent of the soil matrix after it has reacted sufficiently with soil, thus building up the soil P content (Withers *et al*., 2001). This can result in a long-term risk of P leaching, which may require different mitigation strategies from those for recently applied P.

3.2 Mobilisation of P in soil

Mobilisation describes the start of P transfer in soil and includes solubilisation of P to dissolved form and detachment of particles or colloids, and associated P (Haygarth *et al*., 2005). Solubilisation of P is driven by soil chemical and/or biological processes such as sorption/desorption and mineralisation/immobilisation. It can also be affected by plants in soil. Detachment of soil PP and colloid P is driven by the physical force exerted by moving water. Operationally, dissolved P and PP are often differentiated by passing water samples through 0.45 or 0.2 µm filters (depending on different operating methods). Dissolved P, consisting of dissolved reactive P (DRP) and dissolved organic P (DOP), is more biologically available to algae than PP.

Haygarth *et al.* (2005) and Gburek *et al.* (2005) thoroughly reviewed factors affecting mobilisation of dissolved P, including recently applied P and established soil P. When fertiliser or manure is applied to soil without incorporation or immediately before a rainfall event, a large P pool is available for losses. Sorption of dissolved P mainly occurs to clay particles, $CaCO_3$, Al and Fe oxides and hydroxides, and organic matter. Phosphorus adsorbs to Fe and Al oxides by surface complexation, which is highly dependent on the pH of the soil solution. Adsorption is greatest at low pH and decreases with increasing pH. At high pH, P adsorbs to surfaces of $CaCO_3$, followed by precipitation of secondary Ca phosphates.

Once the applied P is in sufficient contact with the soil matrix, the P concentration in the soil solution and its potential subsequent loss greatly depend on processes of sorption/desorption of DRP. The degree of P saturation (DPS), defined as the percentage of a soil's P sorption sites already occupied by P, ultimately controls equilibrium between sorption and desorption of P (Börling, 2003). Mobility of DRP in the soil can be reduced by increasing soil PSC through management practices, for instance, amending soils with industrial by-products containing Al (Ulén *et al*., 2012a). Calcium in manure applied is suggested to change P sorption characteristics and increase the PSC of the soil (Sharpley *et al*., 2004). Liming with CaO and CaOH, mainly used to improve soil aggregate stability and other soil structural properties and thereby reduce PP leaching (Ulén *et al*., 2012b), may also contribute to PSC to some extent. Under specific conditions, mineralisation of organic matter may be critical in P mobilisation. For instance, Reddy (1985) found P leaching from some organic soils in Florida to be as high as 16-168 kg P ha^{-1} yr^{-1} due to mineralisation of organic matter.

Crops, including cover/catch crops, may also affect the mobility of P in soil. Roots can considerably deplete the most mobile fractions of soil inorganic P in the rhizosphere due to uptake of P. On the other hand, the roots may release exudates such as protons or organic anions such as citrate, resulting in dissolution of P (Hinsinger, 2001). It has even been suggested that improving root capability to increase P solubility in soils may be a solution for more sustainable use of limited P resources (Stutter *et al*., 2012). In general, however, little is known about the extent to which crop roots affect P mobility in terms of losses.

Detachment of soil PP and colloidal P is often linked to soil erosion, both in the soil and on the soil surface. The mobility of P attached to soil particles is related to both the amount of P associated with the different size fractions and the dispersibility of soil particles as a function of soil properties and management practices (Gburek *et al*., 2005). Soil erosion is a size-selective process with a preference for smaller-sized particles (Issa *et al*., 2006; Sutherland *et al*., 1996) and the total P associated with soil particles generally increases with decreasing particle size (Sinaj *et al*., 1997). This may result in greater P content and reactivity of eroded materials than the source soil. Clay soils are usually highly enriched in P due to large specific area of fine particles.

3.3 Pathways of P leaching

Leaching of P occurs through two pathways, matrix flow and preferential flow. Matrix flow, also called micropore flow, is ideally uniform movement of water and solutes vertically through the whole pore volume of a soil profile, whereas preferential flow (*e.g.*, macropore flow) involves only a small part of the total pore volume (consisting of *e.g.*, root and earthworm channels, fissures and interaggregate voids) and triggers rapid transport of water and solutes (Jarvis, 2007). Dissolved P is the predominant form of P transported through matrix flow pathways, while both dissolved P and PP are transported through preferential flow pathways.

The transport pathways can to a large extent be determined by the type of soil. For instance, Bergström & Shirmohammadi (1999) and Glæsner *et al.* (2011) demonstrated that soil texture greatly affects active flow volume in soil, which is of great importance for water and solute transport. In general, matrix flow is predominant in sandy soils and preferential flow is expected to occur in well-structured clay soils (Jarvis, 2007), and also in organic soils (Bergström, 1995). Substantial amounts of recently applied P can be lost through preferential pathways by which P bypasses the soil matrix where sorption sites are located. Comparing P leaching through a clay soil and a sandy soil, Djodjic *et al.* (1999) found that the average total-P leaching load was 4.0 kg ha^{-1} in clay lysimeters and only 0.06 kg ha^{-1} in sand lysimeters under identical climate conditions. Preferential flow may also occur in sandy soils to a minor extent, *e.g.* due to water repellency caused by high amounts of organic matter in the topsoil (Larsson *et al.*, 1999). In addition, water and P transport can be accelerated by initial wet soil conditions (Kramers *et al.*, 2012) and high precipitation intensities (Köhne & Gerke, 2005).

4 Methods for assessing P leaching

4.1 Relating P leaching to soil P content and added P sources

Soil P content, which was originally quantified for agronomic purposes to assess the amounts of plant-available P in soils, is now being widely tested as an indicator for estimating P losses to water. By tradition, different countries use different testing methods to quantify soil P content. For instance, Olsen-P (Olsen *et al*., 1954) is widely used in the United Kingdom and the Mehlich 3 method (Mehlich, 1984) in the United States. In Sweden, the ammonium lactate method (P-AL) is commonly used, where soil P is extracted using 0.01 M ammonium lactate and 0.40 M acetic acid solution at pH 3.75 with a soil/solution ratio of 1:20 (Egnér *et al*., 1960). A number of studies have demonstrated a clear relationship between soil P content quantified with various methods and potential release of DRP (Börling *et al*., 2004; Maguire & Sims, 2002; Torbert *et al*., 2002; Pote *et al*., 1999; Heckrath *et al*., 1995). However, so far no test has proven superior to all others and more research is needed to identify a common method with high precision in predicting P losses (Eriksson *et al*., 2013; Bundy *et al*., 2005).

For more precise estimates of P losses, measurements of soil properties accounting for mobility factors such as PSC should be considered, in addition to measurements of soil P content. Calculation of DPS is one widely-used method. It was first developed by van der Zee *et al*. (1990) as $P_{ox}/((Fe_{ox} + Al_{ox}) \times \alpha) \times 100$, where the content of P_{ox}, Fe_{ox} and Al_{ox}, expressed on a molar basis, are measured in the same extract by ammonium oxalate according to Schwertmann (1964). P_{ox} represents soil P content and Fe_{ox} and Al_{ox} are used for estimating PSC. The coefficient α ranges from 0 to 1, with a value of 0.5 recommended for soil conditions in the Netherlands (Breewsma & Silva, 1992). Strong correlations have been found between soil DPS values and concentrations of dissolved P in various types of solutions, *e.g.*, in leachate from lysimeters (Leinweber *et al.*, 1999). In Sweden, Ulén (2006) found a good correlation between Fe and Al extracted with ammonium lactate and with ammonium oxalate for 40 clayey, loamy or sandy soils from Swedish long-term experimental fields, and modified the calculation of DPS-AL to P-AL/(Fe-AL + Al-AL) x 100 on a molar basis for Swedish acid soils. Besides measuring soil Fe and Al contents, P sorption index (PSI) is also widely used to estimate PSC (Börling *et al.*, 2004, 2001). Based on P sorption isotherms, Bache & Williams (1971) developed a simple method to determine PSI where a single addition of 19.4 or 50 mmol P kg^{-1} soil is used and PSI is calculated as X/log C, where X is the amount of P sorbed by the soil (in mmol kg^{-1} soil) at equilibrium and C is the equilibrium P concentration in the solution (in mmol L^{-1}).

In general, recently applied P, especially in large amounts, can affect potential P leaching. For instance, Weaver *et al.* (1988) clearly demonstrated that soil solution P concentration significantly increases with the application rate of P in different types of superphosphate fertilisers. The increase was greatest for the fertiliser with the highest proportion of water-extractable P. Chardon *et al.* (2007) also observed an increase in P leaching after application of cow manure patches on a sandy soil. Moreover, the forms of P in manure can affect the potential for P leaching. Sharpley & Moyer (2000) reported that P leached from dairy manure, dairy manure compost, poultry manure, poultry manure compost, and pig slurry significantly correlated to water-extractable inorganic P or organic P in the corresponding material. However, application of P does not necessarily cause an increase in P leaching. Some studies have even shown an opposite trend, with smaller losses of P after adding mineral fertiliser P or manure compared with soil with no P application (Bergström & Kirchmann, 2006; Sharpley *et al.*, 1999). These contradictory results on P leaching after recent P application indicate that additional parameters, such as soil properties and transport pathways (Djodjic *et al.*, 2004), must be included in assessing P leaching.

4.2 Measuring P leaching at different scales

Leaching of P with drainage water can be measured in lysimeters, field plots and fields, where combinations of source, mobility and transport factors are included. For scales larger than fields, measuring P leaching losses with accuracy is difficult, but possible under certain circumstances. For instance, in the Swedish Vemmenhög catchment (900 ha), where most of the fields are extensively drained and drainage water is collected together with surface runoff in a main culvert (Kreuger, 1998), the P concentration in culvert water has been measured since 1992.

Lysimeters are defined as containers of soil (with or without plants) representing the field environment. They were originally used to determine the evapotranspiration of a growing crop or evaporation from bare soil (Aboukhaled *et al.*, 1982). Lysimeter studies allow relatively rapid generation of results and reliable comparisons between treatments of particular interest, since they represent relatively controlled conditions. They have become an important experimental method for measuring leaching of nutrients (including P) and pesticides in recent decades. According to different soil-filling techniques, lysimeters can be categorised as undisturbed lysimeters or repacked lysimeters, with undisturbed lysimeters being recommended for leaching studies (Winton & Weber, 1996; Bergström, 1990). Lysimeters can range in size from 0.05 to 2 m in diameter and from 0.1 to 2 m in depth and they can be placed indoors or outdoors according to availability of experimental facilities required for irrigation and measuring water discharge. For studying P leaching, the most commonly used lysimeters are topsoil lysimeters sampled from the plough layer (0.2-0.3 m depth, Glæsner *et al.*, 2011; Kleinman *et al.*, 2009) and lysimeters including both topsoil and subsoil, which are sampled to a depth approximating where tile drains are installed (0.9-1 m deep, Andersson *et al.*, 2013; Djodjic *et al.*, 2004). Studies with topsoil lysimeters are commonly referred as column studies, where the lysimeters are often placed indoors and receive artificial rainfall (Figure 4).

Leaching of P is also often measured at plot and field scale, for which long-term field experiments provide a valuable opportunity to evaluate the effect of different management practices on P leaching. Several such field experiments with separately tile-drained plots have been established in central and southern Sweden since the 1970s. These experiments cover different soil types and various management practices, such as different cropping and tillage systems and use of animal manure and catch crops in both conventional and organic farming systems (Ulén *et al.*, 2006). Drainage water from each plot is directed to an underground measuring station, with flow recording and water sampling (Figure 5). The plots are usually separately tile-drained at a depth of 0.9-1.0 m. Discharge rates from each plot are recorded with tipping buckets connected to a data logger. For analysis of P in water, discharge from each plot is flow-proportionally sampled, *i.e.*, a smaller water volume representing a certain proportion of all water that passes through is sampled.

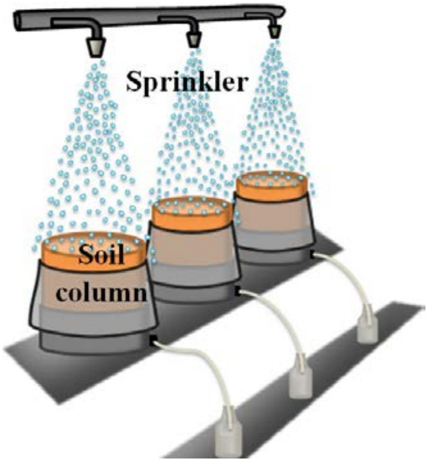

Figure 4. Diagram of indoor lysimeters for studying P leaching (figure made by Eriksson A.K.).

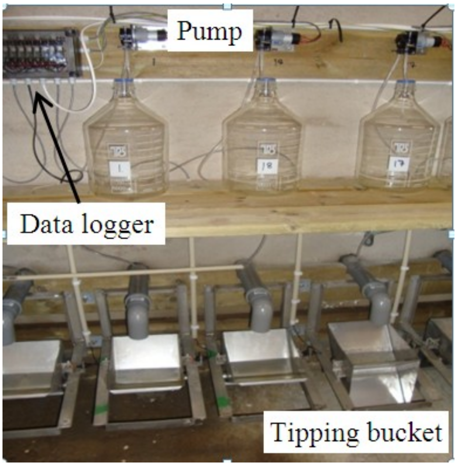

Figure 5. Recording water discharge and flow-proportional sampling in the field.

4.3 Model tools for assessing P leaching

There is increasing interest in the use of computer models that comprehensively account for P source, mobility and transport factors, in order to identify risk areas of P losses and to predict P loads to surface waters and/or groundwater. For example, model calculations are required for large-scale estimates of nutrient leaching for reporting according to international conventions, such as the Helsinki Commission for the Baltic Sea (HELCOM). Models are also widely used for evaluation of mitigation programmes and for prediction of long-term effects. Moreover, models can become an excellent tool for our understanding of the complex processes involved in the soil.

Phosphorus models cover a spectrum from static risk-based index models such as P-index (Heckrath *et al.*, 2008) to more complex, process-based and dynamic simulation models such as GLEAMS (Knisel & Davis, 1999), SWAT (Arnold *et al.*, 1998) and ICECREAM (Rekolainen & Posch, 1993). These models have been developed to focus on different areas, and they have been shown to work well enough for certain purposes. In Sweden, P leaching through the soil profile normally constitutes a large proportion of P losses. Hence, processes of water and P transport through the soil have to be considered in any model used for Swedish conditions. The ICECREAM model, simulating surface and subsurface P losses in both dissolved and particulate form, is officially used for calculating P leaching losses from Swedish agricultural soils at both regional and national scale (Johnsson *et al*., 2008). The ICECREAM model is basically derived from the CREAMS model (Knisel, 1980), and has been modified by incorporating snow and soil frost processes to suit Nordic conditions (Tattari *et al*., 2001; Rekolainen & Posch, 1993). Larsson *et al*. (2007) incorporated a component to represent preferential flow pathways in the model. The model simulates a full water balance including precipitation, evapotranspiration, surface runoff and percolation between layers and out of the root zone. Percolation losses are partitioned between preferential flow and matrix flow, and between losses through tile drains and deep percolation. Larsson *et al*. (2007) found that ICECREAM generally worked well for estimating P losses from well-structured soils, but they also pointed out that the model failed to simulate some events, most likely because it did not account for P sorption to free Fe and Al.

The ICECREAM model and many other currently widely used models simulate soil P cycling based on the model of Jones *et al*. (1984). Six soil P pools are included in ICECREAM (Figure 6): three pools representing stable (P_S), active (P_A), and labile (P_L) inorganic P forms, and three organic pools representing manure P (P_{MAN}), fresh organic matter P (P_{FO}) and slowly mineralisable humus P (P_{SO}). All soil P pools contribute to PP losses. P_L is the source of DRP and it can be taken up by plants (P-PLANT), immobilised into P_{FO}, or lost through surface runoff and subsurface drainage. Additions of manure are placed into P_{MAN} and mineral-P fertiliser into P_L. Phosphorus is transferred to P_L from the organic-P pools through mineralisation and from the mineral-P pools through desorption and dissolution processes. Overall, sorption/desorption processes often dominate P reactions in soil.

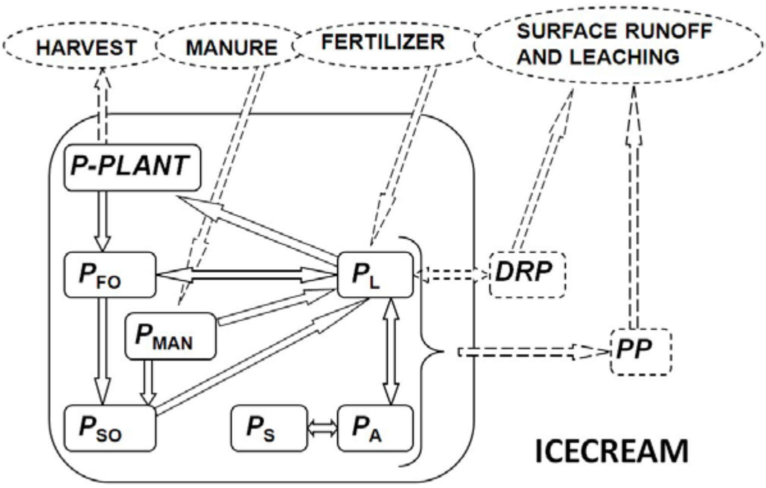

Figure 6. Phosphorus pools and flows in the ICECREAM model (Larsson *et al*., 2007).

The model user enters estimates for total soil P pools and selects equations for calculating P sorption distribution coefficients, which control the relative sizes of different inorganic P pools, as well as P flow between the pools. These equations are estimated from soil properties, but they have been limitedly updated since the 1980s (Vadas *et al.*, 2013), which may lead to errors in estimating P losses. As the ICECREAM model is widely used, it has to be thoroughly tested for field-scale applications on soils with different P sorption properties. A field study with a sandy soil, which has high PSC and received different amounts of liquid manure and mineral P fertiliser, was used to test the applicability of the ICECREAM model in this thesis.

5 Manure studies

5.1 Experimental design

Three studies were carried out to examine the effects of manure application on P leaching from soils with different properties, and to suggest appropriate mitigation strategies. A summary of the studies is presented in Figure 7 and the results are presented in Papers I-III.

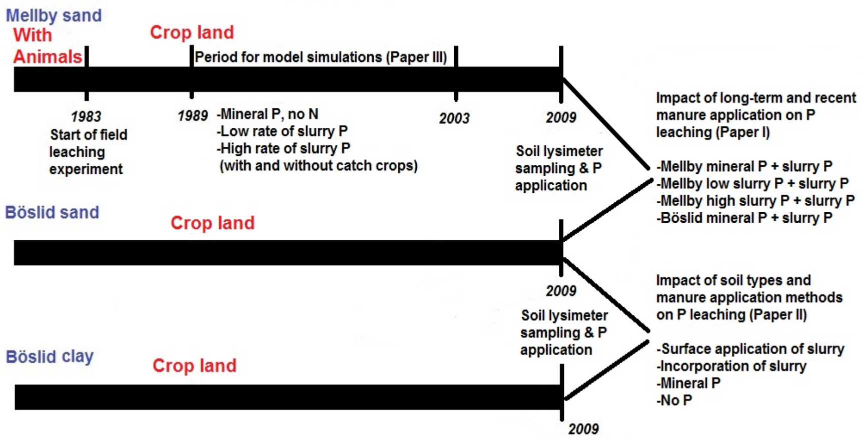

Figure 7. Summary of manure studies in Papers I-III and the history of the soils used.

Two experimental sites, Mellby (56°29´N, 13°00´E) and Lilla Böslid (56°35´N, 12°56´E), both located in south-west Sweden (Figure 8), were involved in these studies. The Böslid site has a sandy and a clay soil, and the Mellby site has a sandy soil. The two sandy soils have similar physical properties. Separately tile-drained plots were established on the Mellby sand in 1983 to study the impact of different manure treatments, in combination with and without catch crops, on nutrient leaching. Before 1983, the Mellby farm

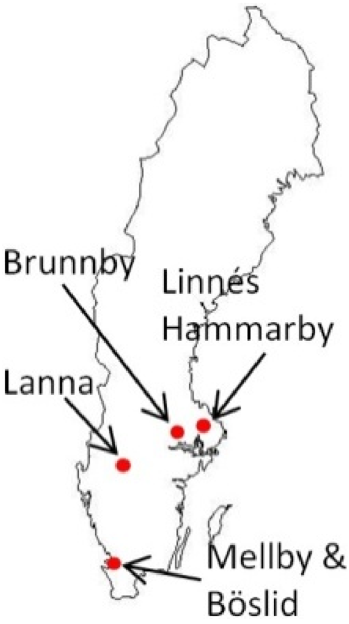

Figure 8. Locations of field experiments and lysimeter sampling.

has had animals for a long time, which means that the site received large amounts of manure. In contrast, the Böslid site was used only as a crop land fertilised with mineral P. Different historical loads of P to these soils and experimental treatments at Mellby resulted in different soil P contents and DPS values.

In Paper I, leaching studies with intact topsoil lysimeters were conducted to examine the impact of both long-term and recent manure applications on P leaching from topsoils and to determine the influence of soil DPS-AL on P leaching. The lysimeters were sampled from the Mellby and Böslid sandy soils after harvest in September 2009. At Mellby, the lysimeters were taken from experimental plots (without catch crops) which received a low rate of pig slurry (24 kg slurry P ha^{-1} yr^{-1} + 6 kg mineral P ha^{-1} yr^{-1}), a high rate of pig slurry (41 kg slurry P ha^{-1} yr^{-1} + 3 kg mineral P ha^{-1} yr^{-1}) and only mineral P (22 kg mineral P ha^{-1} yr^{-1}). The low rate of slurry represents manure amounts produced on a farm with the maximum permitted animal density in Sweden. The Böslid lysimeters were used as the control. The leaching experiments were conducted in the laboratory in two sequences, before and after incorporation of pig slurry into the lysimeters at a P rate of 22 kg ha^{-1}. These were to investigate effect of long-term and recent applications of manure, respectively.

In Paper II, leaching studies with topsoil lysimeters were conducted to examine the impact of recent manure application on P leaching from topsoil, as influenced by soil type, application method and source of P. This study included the lysimeters from the Böslid sand and clay soils, which received 30 kg P ha^{-1} in pig slurry (incorporated or not), 30 kg mineral P ha^{-1}, or no P (control). As in Paper I, the laboratory leaching experiments were conducted both before and after P application.

In Paper III, measurements of P leaching from the Mellby plots for the period 1989-2003 were evaluated and used in simulations with the ICECREAM model to study long-term effects of manure application on P leaching. The main objectives were to examine the importance of different soil characteristics (soil P, Fe, Al and Ca content and DPS) and processes (water flow and P sorption/desorption) on P leaching, and to test application of the

ICECREAM model on this type of soil. Three fertilisation treatments, including the two slurry P treatments as in Paper I, as well as one treatment with mineral P but without N, were included in this study.

The sorption distribution coefficient (k_{dl}), which determines P sorption/desorption between P_L and P_A and between P_A and P_S (different P pools described in section 4.3) was calculated according to Siimes *et al.* (1998), where k_{dl} is a function of pH, degree of base saturation (*bsat*) and clay content (*solcly*):

$$k_{dl} = 0.0025\, solcly\, (0.46 - 0.0916\, log(100\, slocly) + (0.35 - 0.0025\, solcly)\, (0.0054\, bsat + 0.116\, pH - 0.73) \quad [1]$$

The distribution of P between P_L and DRP is described by a linear sorption isotherm assuming instantaneous equilibrium and with the sorption distribution coefficient (k_{dw}) given as a function of the clay content (Knisel, 1993):

$$k_{dw} = 100 + 250\, solcly \quad [2]$$

The simulations were carried out in three steps. First, the hydrological part of the model was calibrated on one selected plot to achieve good agreement between simulated annual cumulative drainage and daily drainage and the measured values. The calibration was carried out by accounting for 17% of the drainage water bypassing the tile drains (Torstensson & Aronsson, 2000) and occurrence of preferential flow to a minor extent, probably as a result of water repellency caused by the high organic matter content in the topsoil (Larsson *et al.*, 1999). Thereafter, daily P leaching from each treatment was simulated with parameterisation of P pools based on measured soil P properties to estimate the potential P leaching as given by the soil P content. Initial mineral P content was estimated from measured soil P values (P-HCl multiplied by 1.44) for each treatment. Finally, the effect of sorption/desorption processes in the model was tested by running simulations with the soil P pools initially set to zero.

The SAS programme (Version 9.1 & Version 9.2) was used for statistical analysis. The Mixed Model for repeated measurements (Littell *et al.*, 2006) was used to compare treatment effects on variables (*e.g.*, P concentrations and losses) in Papers I and II. A "repeated" procedure was used in the model to realise repeated irrigations or extractions on the same subject. The General Linear Model (GLM) was used to compare treatment effects in Paper III and used for regression analysis in all the studies. When needed, the data was log-transformed to obtain normal distribution of the residuals. A significance level of $\alpha = 0.05$ was used in all the studies unless noted otherwise.

5.2 Soil type and long-term manure application influence the risk of P leaching from topsoil

The lysimeter studies in Papers I and II confirmed that P transport pathways have a great influence on P leaching associated with recent P application. Transport pathways of P are dependent on soil texture and soil structure (the organisation of individual soil granules including the arrangements of soil pores between them). In addition, data on soil P content and PSC must be combined with information about P transport pathways to assess the risk of P leaching. In general, recent P applications, even at moderate rates, to well-structured clay soils containing preferential flow pathways cause a high risk of P leaching compared with sandy soils, where matrix flow dominates. Preferential flow results in rapid transport of P and in a smaller active pore volume, which makes P bypass sorption sites on the soil matrix. In this way, a certain amount of P that is applied on the soil surface may be directly washed away.

The Böslid clay and sand used in this thesis both have high PSC and they were applied with 30 kg slurry P ha^{-1} on the soil surface. This P application elevated the concentration of total-P in the leachate from the clay soil 18-fold compared with the control, while it had no influence on the total-P concentration in leachate from the sand (Figure 9a & 9b). Elsewhere, Djodjic *et al*. (1999) and van Es *et al*. (2004), among others, have also observed larger P leaching losses from clay soils than from sandy soils under identical weather conditions and management practices. In addition, Glæsner *et al*. (2011) and Sørensen & Rubæk (2012) reported that the risk of P leaching resulting from application of P to coarse-textured soils without macropores is low due to adsorption of P to the soil.

However, not all sandy soils have a low risk of P leaching. Potential P leaching may greatly increase when the soil has a high DPS, resulting from low PSC of the soil (Elliott *et al.*, 2002; Weaver & Ritchie, 1994), or high soil P content (De Bolle *et al*., 2013). A tendency for an increasing risk of P leaching after a recent single slurry application was also observed in this thesis for the Mellby topsoil, which has a relatively high DPS due to long-term loading with manure (Figure 10). Furthermore, the surplus added P can move downward through the soil (Koopmans *et al.*, 2007). This is of particular concern in regions with intensive and specialised livestock production, where application of manure exceeding crop requirements for P often occurs year after year (Bergström *et al.*, 2005). Many such areas exist around the world, also in Sweden (OECD, 2008).

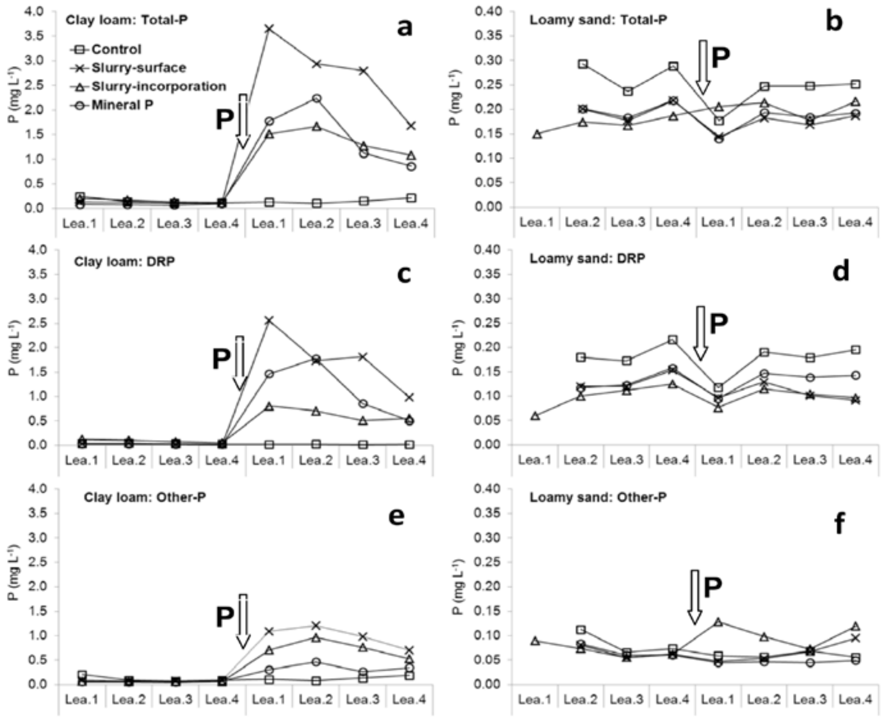

Figure 9. Mean concentration of total-P, DRP and other-P (sum of DOP and PP) in each effluent sample before and after P application to the Böslid clay loam and loamy sand topsoil lysimeters (n = 3 or 4). a) Total-P concentration in the clay loam, b) Total-P in the loamy sand, c) DRP in the clay loam, d) DRP in the loamy sand, e) Other-P in the clay loam and f) Other-P in the loamy sand (note that the scale of the Y-axis differs between soils).

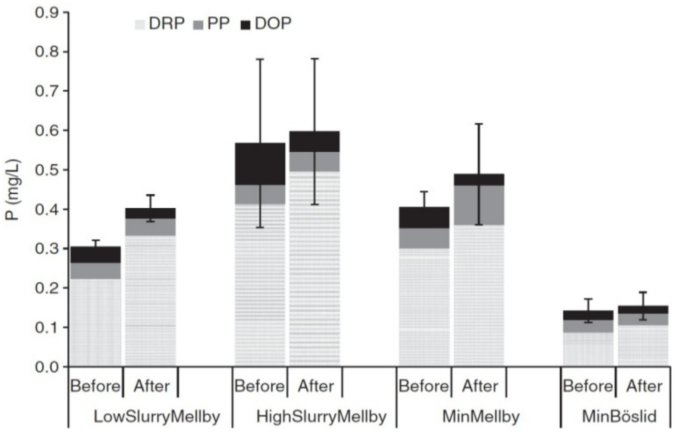

Figure 10. Mean concentration of P in leachate before and after slurry application to the Mellby and Böslid sandy soils. Bars represent standard deviation of total-P (n = 4 except for the LowSlurryMellby treatment, where n = 3).

Long-term manure application, which builds up soil P content and thus increases soil DPS, also has a great impact on the risk of P leaching. This risk was evaluated in this thesis in the lysimeter leaching studies with topsoil before slurry application in the laboratory, as presented in Paper I. Many years' loading of large amounts of manure to the Mellby sand have resulted in a high P content and DPS in the topsoil. This makes the Mellby sand a high risk soil in terms of P leaching compared with the Böslid sand, which has similar physical properties, but has received only mineral fertilisers with P amounts approximating those removed by crops. The risk of P leaching from the Mellby topsoil increased with increasing amounts of P applied during the field experiments since 1983 (Figure 10). Several other studies have also demonstrated that, as for the Mellby soil, long-term manure P application in large amounts contributes to build-up of soil P (Maguire *et al*., 2009; Nelson *et al*., 2005).

High soil P content increases the risk of P losses to drainage water and groundwater when the PSC of soil approaches saturation (Schoumans & Groenendijk, 2000). For all the sandy topsoils studied, the concentration of DRP, which was the dominant form of P in the leachate, increased significantly with increasing soil DPS-AL values (R^2 = 0.95, p < 0.0001; Figure 11a). The increase in DRP concentration after a single slurry application was greater with higher DPS-AL values (R^2 = 0.79, p < 0.0001; Figure 11b). These differing DPS-AL values were caused by different manure application histories before 1983 and subsequent experimental treatments. Principally due to relatively low soil P content and low DPS-AL, the Böslid clay topsoil had lower background leaching of total-P and DRP than the two sandy soils.

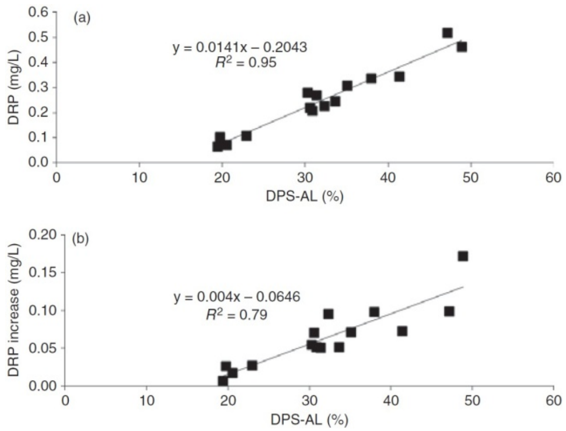

Figure 11. Regression lines between DPS-AL in the Mellby and Böslid sandy topsoil and a) mean concentration of DRP in leachate before slurry application to the topsoil lysimeters, and b) increase in DRP concentration after slurry application (n = 15).

5.3 Management of manure applications to reduce P leaching

As discussed previously, there is a high risk of P leaching associated with recently applied manure P from clay topsoil compared with sandy topsoil. Also, in a two-year study in the fields from which the lysimeters used in this thesis were collected, much higher P leaching was observed from the Böslid clay than from the Mellby sand (Table 1). Drainage amount was also higher from the Böslid clay, indicating rapid water transport. Incorporation of pig slurry into the soil seems to be an effective mitigation strategy to reduce the risk of P leaching from the topsoil (Paper II), which is also indicated in the field study (Table 1). In our topsoil lysimeter studies (Paper II), incorporation of slurry into the soil significantly reduced the concentration of total-P in the leachate from the Böslid clay topsoils by 50% and DRP by 64% compared with surface application (Figure 9). This reduction in P leaching is probably due to two factors, enhanced sorption of labile P in the slurry to the soil matrix and disruption of the continuity of macropores. Other studies have also reported that mixing P with the topsoil or injecting slurry into the soil, efficiently reduces the risk of P losses by leaching (Glæsner *et al.*, 2011; Djodjic *et al.*, 2002) and in surface runoff (Uusi-Kämpää & Heinonen-Tanski, 2008; Kleinman *et al.*, 2002).

The reduction in total-P leaching losses increases with increasing disruption of macropores (Geohring *et al.*, 2001). However, it should be noted that the remaining DRP leaching after incorporation of slurry was still considerably high and other-P (sum of PP and DOP) leaching was not reduced in our lysimeter study (Figure 9). This suggests the need for additional mitigation strategies besides slurry incorporation to further reduce the risk of P leaching from clay soils, where macropore flow is likely to occur. This includes avoiding manure application during the autumn in cold and wet regions, and adopting improved tillage and/or cropping systems which reduce P leaching via macropore flow pathways.

Table 1. *Two-year (2010-2012) mean of drainage amounts and concentrations and transport of P in drainage water from Böslid clay and Mellby sandy soil, where spring cereals were grown and pig slurry was applied each year (Aronsson, unpublished observations)*

Site	Slurry treatment	Drainage	DRP	Total-P	DRP	Total-P
		(mm)	(kg ha^{-1} yr^{-1})		(mg L^{-1})	
Böslid	Surface-applied in spring	382	0.077	0.488	0.020	0.127
Böslid	Incorporated in spring	387	0.071	0.408	0.018	0.107
Böslid	Incorporated one month after application in autumn	369	0.154	0.571	0.041	0.153
Mellby	Surface-applied in spring	247	-	0.092	-	0.026

In contrast to the clay soils, single slurry application at a moderate P rate did not cause a risk of P leaching from the Böslid sand. This soil has medium soil P content in Swedish terms and sufficient PSC (Paper II). The 15-year field leaching measurements on the Mellby sand (Paper III) demonstrated a low risk of P leaching from this soil, even from plots applied with high rates of slurry P. This is because the soil has a high PSC, as indicated by direct measurements of soil properties and simulations with the ICECREAM model (Paper III). However, there is a considerable risk of P leaching from the Mellby topsoil as a result of long-term manure application and this risk will increase with additional manure applications, as already observed for DRP (Paper I). Therefore, manure application even to sandy soils should be restricted. Manure should preferably be applied at a P rate in balance with crop removal, because both the long- and short-term risks of P leaching may increase as surplus P continues to saturate the soil. For high-risk sandy soils with a high soil P content and DPS in the subsoil, or restricted P sorption in the subsoil, besides minimising P applications, additional mitigation strategies may be needed. These strategies may be aimed at mining P from the soil or increasing P fixation in the soil.

The results in Paper II also suggest that it does not seem necessary to incorporate manure into a sandy soil such as that at the Böslid site, with the aim of reducing P leaching. However, incorporation of manure is very important in order to decrease losses of N through ammonia volatilisation (Sommer & Hutchings, 2001), and is therefore still recommended for circumstances where ammonia volatilisation is a concern.

The potentially large effect of P in slurry on the risks of P leaching from different soils was expected, because of the high mobility of slurry P. In another topsoil lysimeter study where P was applied at a very high rate (167 kg ha^{-1}), Tarkalson & Leytem (2009) demonstrated that P mobility in a sandy soil followed the order: liquid dairy manure > monoammonium phosphate > solid dairy manure. The pig slurry used in Papers I and II had a high labile P content (50% NH_4-Cl-extractable) and incorporation of this slurry into clay and sandy soils caused an overall risk of P leaching from both soils, similar to that caused by application of mineral P fertiliser (Figure 9). However, in the 15-year field leaching measurements at Mellby (Paper III), application of slurry (even at high rates) did not increase P leaching compared with mineral P application, rather the opposite.

Mean annual concentration of total-P in drainage water from the plots receiving mineral P, but not N, was significantly higher than in water drained from the plots applied with twice the amount of P in pig slurry (Figure 12). This was most likely because of poor crop development when no N was applied, which indicates that the P use efficiency of the crop plays a role in reducing P leaching. In addition, manure is regarded as having a long-term equivalent value to mineral fertilisers in supplying P for crops (Smith *et al.*, 1998; Smith & van Dijk, 1987). Therefore, in conditions where animal manure has to be dealt with, such as on livestock farms, it is recommended that the manure be used as a substitute for mineral P fertilisers on nearby arable land. However, the amount of P that is applied with manure should balance crop P removal to minimise the potential for P losses. It should also be borne in mind that additional N may be needed in P-based application of manure, which generally has a low N:P ratio (2:1-8:1) compared with the needs of most crops (≈8:1).

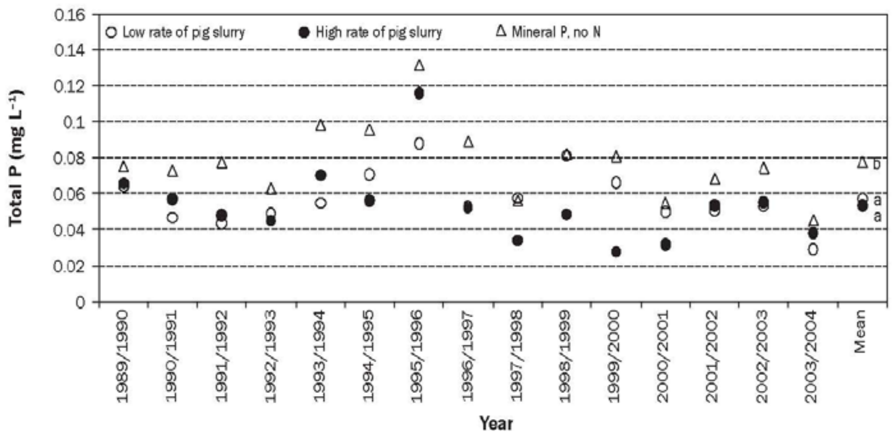

Figure 12. Measured mean annual concentration of total-P in drainage water from the Mellby sand in different years and mean values for the whole period. Different letters (a, b) indicate significant differences between the different treatments.

5.4 Implications of use of models for simulating P leaching

Application of the ICECREAM model to simulate P leaching associated with manure applications from sandy soil with high PSC was tested on the Mellby soil for a 15-year period (Paper III). Simulated drainage values were in good agreement with measured values, but the model substantially overestimated total-P leaching, by a factor of 5-9 for different treatments (Figure 13). However, when the scenario for the soil with low desorption of P was simulated by setting the initial mineral P pools in the model to zero, the total-P leaching loads simulated by the model were rather similar to the measured loads. The modelling work confirmed that for sandy soil without macropores, soil P sorption/desorption characteristics are far more important for leaching than application of P.

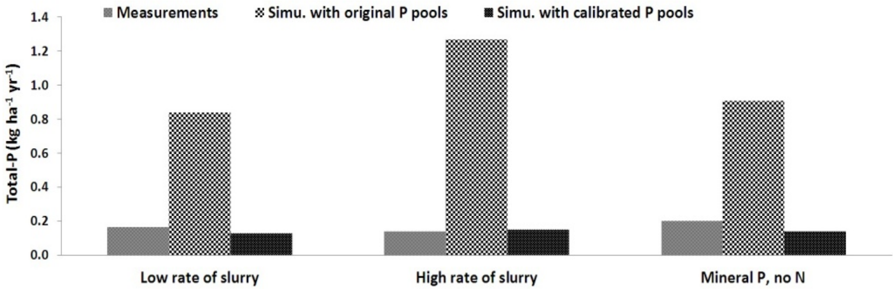

Figure 13. Measured and ICECREAM-simulated mean annual total-P leaching from different fertilisation regimes for the period 1989-2003 at Mellby.

The results also indicated that ICECREAM cannot describe sorption/desorption processes in an accurate manner for soils such as Mellby. The substantial overestimation of P leaching was attributed mainly to high desorption from the more stable P pools, while both the mineralisation of P from the organic pools and the water transport capacity were reasonable. The functions for sorption/desorption processes in the current version of the ICECREAM model are based on pH, clay content and degree of base saturation. For further use of the model, and other models with the same problem, sorption/desorption capacity of soils due to Fe and Al oxides should be considered. This has also been suggested by Yli-Halla *et al*. (2005) and Larsson *et al*. (2007) in studies with the ICECREAM model on other soils. Inclusion of recent work by Vadas et al. (2007 & 2012) to provide updated P fate and transport subroutines into ICECREAM will go a long way to addressing these model limitations.

6 Catch crop studies

6.1 Experimental design

Two studies were carried out to investigate potential P uptake by catch crops and leaching of P from the crops after freezing-thawing. In one study (Paper IV), eight catch crop species were grown in the greenhouse and the P amounts released from their shoots and roots were determined in different freezing-thawing treatments. The amounts of roots and root morphology were also determined. The other study investigated field growth and uptake of P by these catch crops on three clay soils, and P leaching from topsoil lysimeters of the catch crops taken from these soils (unpublished work, with some results presented in this section of the thesis). A summary of the studies is presented in Figure 14 and the detailed experimental design is described below.

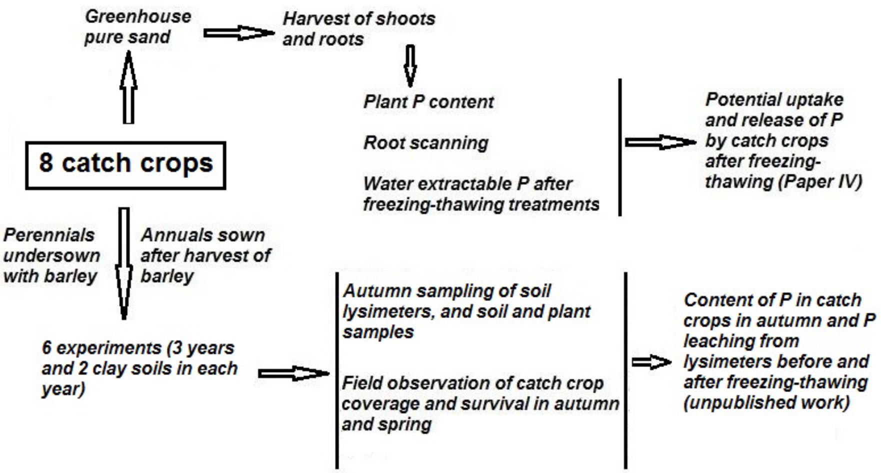

Figure 14. Summary of the catch crop studies (Paper IV and one unpublished study).

6.1.1 Catch crops studied

The eight catch crop species studied were the perennial crops perennial ryegrass, cocksfoot (*Dactylis glomerata* L.), chicory and red clover (*Trifolium pratense* L.), and the annual crops phacelia, white mustard, oilseed radish (*R.* var. *oleiformis* ‘Adios’) and white radish (*R.* var. *longipinnatus* ‘Structurator’) (Figure 15). The two forage grasses (perennial ryegrass and cocksfoot) are winter-hardy for the study region. They have fibrous roots, which can efficiently extend and use nutrients available in the upper part of the soil profile, while the root intensity rapidly decreases with soil depth (Thorup-Kristensen, 2001). Perennial ryegrass, under-sown in cereal crops in spring, is a very suitable catch crop for reducing N leaching in Scandinavia (Torstensson & Aronsson, 2000; Hansen & Djurhuus, 1997). The forage legume red clover, which is commonly used as a forage crop, is also relatively frost-tolerant and has a deep taproot. Chicory has a stout taproot with a high dry matter content and can survive exposure to low temperatures (down to -7 °C) for several weeks (Neefs *et al.*, 2000). Phacelia is an annual herbaceous plant with extensive, fine roots (Stivers-Young, 1998), and is reported to have high N scavenging ability due to its fast growth and high dry matter production (Gilbert, 2003). However, it is sensitive to frost and releases large amounts of N after frost damage (Hansen *et al*., 2000), and therefore has a limited period for growth in autumn in Swedish conditions. White mustard, oilseed radish and white radish belong to the Brassicaceae and share many common characteristics such as a deep taproot, sensitivity to frost and rapid decomposition. The roots of white radish have better ability to penetrate through dense soil than those of oilseed radish, but both crops are receiving attention for their ability to improve soil structure on compacted clay soils (Chen & Weil, 2010).

6.1.2 Greenhouse study

The eight species described above were sown in a pure sand in the greenhouse (Paper IV), at a seed rate equivalent to field practice in Sweden (≈ 500 seeds m^{-2}). The catch crops were supplied with 110 kg N and 21 kg P ha^{-1} and sufficient amounts of other necessary elements during growth. The catch crop shoots and roots were harvested separately, and the roots were collected in a 2-mm mesh by washing away the sand carefully with tap water. Both shoots and roots were sampled for determination of dry matter content and plant P content. In addition, general root morphological features, including root length, root surface area and root volume, were measured.

Figure 15. The eight experimental catch crops studied in Paper IV and one unpublished study.

To determine potential P leaching from fresh plant materials after freezing-thawing, samples of catch crop shoots and roots were exposed to four treatments, followed by water extraction of P. The treatments, where freezing took place at -18 °C and thawing at 18 °C, simulated some extreme conditions of the Nordic winter climate.

- Treatment sFTC (one single FTC with long-lasting freezing and thawing followed by repeated water extractions): representing extreme cold winter followed by one melting period.
- Treatment cFTCs (continuous FTCs, repeated water extractions after completion of FTCs): representing several deep frost events but only one final period with snowmelt/rain.
- Treatment dFTCs (discontinuous FTCs, water extraction after each FTC): representing several deep frost events, each of which is always followed by snowmelt/rain.
- Treatment without freezing.

Red clover was excluded from the FTC studies owing to its relatively low germination rate and poor biomass production. The Mixed Model for repeated measurements in the SAS programme (Version 9.2) (Littell *et al.*, 2006) was used to compare treatment effects on P concentrations in water extracts, as described in section 5.1 for the statistical method used for Papers I and II.

6.1.3 Field growth and laboratory lysimeter leaching study

The catch crops were grown on clay soils in six field experiments (during three years and two experiments in each year) at Brunnby (59°36'N 16°39'E), Linnés Hammarby (59°49'N 17°48'E) and Lanna (58°21'N 13°10'E) (Figure 8). Brunnby and Linnés Hammarby are located in the same crop production region, with 30-year (1961-1990) mean annual temperature of 5.3 °C and precipitation of 565 mm. Lanna is located in a different region, in south-west Sweden, with mean annual temperature of 6.1 °C and precipitation of 560 mm for the same 30-year period. For the experiments at the same site, different fields were used in different years to avoid the spread of disease from crops in the same family used in the previous year. These experimental fields generally had similar clay content and soil chemical properties, but the Linnés Hammarby field used in 2010/11 (Linnés H. I) had a much higher topsoil P-AL content and the Linnés Hammarby field in 2011/12 (Linnés H. II) had higher total-C and total-N contents and lower pH than the other fields (Table 2).

In all experiments, the perennial species were under-sown in spring barley (*Hordeum vulgare* L.) in May and the annual species were sown after harvest of barley in August, at seed rates equivalent to normal field practice. A randomised block design was used, with one plot (12 m x 1.5 m) of each different crop species and an additional control plot without a catch crop randomly distributed within each of four blocks. Mineral fertiliser supplying 80 kg N ha^{-1} and 20 kg P ha^{-1} was applied to barley in spring and an additional 25 kg N ha^{-1} was applied at sowing of the annual species to ensure catch crop growth. The same species were used in different years and at different sites, except that phacelia was used only in 2009/10, while red clover and white mustard were not used in that year.

To study the influence of catch crops, in particular after FTCs, on P leaching, soil lysimeters (0.25 m long, 0.188 m inner diameter) with intact catch crops were sampled in late autumn in all six field experiments. Leaching studies were carried out in two sequences, before and after the lysimeters were exposed to seven FTCs. Each FTC consisted of freezing at -18 °C for 12 hours and thawing at 18 °C for 12 hours. In each sequence, the lysimeters were irrigated with 70 mm water during 4 days, at an intensity of 10 mm hr^{-1}. Statistical differences in the P concentrations in water leachates among the treatments were tested with the Mixed Model for repeated measurements in the SAS programme (Version 9.2) (Littell *et al.*, 2006), as described in section 5.1 for the method used for Papers I and II. When the soil lysimeters were extracted, aboveground plant material and soil samples for determination of roots were also collected. Shoot samples were taken from each plot in every experiment, but the root samples (0.25 m deep) were taken only in 2010, due to the work load involved in washing the roots. The root:shoot biomass ratio and root P concentrations from this year were then used for calculating the whole-plant biomass and content of P in the other two years. Survival rates of catch crops on the soil surface were observed in the field in spring.

Table 2. *Experimental sites and years and selected physical and chemical properties of the topsoil (0-0.25 m) in the experimental fields*

Exp.	Site	Year	Clay[#] %	pH (H_2O)	Total-C %	Total-N %	P-AL[¶] mg kg^{-1}
Br-09/10	Brunnby	2009/10	44	6.3	1.7	—	41
LH-I-10/11	Linnés H. I	2010/11	44	6.4	1.9	0.18	142
LH-II-11/12	Linnés H. II	2011/12	44	5.8	6.1	0.47	50
La-09/10	Lanna	2009/10	45	6.5	2.2	0.16	34
La-10/11	Lanna	2010/11	45	6.9	—	—	39
La-11/12	Lanna	2011/12	45	6.8	—	—	42

#: Fraction <0.002 mm; ¶: P extracted with ammonium lactate (Egnér *et al.*, 1960)

6.2 Catch crops as a mitigation option for P leaching

Currently, catch crops are mainly used for mitigating N leaching and preventing soil erosion when there is otherwise no crop cover (Thomsen, 2005; Morgan, 2005). However, their use in reducing P leaching has not been intensively studied and their efficiency in this regard is not clear. In our long-term field experiment at Mellby, the perennial ryegrass catch crop did not influence P concentrations in the drainage water at all. In contrast, Wang *et al.* (2005) reported that summer cover crops reduced both N and P leaching in a subtropical area. However, their study was conducted under conditions greatly differing from the field. For example, the crops were planted in pots at triple the seed rate used in the field.

The role of catch crop P uptake in reducing P leaching has received little research attention. Phosphorus uptake by a catch crop may reduce P leaching if P is preserved in the plants during the drainage period, but may also be a source of losses if released later from the plant materials (Riddle & Bergström, 2013; Bechmann *et al.*, 2005). Moreover, roots play an important role for P uptake and dynamics, but this is also not well understood. Paper IV showed that catch crop roots differ greatly owing to the morphological properties of different species. For instance, the concentration of P in the taproots of the five taprooting species, as well as P release after freezing-thawing, increased with increasing specific root length, specific surface area and specific volume (Figure 16). The roots made up 15-70% of total-P in the catch crops on clay soils (unpublished work). Thus they certainly need to be considered in evaluation of catch crop effects on P uptake and release.

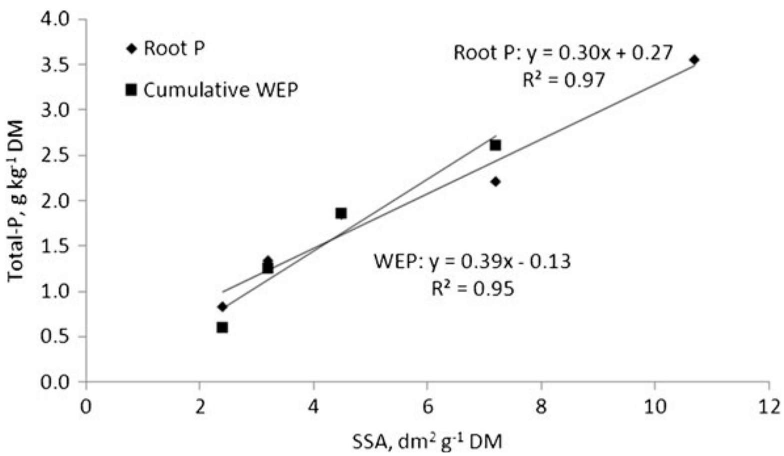

Figure 16. Correlation between concentration of total-P in the roots and specific root surface area (SSA) for the greenhouse-grown catch crops with taproots (n = 5); and between cumulative P losses after five extractions with water in the discontinuous FTCs treatment and SSA of the taproots (n = 4) (Paper IV).

In the clay topsoils with catch crops extracted from the six field experiments, mean total-P concentration in the leachate from the lysimeters before and after freezing-thawing differed significantly with experiments, and the performance of each species was not consistent among the experiments (Figure 17). Despite this, the results revealed some distinct trends. For example, chicory tended to decrease total-P concentration compared with the control in five of the six experiments, while oilseed radish tended to increase total-P concentration in five experiments. In 95 out of 140 lysimeters, the total-P concentration increased after FTCs compared with before, but great variations were found among the lysimeters (Figure 18). Freezing-thawing of both the soil and plants contributed to P losses in many cases. Ryegrass and oilseed radish were the most sensitive species to frost in terms of causing the largest increase in total-P concentrations compared with the control. As these two species are commonly grown as catch crops for N in the Nordic countries, their susceptibility to increased P losses when exposed to severe frost should be considered in the selection of catch crop species. In contrast, chicory, cocksfoot and white radish were the least sensitive crops and caused no significant increase in P concentrations after FTCs.

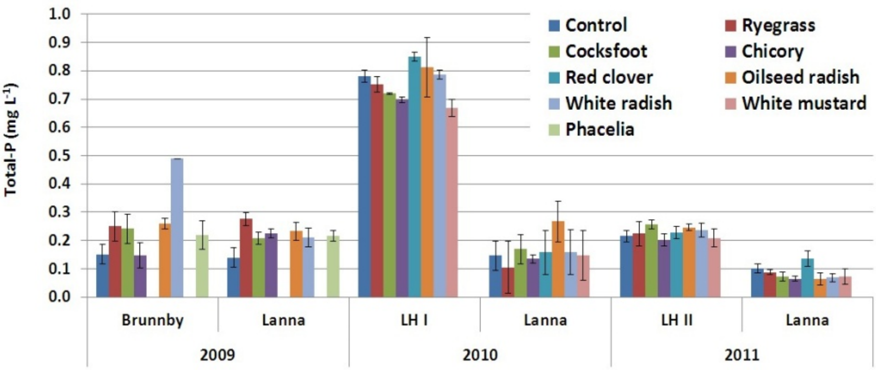

Figure 17. Concentration of total-P in the leachate from soil lysimeters with catch crops, as means of before and after FTCs, for different years and sites. Bars represent standard errors (n = 2-4). LH = Linnés Hammarby.

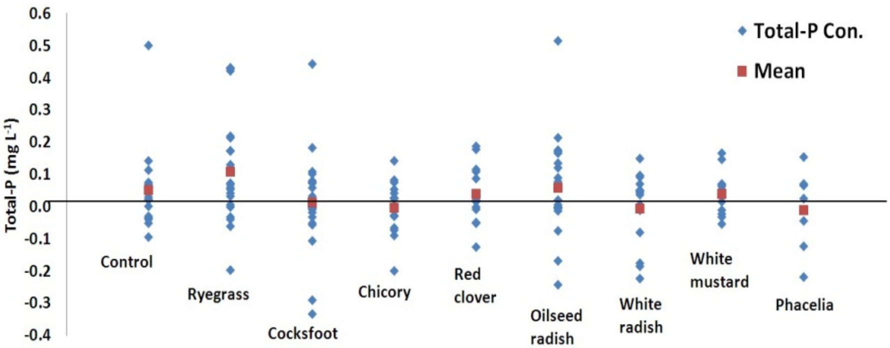

Figure 18. Net change in the concentration of total-P in the leachate from soil lysimeters after FTCs compared with before (phacelia: n = 7; the others: n = 11-20).

Overall, the concentration of total-P in leachate from the lysimeters was significantly correlated with the total-P content in the catch crop (Figure 19). However, this does not necessarily mean that the P in the leachate originated from the plants, because a similar correlation was found even before freezing-thawing of the lysimeters. It is more likely that the soils which permit good P uptake by catch crops are also susceptible to P leaching. The catch crops took up significantly more P (6-15 kg P ha^{-1}) from the soil at Linnés H. I, which had a high soil P-AL content, than from the other soils (0-6 kg P ha^{-1}), which had much lower soil P-AL. The concentration of total-P in leachate from Linnés H. I soil was also significantly higher than that from the other soils (Figure 17). These results indicate that soil P content is more important than catch crop species for overall P leaching.

In particular, the work in this thesis showed that use of catch crops for P capture under cold climate conditions needs careful consideration. Paper IV showed that all the P in the catch crop plant tissues could potentially be leached out after several severe freezing events and that the potential P release was strongly correlated to total-P concentration in the plants (Figure 20). It appears that the concentration of P in plants is more important than species differences in influencing P losses from plant materials. Paper IV also showed that perennial species released less P than annual species, with the lowest release from chicory of all species tested. However, in a lysimeter study with cut plant materials of catch crops grown in a greenhouse, Riddle and Bergström (2013) observed much higher P losses from chicory and oilseed radish than from phacelia and ryegrass. These contradictory results are most likely due to differing plant P concentration, which varies greatly with amounts of P supplied in the greenhouse. “Luxury uptake” of P, *i.e.*, uptake beyond need for balanced growth, may occur when the catch crops are supplied with large amounts of P. This part of P uptake is also likely to be easily released after exposure to FTCs. Our results also showed that release of P, especially from the plant shoots, increased with increasing number of FTCs to which catch crops were exposed, each followed by water extraction. Such repeated events seemed to cause more P release than one long freezing period. However, it should be borne in mind that under field conditions, the contribution of catch crops after frost damage to P leaching is most likely small because of sorption of P by the soil. In addition, perennial species can often survive the winter (55-76% survival rate in the present work), and thus do not lose all their P to the soil.

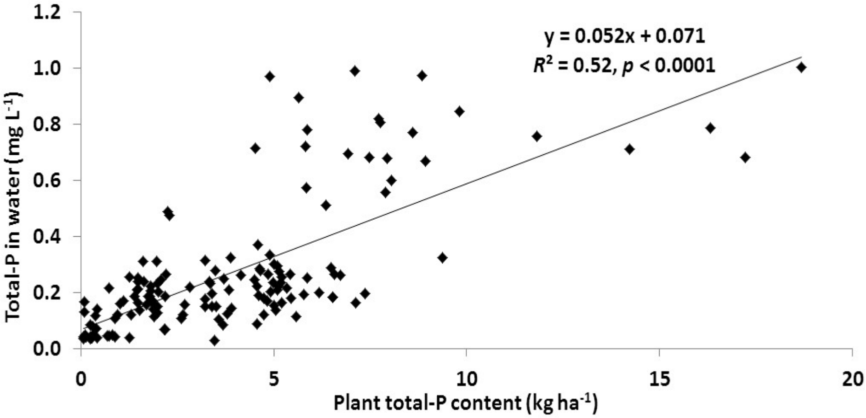

Figure 19. Correlation between concentration of total-P in the leachate from lysimeters (mean of before and after FTCs) and catch crop total-P content (n = 154).

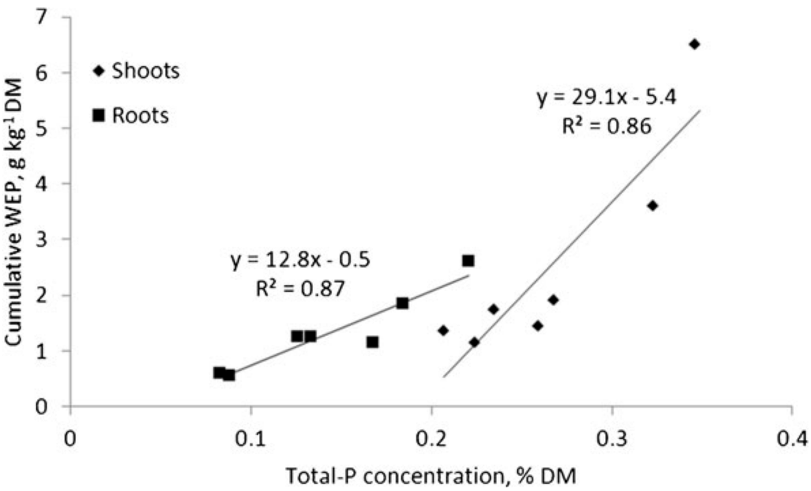

Figure 20. Correlation between cumulative P losses after five extractions with water in the discontinuous FTCs treatment and concentrations of total-P in the shoots and the roots of the greenhouse catch crops (n = 7).

7 Evaluation of the study methods

For critical evaluation of the results, it is important to understand the advantages and limitations of the methods used. For example, leaching studies carried out in indoor conditions allow excellent possibilities for comparing different treatments and for mechanism studies and such studies can be carried out rather rapidly at a relatively low cost. However, in most cases the quantitative values obtained from such studies cannot be directly translated to field conditions. In contrast, field studies can provide more realistic quantitative results based on management practices under natural conditions, but it is often difficult to understand the mechanisms underlying the effects observed. It is also very costly to run field experiments, resulting in few replicates. Moreover, technical limitations may exist in any type of study, as water bypassing tile drains in the field and exclusion of groundwater intrusion and surface runoff in lysimeters.

Results presented clearly show that laboratory studies and field studies need to be combined in order to understand the processes behind P losses and lay the foundations for developing models. Model simulations represent another type of study that can rapidly generate results, indicate soil processes and be applied at different scales. However, the updates made to these models, *e.g.*, sorption/desorption processes dominated by Fe and Al oxides (Paper III), are always later than advances in experimental research. Nevertheless, updates are very important if models are to be used as decisions support tools for mitigation programmes.

The work in this thesis demonstrated a good example of a problem that can arise in many topsoil studies, namely that the P leaching results from topsoil studies may fail to give realistic results typical of field conditions due to the critical role of the subsoil (Andersson *et al.*, 2013; Sinaj *et al.*, 2002). Improvement of the models may give the opportunity to use topsoil results instead of field measurements. More importantly, however, the work demonstrated the necessity of combining topsoil studies, which show the potential for P leaching, with field studies, which give the actual magnitude of P leaching. Our lysimeter study showed a high risk of P leaching in the Mellby topsoil, which is reasonable since large amounts of P in the form of manure have been applied to this soil over many years. Nevertheless, the actual leaching of P from this field was quite low, due to efficient sorption of P in the subsoil. Without the field study, the risk of P leaching from this soil would have been exaggerated, as also shown in the model simulations, and efforts for reducing P leaching from this soil would not be cost-effective. On the other hand, there is still a risk with additional P applications and this risk would have been overlooked without the topsoil study. Thus recommendations to farmers would be wrong to some extent if only the results from one type of study had been considered.

Other factors might also have affected the accuracy with which the laboratory studies represented field conditions. For example, the lysimeters were irrigated with tap water at a rain intensity representing worst-case scenarios, and the slurry was more thoroughly mixed with the topsoil than in the field, but at shallower depth. In one catch crop study (Paper IV), the crops were grown in the greenhouse under optimum growing conditions and were not winter-hardened before the leaching experiment. Therefore, the results from these studies were interpreted with caution.

8 Conclusions, practical recommendations and future research

In summary, the work in this thesis studied the influences on P leaching of two important Swedish agricultural practices; application of animal manure and use of catch crops. The results allowed corresponding mitigation strategies to reduce P leaching and improved manure application and catch crop management to be formulated. The main conclusions and advice to farmers are as follows:

1. Recent manure applications to clay soils with macropore flow pathways cause a high risk of P leaching. The risk can be reduced by incorporating the manure into the soil, but it will not be eliminated. Therefore, applications of P under wet conditions always constitute a risk of P leaching (Paper II).
2. Moderate rates of P (20-30 kg P ha^{-1}) in pig slurry can be applied to sandy soils that have sufficient P sorption capacity in the soil, without increasing the risk of P leaching (Paper II). However, surplus P applied over time will gradually saturate the soil sorption capacity and elevate the risk of P leaching (Paper I). Therefore, P applications to low-risk sandy soils should be at a P rate in balance with crop removal.
3. When pig slurry (50% of the P was NH_4-Cl-extractable in this study) is incorporated, it does not pose a high risk of P leaching compared with mineral P fertilisers (Papers I, II and III). Therefore, pig slurry can be applied as a substitute for mineral P fertilisers, at the same P rate.
4. Phosphorus sorption/desorption processes dominated by Fe and Al oxides are very important in regulating P mobility in many soils, and therefore descriptions of these processes should be included in P models. This includes the ICECREAM model, which is commonly

used in Sweden, *e.g.*, for calculating national P loads to the Baltic Sea in reporting to HELCOM (Paper III).

5. Effect of catch crops on reducing P leaching was not clearly demonstrated in this study. However, different species of catch crops, especially ryegrass and oilseed radish, which are commonly used for mitigating N leaching in the Nordic countries, can become sources of P losses after exposure to freezing-thawing. This should be considered when choosing catch crops to reduce nutrient losses from soil (Paper IV and unpublished work).

In future, more investigation on mitigation strategies to minimise P leaching losses is needed, especially from clay soils which often have a relatively high risk of P leaching associated with recent P applications. The complex effects of organic fertilisers, as manure, on P turnover and transport in the soil need further investigations. Catch crops are and will be important for development of sustainable cropping systems in future. To identify the species suitable for both N and P uptake and retention in the soil is one important part. The role of catch crops, in particular the roots, in influencing P leaching needs to be more investigated under the field conditions and for longer time period than the present study (at least one growing season). Moreover, development of methods for accurately assessing risk of P leaching is needed. This includes both experimental methods that can be easily and economically operated to quantify or estimate P losses and improved models that can be used for large scale applications with sufficient accuracy. For example, as was shown in this work, the role of the subsoil needs further attention, including inclusion of subsoil information in model applications. The findings obtained from this work will hopefully be valuable for improvement of simulation models used in both field and watershed scales.

9　中文摘要 (Chinese Summary)

动物厩肥施用和填闲作物种植对土壤磷素淋溶损失的影响

研究背景：氮磷等营养元素过量富积引起的水体富营养化是一个存在于全球多地区的、严重的环境问题。如美国的切萨皮克湾（Chesapeake Bay），北欧的波罗的海（Baltic Sea）和中国的太湖、巢湖和滇池等内陆湖以及沿海水域如渤海湾等近年来时有藻类大量暴发，对水体质量和渔业造成严重威胁。随着生产技术和污水治理技术的改进和成熟，来源于工业点源的氮磷排放量大大减少；相应地，农业和林业等面源污染在全部污染中所占的比例有所上升。在很多国家和地区，农业是地表水的主要氮磷污染源。磷素被公认为是内陆水域和类内陆水域（如波罗的海）富营养化的限制因素，因而近年来逐渐成为研究热点。在西方发达国家，自二战之后动物厩肥和无机肥料的大量施用导致大多数农田土壤存在磷素过量累积的问题。比如，土壤养分测定显示瑞典 50%的农田具有较高或很高的磷素水平，进而存在磷素损失的风险。大多数发达国家和一些发展中国家已经意识到农田磷素损失所引发的水环境问题，并寻求解决办法，其中包括规范农业生产和进行农业补贴等。对此，美国和欧盟相应的学术和研究网络（如 SERA-17，EU COST Action 869）分别提出了很多建议以减少磷素从农田系统中的流失。

土壤中磷素的流失是磷源、转化和运移等因素的综合结果，并最终在磷限制的水体中造成富营养化。流失类型包括通过地表径流与侵蚀损失和淋溶损失。以哪种类型为主主要由天气状况、地形和土壤特征决定。在瑞典，大多农业用地坡度都比较小，并且具有良好的天然或人工排水系统，因此，磷的淋溶是很重要的损失类型。在欧美包括瑞典，动物厩肥是农业生产中非常重要的磷源，也是农业向水体排放磷素的重要贡献者，引起了水质管理研究者的广泛关注。填闲作物是种植在两季主要作物之间的短期生长的作物。主要用于防止土壤侵蚀和减少土壤中氮素淋溶损失，但对磷素损失的效用还不清楚。相反，在北欧冬天存在冻融的情况下，作物储存在体内的磷可能会伴随由冻害引起的细胞破裂而释放出来，进而流失到水体。由于有政府的补贴，

填闲作物在瑞典和丹麦广泛种植，因此，很有必要研究其在冻融条件下可能产生的负面环境效应。

研究目标：研究在瑞典农业中，动物厩肥的短期和长期施用以及填闲作物的种植如何影响土壤磷素的淋溶损失。在此基础上，制定相应的减少磷素损失的策略。

研究方法：在厩肥项目中，应用原状土柱渗漏法（lysimeter）研究了土壤类型、厩肥施用方法和长期厩肥施用对耕层土壤中磷素淋溶的影响。此外，应用 ICECREAM 模型对磷素从施用厩肥的大田中长期淋溶的结果进行了模拟，并以此确定控制磷素淋溶的关键过程。在填闲作物项目中，研究了 8 种作物在温室和大田条件下对磷素的吸收，并分别应用温室种植和原状土柱渗漏法研究了冻融条件下磷素的损失。

主要结论：

（1） 厩肥在具有大孔隙流的粘土上的近期施用会造成较大的磷素淋溶风险。通过把厩肥混入土壤，该风险可以降低，但不会完全消除。因此，在这种土壤条件下，特别是在雨季，厩肥应该被混入土壤或免施。

（2） 中量的厩肥在具有足够吸磷能力的沙土上的施用不会造成磷素淋溶风险。因此，厩肥可以施用到这样的土壤上，但施磷量要与作物移除量平衡。

（3） 在同样施磷量的情况下，猪液体厩肥不会比无机磷肥造成更高的磷素淋溶风险。

（4） 在很多土壤中，磷素的吸附/解吸过程是由铁铝氧化物控制的。这个过程应该被包括在磷素模拟模型中，比如本论文中用到的 ICECREAM 模型。

（5） 在冻融条件下，填闲作物会成为磷素损失源，可能增加磷素向水体的损失量。因此，在存在冻融的地区种植填闲作物时要考虑到这一点。

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