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Size and dynamics of fast- and slow-desorbing phosphorus pools

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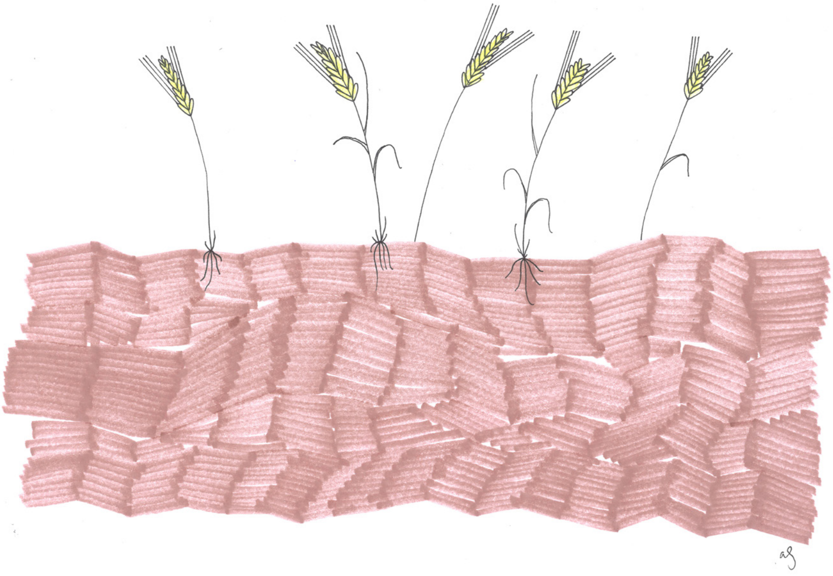

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Size and dynamics of fast- and slow-desorbing phosphorus pools

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Long-term phosphorus supply in agricultural soils: Size and dynamics of the fast- and slow-desorbing phosphorus pools

Abstract

To improve phosphorus (P) fertiliser management, a better understanding of inorganic P exchange between the soil solution and solid phase is needed. This thesis examined the dynamics of this exchange, distinguishing between pools of P that are fast- and slow-desorbing, and compared methods for quantification of these pools. This was done using soil and data from six locations in the Swedish long-term soil fertility trials. Treatments with four levels of P addition, from zero P to replacement + 30 kg P ha^{-1}, were sampled. Isotopic exchange kinetics (IEK) were used to study the dynamics and size of the isotopically exchangeable P pools. The size of the isotopically exchangeable pool at t=1 min ($E_{1\ min}$) was affected by exchangeable Ca^{2+}, while that of the $E_{1\ day} - E_{1\ min}$ and $E_{3\ months} - E_{1\ day}$ pools was affected by soil pH and Al-ox + Fe-ox. The change in P-Olsen and P-ox over time was also related to exchangeable Ca^{2+}. Phosphorus desorption kinetics were tested with iron(hydr)oxide-coated papers as an 'unlimited' sink. The P desorption values were fitted to the Lookman two-compartment model, giving information about the size and desorption rate of the fast- and slow-desorbing P pools (Q_1 and Q_2). The desorption experiments was shown to deliver similar information as the IEK, even if they assess different mechanisms.

Two extraction methods (AL and Olsen) were tested for their ability to quantify the fast-desorbing P pool, by incubation of soil with radioactive ^{33}P before extraction. This revealed that AL extraction dissolves more stable P forms, which was further proved by the relationship between P-AL and Q_1 ($r^2=0.63$) being weaker than for P-Olsen and Q_1 ($r^2=0.96$).

A positive P balance increased the amount of 'P bound to Al and Fe', and/or CaP, (according to P K-edge XANES), the desorption rate from the slow-desorbing P pool and the fraction of total P present in the fast-desorbing pool. It did not increase wheat, barley, or oat grain yield. With no P fertiliser, the extractable and exchangeable P pools decreased, but about half locations had significantly lower grain yield. This shows that the P contribution from the slow-desorbing P pool is important for plant P uptake, and that this pool can supply P for a long period. When replacement P was added, yields was not affected but P-AL and P-Olsen decreased, making 'P in balance' a possibly useful strategy to lower soil P levels without grain yield loss.

Keywords: phosphorus desorption, isotopic exchange kinetics, ^{33}P, long-term field experiments, P K-edge XANES, phosphorus balance, grain production

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Långsiktig fosfortillgång i jordbruksjordar: Storlek och dynamik av de snabbt och långsamt desorberande fosforpoolerna

Sammanfattning

För att förbättra användningen av fosfor (P) i lantbruket krävs en utökad kunskap om utbytet av oorganiskt P mellan marklösningen och den fasta fasen. Målet med detta arbete var att studera dynamiken av detta utbyte, separerat mellan pooler av P som är snabbt och långsamt tillgängliga till desorption, samt att jämföra metoder för att kvantifiera dessa pooler. Detta gjordes genom studier av jord och data från sex platser inkluderade i de svenska bördighetsförsöken. Behandlingar med fyra nivåer av P tillförsel provtogs, från noll P till ersättning + 30 kg P ha^{-1}. Isotoputbytes-kinetik (IEK) användes för att studera dynamik och storlek av de isotop-utbytbara poolerna för olika tidsperioder (E_t). Storleken av $E_{1\ min}$ var kopplad till mängden utbytbart Ca^{2+}, och $E_{1\ dag} - E_{1\ min}$ samt $E_{3\ månader} - E_{1\ dag}$ var kopplat till markens pH och innehåll av Al-ox + Fe-ox. Förändringen i P-Olsen och P-ox över tid var också relaterad till koncentrationen av utbytbart Ca^{2+}. Kinetiken för desorption av P undersöktes med hjälp av järn(hydr)oxid-täckta papper som fungerade som ”oändliga” sänkor, och desorptionen av P modellerades med Lookmans två-facks modell som ger information om storlek och desorptionshastighet för den snabba och långsamma poolen (Q_1 och Q_2). Desorptionsexperimenten visade sig leverera liknande information som IEK, trots att de utvärderar olika mekanismer.

Förmågan av de två extraktionerna AL och Olsen att kvantifiera den snabbt desorberande poolen undersöktes genom att inkubera jord med radioaktivt ^{33}P innan extraktion. Detta visade att AL metoden extraherar mer stabila P former. Vidare så var relationen mellan P-AL och Q_1 (r^2=0.63) svagare än mellan P-Olsen och Q_1 (r^2=0.96).

En positiv P balans ledde till en större mängd ”P bundet till Al och Fe” och/eller CaP (enligt P K-edge XANES), en högre desorptionshastighet from den långsamma poolen, och en större andel av total P i den snabbt desorberande poolen. Dock ledde det inte till ökade skördar av höstvete och vårkorn. Utan P-gödsel minskade de extraherbara och utbytbara poolerna i storlek, men bara hälften av platserna hade signifikant mindre medelskördar. Det visar att tillförseln av P från den långsamma poolen är viktig för växtupptaget av P, samt att den långsamma poolen kan tillföra P under en lång tidsperiod. När P återfördes efter skörd fanns ingen skördeförlust, men P-AL och P-Olsen minskade, vilket gör ”P i balans” till en möjlig strategi för att minska markens P nivåer.

Keywords: desorption, isotoputbyte, ^{33}P, långvariga försök, höstvete, vårkorn, P K-edge XANES, fosforbalanser

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Dedication

To Arvid, Henning, my parents, and my friends. I could not have done it alone.

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. Braun, S.*, Warrinnier, R., Börjesson, G., Ulén, B., Smolders, E. & Gustafsson, J.P. (2019). Assessing the ability of soil tests to estimate labile phosphorus in agricultural soils: Evidence from isotopic exchange. *Geoderma* 337, 350-358.
II. Braun, S.*, McLaren, T., Frossard, E., Tuyishime, J.R.M., Börjesson, G. & Gustafsson, J.P. (2020). Phosphorus desorption and isotope exchange kinetics in agricultural soils. *Soil Use and Management.* Accepted Author Manuscript.
III. Braun, S.*, McLaren, T., Oberson, A., Börjesson, G. & Gustafsson, J.P. Long-term cropping with and without phosphorus fertiliser: Effects on isotopic exchangeability, soil phosphorus speciation and grain yields. Manuscript.

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

* Corresponding author.

The contribution of Sabina Braun to the papers included in this thesis was as follows:

I. Planned the study together with the co-authors. Performed the experimental work together with the second author and laboratory staff. Performed the data analysis and writing, with assistance from the co-authors.

II. Planned the study together with the co-authors. Performed the experimental work with the assistance of the co-authors and laboratory staff. Performed the data analysis and writing, with assistance from the co-authors.

III. Planned the study together with the co-authors. Performed the experimental work and data collection with the assistance of the co-authors and laboratory staff. Performed the data analysis and writing, with assistance from the co-authors.

1 Introduction

World agriculture now supplies food to four times as many people as in the early 1900s, partly because of improved access to inorganic phosphorus (P) fertilisers (Roy *et al.*, 2006). However, the use and production of P fertilisers is associated with various environmental and social issues. One of the most serious environmental issues is that agriculture is a major non-point source of P in water, leading to eutrophication of freshwater and oceans, with consequences such as algae blooms and disturbance of marine ecosystems (Djodjic *et al.*, 2004; Schindler, 1977). This is due in many cases to the large amounts of P fertilisers that have been applied to Western agricultural soils during the past century, leading to build-up of soil P concentrations (Kleinman *et al.*, 2011; Sharpley *et al.*, 2013). To avoid P losses to water, Sweden and many other countries now have a long-term strategy to reach soil P levels where only the addition of sufficient P to replace what is removed by harvest is needed to maintain crop yields (Jordan-Meille *et al.*, 2012; Kvarmo *et al.*, 2019).

A long-term strategy for P fertiliser management is also needed since future access to high-quality P-rich rock for fertiliser production cannot be guaranteed. This is because the reserves are limited, but also due to political impediments to the mining of P-rich rock (Cordell *et al.*, 2009). Today, the majority of P-containing rock resources are located in only a few countries, with Morocco, the occupied Western Sahara, China and the USA together producing more than two-thirds of all inorganic P for agriculture and industry (de Ridder *et al.*, 2012). This means that food production in the European Union is dependent on P imports from outside Europe, making it vulnerable to political conflicts (de Ridder *et al.,* 2012).

These issues have led to the development of P fertiliser management strategies where regular soil P testing, sometimes combined with soil properties, is used as a base for P fertiliser application recommendations. The soil P test used varies greatly between countries, and is usually calibrated to crop responses in local long-term field experiments (Jordan-Meille *et al.*, 2012). However, when common soil P tests are applied to a large range of soils and crops, they often perform poorly in predicting crop response to P fertilisation (Nawara *et al*., 2017; Speirs *et al*., 2013). To improve fertiliser P management, a better understanding is needed of the transfer of P from solid forms to solution (where plant P uptake occurs). In addition, in order to identify when only replacement P addition is sufficient, the impact of long-term cropping with various levels of P fertiliser on the 'soil P pools' that can replenish the soil solution in the short and long term needs to be thoroughly assessed.

2 Aims and objectives

The overall aim of this thesis was to investigate the exchange of inorganic P between the soil solution and the solid phase, distinguishing between pools of P that are fast- and slowly-desorbing, and to compare different methods for quantification of these pools.

Specific objectives of the work were:

- To evaluate whether two common chemical P extractions, ammonium acetate-lactate (AL) and Olsen, can quantify the amount of P available for short-term desorption in a range of Swedish agricultural soils (Papers I and II).

- To investigate the size and dynamics of the fast- and slow-desorbing soil P pools and identify soil properties that control the dynamics of these pools (Papers II and III).

- To investigate whether changes in extractable P pools and isotopically exchangeable P pools after long-term cropping with various levels of P fertiliser are related to the P balance (added P – removed P), and whether soil properties affect the changes in these pools (Paper III).

- To investigate how long-term cropping with various levels of P fertiliser addition affects grain yield in winter wheat, spring barley, and oats (Paper III).

The work was conducted using six agricultural soils included in the Swedish long-term soil fertility experiments.

3 Background

3.1 Phosphorus in the soil-plant system

During the growing season, plant roots take up soil P in the form of orthophosphate ions from the soil solution (Pierzynski *et al.*, 2005). However, due to the low solubility of P in soils, the amount of P in solution is much lower than total plant P uptake, even in intensively fertilised soils (Pierzynski *et al.*, 2005). Therefore, the ability of a soil to replenish solution P from solid P forms is an extremely important factor for plant P uptake and for soil P concentration (Syers *et al.*, 2008).

The transfer of soil P between the solution and the solid phase is often referred to as ‘sorption’ and ‘desorption’. Sorption may involve chemisorption of P on soil surfaces, penetration of P ions into soil particles and precipitation of secondary P solid phases (Pierzynski *et al.*, 2005). Inorganic P is also added to and removed from the soil solution by microorganisms, via the immobilisation-mineralisation cycle (Condron *et al.*, 2005). These processes, and the distribution of P between the different phases, are affected by environmental factors such as temperature and precipitation, by physical and chemical properties of the soil, by management practices and by time (Goldberg & Sposito, 1984; Hedley *et al.*, 1982; Stutter *et al.*, 2015; Walker & Syers, 1976).

The physical and chemical properties of the soil affect its ability to sorb and desorb phosphorus. Anion exchange and surface complexation are both processes that take place on soil surfaces, such as aluminium (Al) and iron (Fe) (hydr)oxides and 1:1 clay minerals. A higher concentration of these types of surfaces increases the sorption capacity of the soil (Essington, 2004; Yuan & Lavkulich, 1994). Anion exchange is a simple mechanism where a weak electrostatic bond forms between P ions and variably charged soil surfaces (Essington, 2004). Surface complexation (also referred to as ligand exchange) involves a reaction between the P ion and a surface functional group

(Sparks *et al.*, 2008). Since this type of sorption is charge-dependent, chemical properties such as soil pH, redox and ionic strength will affect adsorption of P by altering surface charges.

Dissolution and precipitation of P-containing solid forms is also dependent on the soil chemistry, as well as environmental factors, and the parent material of the soil (Pierzynski *et al.,* 2005). Almost all native P in soils originates from dissolution of P-containing primary minerals, mostly various forms of apatite (Pierzynski *et al.*, 2005). During pedogenesis, these primary minerals weather, so the older the soil, the lower the contribution from primary minerals to plant P uptake (Walker & Syers, 1976). However, if the concentration of P in solution is high, as is the case after addition of water-soluble inorganic P fertiliser, P can precipitate into amorphous or crystalline secondary solid materials together with Al or Fe (Hedley & McLaughlin, 2005; Pierzynski *et al.*, 1990). These secondary solids are usually not stable over the long term and can be a source of P for plant uptake (Hedley and McLaughlin, 2005). In an alkaline soil, various forms of secondary calcium phosphates (CaP) can form if the concentration of P and Ca in solution is high enough (Bell & Black, 1970; Fixen *et al.*, 1983). However, these secondary CaP are often short-lived in soils with pH<8.5 (Hedley & McLaughlin, 2005).

As a soil ages and is subject to weathering, the partitioning of soil P between the different solid phases shifts and the relative importance of the different cycles for plant P uptake changes (Smeck, 1985). Over time, inorganic P transforms into more stable solid forms or penetrates into soil particles, making organic P a larger part of the plant-available P pool (Cross & Schlesinger, 1995; Smeck, 1985; Walker & Syers, 1976). However, the organic P that is easily utilised is quickly mineralised and more stable organic compounds accumulate, meaning that the availability for plant uptake of both inorganic and organic soil P decreases over time if no fresh P is added to the soil (Parfitt *et al.*, 1989; Smeck, 1985). In old and highly weathered soils, the availability of soil P to plants can therefore be very low, and large P additions are required to obtain acceptable crop yield (Baligar & Bennett, 1986; Smeck, 1985).

3.2 Fate of phosphorus fertiliser in soils

3.2.1 Work before 1970

Since the plant availability of P decreases with time and since P is removed by harvest, addition of P fertilisers is essential to maintain long-term soil fertility in agricultural systems (Hedley *et al.*, 1995). During the late 1800s, research in the long-term trials at Rothamsted, England, revealed that to obtain acceptable yield on a soil deficient in P, it is necessary to apply more fertiliser P than is removed by the crop (Johnston, 1970). This raised questions about the fate of the added fertiliser P that is not used by the crop, *i.e.* the ‘residual P’. After calculation of P balance and measurements of soil P concentrations in the Rothamsted trials, it was found that the increase in total P in the top nine inches (~23 cm) of soil corresponded to 80-90% of the positive P balance (Dyer, 1902). However, Dyer (1902) concluded that despite the large amount of P in the soil, it was so strongly fixed that the quantity of P actually available for plant uptake would be insufficient for the needs of the average crop.

In the early 1900s, attempts were made to measure the effect of residual P on crop yield, but using small P additions on soils deficient in P and sometimes also in other nutrients such as nitrogen (N) and potassium (K) (Syers *et al.*, 2008). This led to the conclusion that most of the residual P is irreversibly ‘fixed’ in forms unavailable for plant uptake, but the mechanisms behind this retention were not identified (Johnston & Poulton, 2019; Syers *et al.*, 2008). Much of the early work on P retention was summarised by Wild (1950), who addressed the discussion regarding the relative importance of precipitation of P-containing solids and adsorption of P on soil surfaces. Wild (1950) concluded that high retention of P is positively correlated with soil clay content and with the concentration of acid-extractable iron and aluminium, but the distinction between precipitation and adsorption remained unclear. However, based on the large amounts of P that could be immobilised, a later study suggested that the main reaction of phosphate with Al and Fe is by adsorption, since the concentration of Al and Fe in the soil solution does not seem sufficient to precipitate much P (Sample *et al.*, 1980). In calcareous soils, however, there were proof of formation of CaP after fertiliser application (Wild, 1950).

Early evidence from laboratory experiments and from thermodynamic models suggested that the P equilibrium in soil was controlled by the solubility of crystalline hydroxyapatite (Larsen, 1967). Larsen (1967) presented the hypothesis that P adsorption to surfaces is a combination of precipitation and chemisorption, with microcrystals of apatite adhering to the active surfaces of the soil, the *precipitate-particulate theory*. However, many of the early studies on retention of P by precipitation were performed in laboratories under conditions unlikely to exist in the field, with high temperatures and highly concentrated P solutions (Sample *et al.*, 1980). Sample *et al.* (1980) observed that the nature of the precipitated P compounds had been deduced mainly from indirect evidence, and not from actual isolation of reaction products in soil. Further evidence contradicting the theory that P retention is dominated by precipitation was presented by Kurtz (1953), who noted that when the same reagent was used in sequential extractions, no step-wise decrease in P solubility was found, which would be the case if soil P existed in discrete forms with various solubility.

3.2.2 Work after 1970

In the 1970s and 1980s, a new line of thinking was presented in work by Barrow, Posner and co-workers. They challenged the *precipitate-particulate theory*, where the loss of fertiliser P availability to plants over time is mainly ascribed to precipitation of discrete water-insoluble P compounds. Instead, they put forward the *adsorption-penetration theory*, where the loss is explained by penetration of P into soil particles (Barrow, 1983a; Barrow, 1983b; Posner and Barrow, 1982). This diffusion of P into particles could explain why longer incubation of a soil sample after P addition changes the P sorption/desorption behaviour (Barrow, 1983b). This process has been shown to be reversible, and thus the idea of the majority of residual P being irreversibly ‘fixed’ in soils was rejected (Barrow, 1983b).

In line with the early observations at Rothamsted, more recent studies have estimated that a crop utilises only between 5 and 35 % of added P fertiliser during the first year after application (Mattingly and Widdowson, 1958; McBeath *et al*., 2012; McLaren *et al*., 2016; McLaughlin *et al*., 1988; McLaughlin *et al*., 2011; Sharpley, 1986). However, if not lost by leaching or erosion, the residual P continues to be a source for crop uptake for many years (Barrow, 1980; Barrow, 1983b; Johnston and Poulton, 2019; McLaughlin *et al*., 1988; Syers *et al*., 2008). In both the exhaustion land experiments at Rothamsted and the Danish long-term experiment at Askov, no fertiliser P has been added for more than a century, and plants are still able to recover about 4- 6 kg P ha^{-1} yr^{-1}, supporting the theory that P retention is mostly reversible (Azeez *et al*., 2020; Johnston & Poulton, 2019).

Today, the majority of soil P is thought to be most likely retained by soil components via surface adsorption, followed by penetration into soil particles, leading to soil P existing on a ‘continuum’ of availability to desorption, and not in discrete fractions defined by solubility (Syers *et al*., 2008). However, the relative importance of the different P sorption mechanisms in soils, adsorption-diffusion and precipitation of solid P forms is still debated (Barrow, 2020; Penn & Camberato, 2019). For agronomic purposes, soil P can be divided into different ‘pools’ defined by their accessibility to desorption, extractability by chemical solutions or availability to plants during a set time scale (Frossard and Sinaj, 1997; Syers *et al*., 2008).

3.3 Phosphorus use in agriculture

Manure, human waste, crushed bones and guano (bird and bat droppings) have been collected and used to promote plant growth for at least 5000 years, but the first commercial production of P fertilisers was in 1841, by Sir James Murray (Brock, 2002; Mårald, 1998; Smil, 2000). At the start, the process for manufacturing commercial P fertiliser involved dissolving bones in sulphuric acid and mixing the liquid obtained with other amendments, such as bran and sawdust (Brock, 2002; Murray, 1841). However, soon after the opening of the first fertiliser factory by Murray, Sir John Laws started production of calcium phosphates, commonly called superphosphates, using P-rich rocks as the raw material (Brock, 2002). Soon the demand for P-rich minerals led to mining operations starting everywhere high-quality rock was found (Figure 1) (Smil, 2000; Stewart *et al*., 2005).

After the Second World War, inorganic P fertiliser became easily accessible in high-income countries, and global consumption of P skyrocketed (Cordell *et al*., 2009; Smil, 2000). In recent years, concerns have been raised about the possibility of an impending scarcity of accessible deposits of P-rich rock, and scientists have warned that the current depletion of P rock reserves cannot go on forever (Cordell *et al*., 2009; Li *et al*., 2019; Walan *et al*., 2014). However, increasing demand for animal products such as dairy and meat, a growing world population, economic growth in low- and medium-income countries and increasing demand for biofuel will possibly lead to even higher consumption of P fertiliser in future (Cordell *et al*., 2009; FAO, 2019). With declining P reserves and increasing demand, more effective use and reuse of P in agricultural systems will be essential for future food security.

Figure 1. Train loaded with phosphate rock; mine dumps and workings in background. Metlaoui, Tunisia. Photo by Dennis Jarvis, licenced under CC BY-SA 2.0.

3.4 Assessing soil phosphorus

3.4.1 Chemical extraction methods

Since the mid-1800s, it has been known that even a soil rich in total P may be poor in P available for plant uptake, and that the amount of P extracted with weak citric or carbonic acid solution is a better indicator of soil fertility than total P (Daubeny, 1845; Dyer, 1894). Since then, many different extraction methods for assessing the amount of 'plant-available P' have been developed, as well as extraction methods for assessing other soil P fractions and total P (Fixen & Grove, 1990; Moody *et al.*, 2013). Since chemical extraction methods are relatively cheap and easy, they are routinely used as a base for both P fertiliser recommendations and for leaching risk assessments (Maguire *et al.*, 2005). However, standard methods and interpretation of results both differ greatly between countries (Jordan-Meille *et al.*, 2012).

The chemical extraction methods AL (ammonium acetate and lactate) and Olsen (sodium bicarbonate) compared in this thesis are both standard tests used for estimation of the 'plant-available' P pool. However, the assumed mechanism of extraction is quite different. The acidic AL method is expected to dissolve poorly crystalline forms of Al and Fe (hydr)oxides, and to dissolve reactive CaP. The Olsen extraction is designed to displace P on surfaces by exchange with HCO_3^- and, if possible, to promote dissolution of highly soluble CaP by removing Ca^{2+} from solution by formation of $CaCO_3$ (Barrow & Shaw, 1976; Olsen, 1954). However, it is important to remember that no universal extraction for measuring plant-available P is likely to exist (Moody *et al.*, 2013).

3.4.2 Isotopic exchange kinetics

Phosphorus has one stable isotope (^{31}P) and two radioactive isotopes (^{32}P and ^{33}P) that last longer than a couple of minutes (Audi *et al.*, 2017). These radioactive isotopes have been used for decades to study the dynamics of P in the soil-plant system (Dean *et al.*, 1948; Fardeau, 1996; McAuliffe *et al.*, 1948; Wiklander, 1950). When radioactive P ions are added to a soil suspension, the amount of radioactivity in solution decreases over time due to ionic exchange. This decrease can be fitted to an isotopic exchange kinetics (IEK) model (Fardeau, 1996). The assumptions behind IEK are that: i) the added ^{33}P is such a small amount compared to resident P that the equilibrium is not affected; ii) the behaviour of the added ^{33}P is identical to that of the ^{31}P already in the suspension; and iii) the removal of ^{33}P from solution is due to homoionic exchange with ^{31}P sorbed on soil surfaces (Frossard *et al.*, 2011; Frossard &

Sinaj, 1997). The IEK method can be used to calculate the amount of isotopically exchangeable P on different time scales, known as the E value, the P turnover time and the P sorption capacity of the soil (Fardeau, 1996). For agronomic applications, the pool of exchangeable ions can be divided into different compartments (Frossard & Sinaj, 1997), as shown in Figure 2. Commonly, $E_{1\ min}$ is assumed to represent the pool of free P ions that is considered immediately available to plants, while $E_{1\ day} - E_{1\ min}$, $E_{3months} - E_{1\ day}$ and $E_{>3\ months}$ represent P pools that can replenish the pool of free ions in the short- and long-term (Frossard & Sinaj, 1997) (Figure 2).

Radioactive P can also be added directly to a soil to study plant P uptake, and the ratio of radioactive P to non-radioactive P in plant tissues is referred to as the L-value (Larsen, 1952). By comparing E and L values, plant P uptake has been shown to occur mainly from the isotopically exchangeable P pool (Frossard *et al*., 1994; Morel *et al*., 1994a).

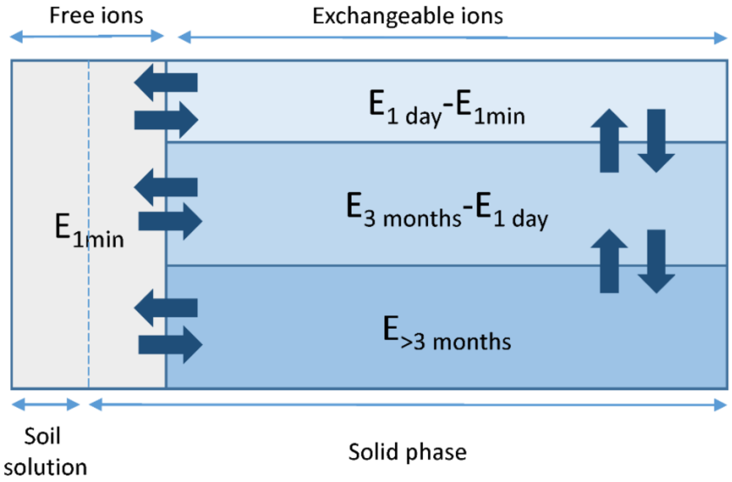

Figure 2. Schematic representation of the multi-compartmental model of isotopically exchangeable soil phosphorus (P), where E_t is isotopically exchangeable P at time *t*. Modified from Frossard & Sinaj (1997).

3.4.3 Sorption and desorption kinetics

Phosphorus sorption data can be collected by adding various levels of P to a soil suspension and measuring the concentration of P in solution after equilibration (Bache & Williams, 1971). The results can then be used to fit a sorption isotherm, commonly Freundlich or Langmuir, which will provide information about the P sorption capacity of the soil. Fitter & Sutton (1975) showed in a study of 29 soils that the best fit to the sorption data was provided by the

Freundlich isotherm, modified with the addition of a factor describing the native soil P. The P sorption capacity of a soil can also be assessed by a single-point sorption index, which has been shown to be well correlated to the P sorption capacity derived from isotherms in Swedish soils (Bache & Williams, 1971; Börling *et al.*, 2001).

Desorption kinetics can be tested in various ways, *e.g.* by lowering the concentration of P in solution by addition of water or a dilute salt solution (Sharpley *et al.*, 1981), by repeated extractions with water or a dilute salt solution, or by a ‘flow-through’ reactor where a solution is percolated though a soil column (Frossard *et al.*, 2014). Another method is to use a P sink such as anion exchange resins or membranes (Andersson *et al.*, 2016), or filter papers covered in iron (hydr)oxide (Fh papers) (Chardon *et al.*, 1996; van Rotterdam *et al.*, 2009). Phosphorus desorption in soil has been described by various empirical and mechanistic models by, among others, Sharpley *et al.* (1981), Barrow (1983a) and Lookman *et al.* (1995a)

3.4.4 Soil phosphorus forms and speciation

In order to identify and quantify the different forms of P in soil, Chang & Jackson (1957) developed a fractionation scheme where the same soil sample is repeatedly extracted with a number of chemical solutions designed to target specific P forms. The fractionation scheme by Hedley *et al.* (1982), and modified versions of it, is probably one of the most widely used systems at present. However, the ability of chemical extraction methods to target specific forms of P has been debated, and today the results are typically not believed to directly represent a specific P form or phase, but are instead referred to as fractions (*e.g.* ‘resin-P’ and ‘HCl-P’) (Condron & Newman, 2011; Hedley *et al.*, 1982). Partitioning soil P into these different fractions has been shown to be useful for approximately dating soils of unknown age and for understanding how management practices change the availability of soil P to extraction (Blake *et al.,* 2003; Walker & Syers, 1976).

Another way to assess soil P speciation is by P K-edge X-ray adsorption near edge structure (XANES) spectroscopy. In brief, the soil sample is exposed to X-ray photons over a set energy range. At the specific binding energy of the atom, absorption of photons occurs because of excitation of an inner-core electron, and when the energy is further increased the absorption decreases again. When X-ray photons are absorbed, the core electrons are excited to a higher energy state. The vacancy from the excited electron is then filled by an electron from a higher energy state, which emits characteristic fluorescence photons. By varying the energy of the incoming X-ray radiation in the energy range in which excitation occurs, an X-ray absorption spectrum is produced and can be used to identify soil P species (Kruse *et al.*, 2015). This synchrotron-based technique has the advantage of being less destructive, since it is applied directly on dry or moist soil samples. However, since many P species lack distinctive features in their absorption spectrum, it can be difficult to distinguish between them (Kruse *et al.*, 2015).

3.4.5 Validation of soil P tests

The purpose of an agronomic soil P test is not to quantify the full amount of plant-available P, but to extract a portion related to the amount of P available for plants (Tiessen & Moir, 1993). According to Tiessen & Moir (1993), a soil P test for 'plant-available' P should be simple to perform routinely, easily measurable, extract a significant proportion of potential plant uptake and not extract significant amounts of P unavailable to plant uptake during the growing season. However, without knowledge of the crop response related to the soil levels of P, the soil P test is close to meaningless for crop production purposes (Beegle, 2005). The calibration of a soil P test should preferably be done for the same crop and under the same conditions as in the field where the test is to be used (Heckman *et al.*, 2006).

In many studies, soil P tests have been compared against each other to assess the capacity of these tests to predict crop response (Bationo *et al.,* 1991; Nawara *et al.*, 2017; Neyroud & Lischer, 2003; Wuenscher *et al.*, 2016). These studies have confirmed that that amount of P extracted differs with the extraction method. However, they also show that many methods are well correlated with one another. Attempts have been made to find formulae to recalculate the results from one soil test to another, either in order to compare data or because of a change in standard method (do Horta *et al.*, 2010; Lončarić *et al.*, 2006; Otabbong *et al.*, 2009). However, the relationships found between P tests in previous studies rarely hold when tested on other types of soils.

Soil tests can also be validated using isotopic methods. Plants grown in soil with a small amount of ^{32}P or ^{33}P added should have the same amount of radioactivity per mg of P, *i.e.* specific activity (SA), in the plant biomass as the SA in the soil extract if the extraction only targets plant-available P (Mason *et al.*, 2013; Six *et al.*, 2012). Soil P test values can also be compared with the amount of isotopically exchangeable P at different time scales, the E value, which has been shown to represent plant available P (Aigner *et al.*, 2002; Frossard & Sinaj, 2006). This means that both the quantity of P and the amount of stable P extracted by the soil test can be investigated with isotopic methods.

3.4.6 Phosphorus fertiliser recommendations

The intensive use of P fertilisers during recent decades has led to enrichment of P in arable topsoils (Eriksson *et al.*, 2010; Kleinman *et al.*, 2011; Sattari *et al.*, 2012). This 'legacy soil P' is now posing a threat to aquatic ecosystems, since P loss from arable soils rich in P is the main contributor to eutrophication of streams, lakes and oceans (Djodjic *et al.*, 2004; Kleinman *et al.*, 2011; Schindler, 1977). Therefore, finding ways to utilise this legacy P and to decrease soil P concentrations without compromising crop yields is an important part of future P management (Andersen *et al.*, 2017; Haygarth *et al.*, 2014; Sattari *et al.*, 2012; Sharpley *et al.*, 2013). Today, most European countries have guidelines and recommendations regarding P fertiliser addition (Jordan-Meille *et al.*, 2012). These recommendations are usually based on a chemical extraction of soil P, but both the measurement method and the interpretation of the results vary greatly between countries (Jordan-Meille *et al.*, 2012).

The Swedish P fertiliser recommendations are based on extraction of the topsoil (0-20 cm) with ammonium acetate-lactate (AL), which should be analysed every 10 years. The soil is then allocated to one of six different classes according to P level, and the appropriate P fertiliser addition is calculated from the soil P class, the requirement of the crop and the expected yield (Kvarmo *et al.*, 2019). However, the Swedish P fertiliser recommendations acknowledge that the acidic AL extraction can overestimate the plant-available P pool in soils with pH >7. For soils with high pH, it is suggested that a lower P class be used. The recommendations also suggest use of the alkaline Olsen extraction (sodium bicarbonate) method on these soils, but since research is lacking there are currently no official Swedish recommendations based on Olsen extraction. In addition, the effects of soil properties or management strategies on the transfer of P from solid phase to solution in Swedish soils are not sufficiently well documented to be incorporated in the recommendations, and the significance of more stable P forms (not extractable with AL) for plant P uptake is unclear. Future P fertiliser recommendations should possibly consider both the size of the 'available' pool and the rates of transport between the solid phase and solution, for a more accurate assessment of the 'plant-available P pool' (McLaren *et al.*, 2014; Tiessen & Moir, 1993).

4 Materials and methods

4.1 Sites, sampling and soil characteristics

4.1.1 The Swedish long-term soil fertility experiments

The increase in inorganic fertiliser use during the mid-1900s, together with a dramatic rise in cropping systems with no livestock, raised concerns in Sweden about the long-term impacts on soil fertility and productivity (Carlgren & Mattsson, 2001). To address these issues, 12 long-term soil fertility trials were started in Sweden between 1957 and 1966, of which nine are still in operation. Five trials each were located in southern and central Sweden and two in the north, with all locations chosen to represent a characteristic Swedish soil type. Half of the sites were placed on land considered to be of good agronomic quality, and the other half on land considered to be of poor quality (Carlgren & Mattsson, 2001).

For each region (south, central, north), two crop rotations deemed typical for the area were defined, one for a dairy farm and one for a farm without livestock. In the ‘dairy farm’ rotation, manure and inorganic fertiliser are used and the straw is removed. The ‘no livestock’ rotation receives only mineral fertiliser and the straw is left in the field after harvest. Both crop rotations are subjected to four different levels of PK fertiliser and four levels of N fertiliser, amounting to a total of 16 treatments, with duplicates. Data on yield, crop nutrient content and crop-specific measures have been collected almost every year since establishment of the trials. Soil pH and soil P and K content have been assessed regularly and dry soil samples have been archived.

4.1.2 Sites and treatments

In the work presented in this thesis, soil samples and data were collected from four treatments (A3, B3, C3, and D3) in the long-term trials at six different locations in Sweden (Figure 3). The selected treatments were from the 'no livestock' rotation and included all four levels of PK fertiliser addition and the highest N fertiliser level (see Table 1). Before establishment of the field trials, all of the locations except Kungsängen were used for crop production and had received inorganic fertiliser and/or manure for at least 100 years. The Kungsängen site was used for grazing until 1907 and then cultivated. All sites except Kungsängen are tile-drained and subjected to annual ploughing, with ploughing depth varying between 20 and 25 cm. Detailed site descriptions can be found in Kirchmann (1991), Kirchmann *et al.* (1999) and Kirchmann *et al.* (2005). A short summary is presented below and in Table 2.

Fjärdingslöv (south)

The experimental site at Fjärdingslöv is located in a slight depression in a flat landscape, with the bedrock consisting of limestone and with soil depth varying between 5 and 20 m. The soil parent material is silty to sandy unsorted glacial sediment consisting of limestone, preCambrian rocks, shales and sandstone. Before the start of the experiments, this site had been cultivated for more than 150 years, but did not receive any large amounts of manure. The site had mean annual precipitation of 660 mm and mean temperature of 7.5 °C during the period 1951-1980. This site is considered favourable for crop production. Fjärdingslöv was limed in 1981 with 2 t ha^{-1} CaO and in 2014 with 2.7 t ha^{-1} CaO.

Ekebo (south)

This site is located on a flat plain and the bedrock consists of sediments from the Upper Trias. The soil parent material is Quaternary deposits of clayey unsorted glacial sediments, to a depth of about 15 m. During 1951-1980, mean annual precipitation was higher than at Fjärdingslöv, 800 mm. Mean annual temperature during this period was 7.4 °C. Ekebo was originally a heath and the soil organic carbon content at this site is still higher than at other sites in the Swedish long-term trials. Despite this, the Ekebo soil is considered unfavourable for cropping. Long ago this site was used for grazing and it was repeatedly burned. However, the site was used for cropping for more than 100 years before the start of the trials. The site was limed in 1981 and 1996, with 1 t ha^{-1} CaO each time, and in 2014 with 2.7 t ha^{-1} CaO.

Högåsa (central)
The Högåsa experimental site is located on a slightly sloping plane, with a bedrock of Ordovician shales and a soil parent material of sandy glacial outwash. The site was cultivated for at least 200 years before the experiments started, and received moderate amounts of cattle manure until 1955. The site is considered poor farmland. Mean annual precipitation during the period 1961-1990 was on average 517 mm and mean annual temperature was 6.1 °C. Snow cover is usually 40-80 days per year.

Vreta Kloster (central)
The site at Vreta Kloster is located on a flat plain, with the soil parent material consisting of glaciofluvial deposits of varved clay. During the 200 years before the start of the experiments, the site was cultivated and received small amounts of cattle manure until 1955. This site is considered to be good farmland. The climate and bedrock are the same as for Högåsa.

Kungsängen (central)
The Kungsängen soil was formed from postglacial sediments (gyttja clay) deposited by nearby rivers, and it has pH<5.5 in the subsoil. The soil is well-structured, with no need for drainage. Mean annual precipitation in the period 1951-1980 was 660 mm. The Kungsängen site was used for grazing until 1907, and thereafter used for grass/clover and cereal production. This site is considered good farmland.

Fors (central)
The soil parent material at Fors is glacial silt deposits together with calcareous material originating from the Bothnian Sea. Mean annual precipitation 1951-1980 was 720 mm. Before the start of the experiments, Fors was used for cereal production and received large amounts of animal manure. This site produces high grain yields, but is considered to be poorer farmland than Kungsängen.

Table 1. *Levels of phosphorus (P),potassium (K) and nitrogen (N) fertiliser applied per year and hectare in the four treatments(A3, B3, C3, D3) in the Swedish long-term soil fertility trials sampled and studied in this thesis. The N level is the average for the rotation, as the amount of N applied each year varies with the crop*

	A3	B3	C3	D3
P	0	Replacement	Replacement + 15 kg (south) Replacement + 20 kg (central)	Replacement + 30 kg (south and central)
K	0	Replacement	Replacement + 40 kg (south) Replacement + 50 kg (central)	Replacement + 80 kg (south and central)
N	150 kg (south) 125 kg (central)	150 kg (south) 125 kg (central)	150 kg (south) 125 kg (central)	150 kg (south) 125 kg (central)

Figure 3. Approximate location of the six sites in the Swedish long-term soil fertility trials studied in this thesis.

4.1.3 Soil sampling and characterisation

Soil samples were taken twice, in autumn 2015 for Paper I and in autumn 2017 for Papers II and III. For each plot, 10 subsamples were taken with a soil corer (Ø = ~2 cm) from the middle of the plot. The 10 subsamples were then pooled into one bulk sample. The final sample was air-dried for a week at room temperature, crushed with a wooden pestle and sieved to <2 mm. Selected soil properties, as means of all treatments, are shown in Table 2. For additional soil properties and differences between treatments, see Table 2 in Paper III. The soil K-AL classification in 2015 was reported to be below class III (indicating K limitation) for Högåsa A3 and B3, Ekebo A3 and Fjärdingslöv A3, B3 and C3.

Table 2. *Selected soil properties in topsoil (0-20 cm) at the six sites in the Swedish long-term soil fertility trials studied in this thesis. Al-ox and Fe-ox is aluminium and iron extracted with oxalate, see Table 3 for method.*

Site	FAO soil order†	Texture class‡	pH$_W$‡	Bulk density†	C-org‡	Al-ox‡	Fe-ox‡
				kg m^{-3}	*g kg*$^{-1}$	*mmol kg*$^{-1}$	
Fjärdingslöv	Haplic Phaeozem	Sandy loam	7.3	1660	13	33	32
Ekebo	Haplic Phaeozem	Loam	7.1	1430	24	81	40
Högåsa	Arenic Umbrisol	Sandy loam	6.5	1380	20	79	56
Vreta Kloster	Haplic Phaeozem	Silty clay	7.0	1440	19	71	34
Kungsängen	Gleyic Cambisol	Silty clay	6.6	1310	21	62	170
Fors	Calcaric Phaeozem	Silt loam	7.6	1490	17	33	31

†From Kirchmann *et al.* (1999); Kirchmann *et al.* (2005); Kirchmann (1991).
‡Average for all treatments included in this work, sampled autumn 2017.

4.2 Soil surface phosphorus balance

In Papers II and III, the soil surface P mass balance was calculated from the year when the experiment was established in its current form (1961 for Ekebo and Fjärdingslöv, 1963 for Kungsängen and Fors, and 1966 for Vreta Kloster and Högåsa). The fluxes included were:

P soil surface balance = P from fertiliser + P from atmospheric deposition – P in harvest (eq. 1)

In Paper II, P from atmospheric deposition was assumed to be zero. For the P balance in Paper III, the estimated input flux of P from atmospheric deposition was included and estimated to be 0.16 kg P ha^{-1} yr^{-1} (Karlsson & Pihl Karlsson, 2018). The significance of atmospheric deposition is low in Sweden, amounting to only 8-9 kg P ha^{-1} during the full duration of the field experiments. For more details about the P balance calculations, see Paper III.

The amount of residual P in the C3 and D3 treatments was calculated as:

Residual P= Total P (treatment) − Total P (B3) (eq. 2)

4.3 Chemical extractions

To investigate the change in extractable soil P pools in the top 0-20 cm of the soils over time, Olsen extractable P (P-Olsen) and oxalate extractable P (P-ox) were determined for archived soil samples from the start of the experiments, and in samples from 2017. For assessing the change in P-AL, data collected during the course of the field experiments were used. The bulk density valued given in Table 2 were then used to calculate the change in kg P ha^{-1}, to enable comparisons with the surface P balances. Chemical extractions was performed as described in Table 3. All extracts were filtered (0.2 µm) before analysis. The degree of P saturation was calculated on a molar basis according to Lookman *et al.* (1995b).

Table 3. *Chemical extraction methods used in this thesis*

Extraction	Liquid:solid ratio	Duration of extraction	Analytical method	Reference
MilliQ water	10	16 h	ICP-MS	Demaria *et al.* (2005)
$CaCl_2$ (0.005 mol L^{-1})	10	2 h	ICP-MS	Houba *et al.* (2000)
Olsen (0.5 mol L^{-1} $NaHCO_3$, pH 8.5)	20	0.5 h	Colorimetric	Olsen (1954)
AL (0.01 mol L^{-1} acid ammonium lactate and 0.4 mol L^{-1}acetic acid, pH 3.75)	20	4 h	ICP-MS	Egnér *et al.* (1960)
Oxalate (0.2 mol L^{-1} oxalate buffer, pH 3.0)	100	4 h	ICP-OES	van Reeuwijk (1995)
Total inorganic P	50	16 h	Malachite green	Walker and Adams (1958)
Total P, extraction with H_2SO_4 after combustion	50	16 h	Malachite green	Walker and Adams (1958)

4.4 Isotopic methods

4.4.1 Relative specific activity

Soil samples were mixed with $^{33}PO_4$ radionuclide solution (half-life ~25 days) and incubated in darkness for one week. After incubation, the P in samples were extracted by water, $CaCl_2$, Olsen, AL or ammonium oxalate (Table 3), to investigate the recovery of ^{33}P in different extracts. For additional experimental details, see Paper I. The specific activity (SA) was calculated as $^{33}P/^{31}P$ (Fardeau *et al.*, 1988). As the SA of $CaCl_2$ was assumed to be equal to the SA that would occur in the soil solution (Fardeau *et al.*, 1988; Six *et al.*, 2012), the relative SA of the extracts was calculated as:

$$\text{Relative SA} = (SA_{extract}/SA_{CaCl_2})\times 100 \qquad \text{(eq. 3)}$$

4.4.2 Isotopic exchange kinetics

To investigate the size and dynamics of the exchangeable P pool, isotopic exchange kinetics experiments were performed. These experiments were performed twice, with some differences in the method. In Paper I, 10 g of soil were mixed with 99 mL 5 mmol L^{-1} $CaCl_2$, equilibrated for 16 h in an end-over-end shaker and then placed on a magnetic stirring plate. To each container, 1 mL carrier-free $^{33}PO_4$ solution containing approximately 0.1 MBq was added. The agitated soil suspensions were sampled at 10 min, 100 min, 24 h and 6 days after addition of the radiotracer. In Papers II and III, ultrapure water was used instead of $CaCl_2$, and sampling was performed at 1, 4, 10, 30, 60 and 90 min after addition of the $^{33}PO_4$ solution. Removal of radioactivity from solution over time by ionic exchange can be modelled as described by Fardeau (1996):

$$\frac{r(t)}{R} = m \cdot \left\{t + m^{1/n}\right\}^{-n} + \frac{r(\infty)}{R} \qquad \text{(eq. 4)}$$

$$\frac{r(\infty)}{R} = \frac{P_w}{P-inorg} \qquad \text{(eq. 5)}$$

where *R* is the amount of radioactivity added (MBq), *r(t)* is the amount of radioactivity in solution at time *t* (MBq), *m* and *n* are fitted parameters, *r(∞)* is the radioactivity remaining in solution at infinity ignoring decay (MBq), P_w is water-extractable P (mg P kg^{-1} soil) and *P-inorg* is P extractable with 0.5 mol L^{-1} H_2SO_4 (mg P kg^{-1} soil).

The amount of isotopically exchangeable P at time *t* is calculated as (Frossard & Sinaj, 1997):

$$E(t) = 10 * C_p * \frac{R}{r(t)} \qquad \text{(eq. 6)}$$

where C_P is the amount of P in solution (mg P L^{-1}) and 10 is the liquid to solid ratio.

The fraction of free P ions ($E_{1\ min}$) derived from residual fertiliser, $E_{1\ min,rf}$, and the fraction of residual P found in the $E_{1\ min}$ pool were calculated according to Lemming *et al.* (2019):

$$E_{1\ min,rf} = \left(1 - \frac{E_{1\ min}(B3)}{E_{1\ min}(\text{treatment})}\right) * 100\ \% \qquad \text{(eq. 7)}$$

$$\text{Recovery of residual P as } E_{1\ min} = \frac{\frac{E_{1\ min,rf}}{100} * E_{1\ min}}{\text{Residual P}}\ x100 \qquad \text{(eq. 8)}$$

where $E_{1\ min}$ and residual P were re-calculated to kg P ha^{-1} using the bulk density values in Table 2.

4.5 Desorption experiment

Desorption of P in the presence of an ‘infinite’ sink was studied using iron (hydr)oxide-coated filter papers (Fh papers, where Fh stands for ferrihydrite, the most likely phase forming on the filters). The papers were prepared according to van Rotterdam *et al.* (2009). Two papers with a total active area of 40 cm^2 were placed in a nylon bag and immersed in a soil suspension consisting of 4 g soil and 40 mL 0.005 mol L^{-1} $CaCl_2$ solution. The papers were removed and fresh papers were placed in the tubes after 2, 4, 8, 26, 48, 78, 145, 221 and 316 hours of shaking time, counted from the start of the experiment. After removal, the papers were rinsed with water, submerged in 40 mL of 0.1 mol L^{-1} H_2SO_4 solution and shaken for 1 h to dissolve all P. The desorption kinetics were described using two discrete pools according to Lookman *et al.* (1995a):

$$\mathrm{Q_{des}}(t) = \mathrm{Q_1}(1 - e^{-k_1 t}) + \mathrm{Q_2}(1 - e^{-k_2 t}) \qquad \text{(eq. 5)}$$

$$\mathrm{Q_1+Q_2=P\text{-}ox} \qquad \text{(eq. 6)}$$

where Q_1 and Q_2 are the amounts of fast- and slow-desorbing P (mg P kg^{-1} air dried soil), respectively, k_1 is the rate of desorption of P per hour from Q_1, and k_2 is the rate of desorption of P per hour from Q_2. The sum of Q_1 and Q_2 was set equal to the amount of P extracted by ammonium oxalate, P-ox (Lookman *et al.*, 1995).

4.6 Phosphorus K-edge XANES spectroscopy

All P K-edge XANES spectroscopic measurements, including collection of standard spectra, were carried out at BL-8 of the Synchrotron Light Research Institute (SLRI), Nakhon Ratchasima, Thailand (Klysubun *et al.*, 2012). Details of sample collection and preparation can be found in Paper III. Data treatment, including merging, normalisation of sample scans and linear combination fitting (LCF) analysis, was carried out in Athena, version 0.9.025 (Ravel & Newville, 2005). Subsequent uncertainty analysis of the LCF weights in Paper III was conducted as described by Gustafsson *et al.* (2020).

4.7 Statistics

Statistical tests and data analysis were carried out with Microsoft Excel or R (R Core Team, 2016). Details about the tests applied are given in the respective paper. Parameter fitting in Paper II was done with R for the IEK and with PEST (Doherty, 2010) for the desorption model. The regression analysis in Paper II was performed by calculation of Pearson's correlation coefficient r, and the two-sided t-test was used to check if r was significantly different from zero.

The IEK experiments in Papers II and III were not duplicated, due to time constraints. However, one soil sample from each location was tested in triplicate to assess the variation between replicates, including an internal soil standard, which revealed minor differences. The standard deviation for C_P ranged between 2 and 13 %, while the standard deviation for r(1)/R ranged between 2 and 4 % (Table S2 in Paper III).

Only one sample per treatment was analysed with P K-edge XANES spectroscopy. Therefore the data cannot be used to infer statistically significant differences in P speciation between treatments, although they can serve as an indicator of likely treatment effects. Chemical extractions, desorption experiments and the isotopic experiments in Paper I were all carried out in duplicate.

5 Results

5.1 Isotopic experiments

5.1.1 Recovery of ^{33}P by chemical extraction (Paper I)

After incubation with ^{33}P, soil samples were extracted with five different solutions to assess their ability to recover ^{33}P, and their ability to extract primarily isotopically exchangeable P. The amount of recovered ^{33}P in the extracts was in the order $CaCl_2$<water<Olsen<AL<oxalate, and the recovery of ^{33}P was always greater for the fertilised samples than for the unfertilised samples from the same location. For the fertilised samples, the oxalate extraction recovered close to 100% of the added ^{33}P, but for the unfertilised samples recovery was between 60 and 92%. The fraction of radioactivity recovered by AL and Olsen showed a significant ($p<0.05$) positive linear relationship with the degree of P saturation.

In the Olsen extracts, the SA relative to SA_{CaCl2} ranged between 54 and 223%, with an average of 103% (Table 4). The relative SA was lower in the AL extracts, ranging between 9 and 40%, with an average of 29% (Table 4). Values of relative SA <100% indicate that the method extracted non-isotopically exchangeable P. Values >100% were probably due to errors in the ^{31}P measurement.

Table 4. *Relative specific activity (SA) of ^{33}P in the Olsen and AL extracts for the unfertilised treatments (A3) and for the treatments receiving replacement P + 30 kg P year^{-1} ha^{-1} (D3) at the six sites in the Swedish long-term soil fertility trials studied in this thesis*

		Relative SA			
Site	Treatment	Olsen		AL	
		Mean	*St. Dev.*	*Mean*	*St. Dev.*
Ekebo	A3	125.1	4.9	32.1	1.9
	D3	71.2	11.1	23.7	1.7
Fjärdingslöv	A3	169.3	18.0	29.9	3.6
	D3	79.4	7.2	28.6	0.7
Vreta Kloster	A3	223.2	70.2	15.8	4.9
	D3	84.6	8.9	38.2	1.9
Högåsa	A3	96.5	2.3	39.7	16.0
	D3	53.8	0.9	28.3	1.9
Kungsängen	A3	108.1	1.7	32.9	15.0
	D3	68.1	3.7	47.1	5.2
Fors	A3	84.1	3.3	9.0	4.7
	D3	69.3	7.3	25.2	0.4
All soils		103.2	49.1	29.2	10.3

Relative SA=(SA(extract) / SA($CaCl_2$))×100, St. Dev.=standard deviation of field replicates.

5.1.2 Isotope exchange kinetics (Papers II and III)

To assess the kinetics of P ionic exchange, the removal of added radioactivity from the solution as a function of time was measured in the soil suspensions, and the results were used to fit the IEK model described by equation 2. The values for the parameter n, which describes the rate of exchange at t=1 min, were significantly lower for the D3 treatment than for the unfertilised A3 treatment ($p<0.05$). For the parameter m, describing the proportion of radioactivity remaining in solution after t=1 min, the opposite trend was found, with significantly higher values in treatment D3 compared with A3. The IEK parameter values for all treatments and locations can be found in Table 6 in Paper III.

5.1.3 Amount of isotopically exchangeable P (Papers II and III)

In previous studies, the majority of plant P uptake has been shown to occur from isotopically exchangeable P forms (Frossard *et al.*, 1994). Therefore, the size of the $E_{1\ min}$, $E_{1\ day} - E_{1\ min}$ and $E_{3\ months} - E_{1\ day}$ pools in the different treatments was used to obtain information about the availability of soil P for potential short- and long-term plant uptake.

The size of the $E_{1\ min}$, $E_{1\ day} - E_{1\ min}$ and $E_{3\ months} - E_{1\ day}$ pools decreased with a negative P balance and increased with a positive P balance (Table 5). The relationship between pool size and P balance was stronger for the $E_{1\ min}$ and $E_{1\ day} - E_{1\ min}$ pools ($r^2=0.58$ and 0.61; $p<0.001$) than for the $E_{3\ months} - E_{1\ day}$ pool ($r^2= 0.13$, $p<0.05$). There were also large differences between sites regarding the effects of P balance on the size of the exchangeable pools. For example, at Högåsa, $E_{1\ min}$ ranged from 1.2 (A3) to 8.8 (D3) mg P kg^{-1}, while at Vreta Kloster $E_{1\ min}$ ranged from 1.6 (A3) to 60.9 (D3) mg P kg^{-1}. The size of the $E_{1\ day} - E_{1\ min}$ and $E_{3\ months} - E_{1\ day}$ pools at Fors was relatively small for all treatments, indicating low long-term availability of P for exchange.

The size of the exchangeable P pools was related to different extractable fractions. A strong relationship was found between $E_{1\ min}$ and P-$CaCl_2$ (exponential, $r^2=0.94$, $p<0.001$), which was not surprising since both methods aim to estimate the pool of free P ions. The size of the $E_{1\ day} - E_{1\ min}$ pool was related to P-Olsen (exponential, $r^2=0.71$, $p<0.001$), and the $E_{3\ months} - E_{1\ day}$ pool was weakly related to P-ox (linear, $r^2=0.29$, $p<0.01$). However, when other soil properties were added in multiple linear regression modelling, a combination of P-Olsen and other predictors gave the highest R^2 values for all E pools.

In attempts to model the $E_{1\ min}$ value by multiple regression, the highest R^2 value was obtained by combining P-Olsen and the concentration of exchangeable calcium ($R^2=0.96$, $p<0.001$), followed by the single regression model including P-$CaCl_2$ mentioned above. A higher amount of exchangeable Ca^{2+} was related to a larger $E_{1\ min}$ pool at a given P-Olsen value, perhaps because a higher concentration of calcium increases the net charge of soil particles and promotes P adsorption. For the $E_{1\ day} - E_{1\ min}$ pool, a model including P-Olsen and soil pH as predictors gave the highest R^2-value ($R^2=0.89$, $p<0.001$), closely followed by P-Olsen combined with the sum of oxalate-extractable Al and Fe ($R^2=0.88$, $p<0.001$). The same predictors, pH and Al-ox + Fe-ox, also gave the two highest R^2 values when modelling the $E_{3\ months} - E_{1\ day}$ pool ($R^2=0.75$ and 0.76, respectively, $p<0.001$). At a given P-Olsen level, both of these pools were larger at lower pH values and at a higher amount of Al-ox + Fe-ox. Soil pH and the amount of Al and Fe(hydr)oxides are both properties related to P sorption capacity, which can explain the effect of these properties on the exchangeable P pools. In all models, the data were log-transformed to get approximately normally distributed data. For R^2 and *p*-values for all models tested, see Table S5 and S6 in Paper III.

The values for $E_{1\ min,rf}$, the percentage of $E_{1\ min}$ derived from residual P (fertiliser P that has been retained in the top 0-20 cm of the soil), were usually higher in the D3 treatment compared with the C3 treatment, but at Högåsa and Fors the value for $E_{1\ min,rf}$ was similar for C3 and D3 (Table 5). No significant relationship was found between $E_{1\ min,rf}$ and the P balance, but there was an inverse linear relationship between $E_{1\ min,rf}$ and the P-Olsen/P-$CaCl_2$ ratio (r^2=0.63, p<0.01) and a positive linear relationship between $E_{1\ min,rf}$ and exchangeable Ca^{2+} (r^2=0.47, p<0.05). The percentage of residual fertiliser P that could be found in the $E_{1\ min}$ pool was similar for treatments C3 and D3 at the same location. The percentage of residual fertiliser P also showed no relationship with the P balance. However, as for $E_{1\ min,rf}$ there was an inverse relationship between the fraction of residual P in $E_{1\ min}$ and the P-Olsen/P-$CaCl_2$ ratio (exponential, r^2=0.84, p<0.001) and a positive relationship with exchangeable Ca^{2+} (exponential, r^2=0.51, p<0.01). This means that a soil with a larger percentage of residual P present in E_{1min}, such as Vreta Kloster and Fors, also had a larger fraction of the fast-desorbing P pool in the solution phase. This indicates that the P-Olsen/P-$CaCl_2$ ratio can be used to estimate the availability of residual P for short-term desorption.

Table 5. *The different compartments of isotopically exchangeable phosphorus (P), the fraction of* $E_{1\,min}$ *originating from residual fertiliser and the fraction of residual P found in the* $E_{1\,min}$ *pool at the six sites in the Swedish long-term soil fertility trials studied in this thesis. Residual P, meaning the amount of fertiliser P left in the top 0-20 cm layer of the soil, is calculated as total P(treatment) − total P(B3)*

		E_{1min}	$E_{1day} - E_{1min}$	$E_{3months} - E_{1day}$	$E_{1min,\ rf}$	% of residual P in E_{1min}
			mg P kg^{-1}			
Fjärdingslöv	A3	1.9 (0.3)	17.1 (1.4)	48.5 (8.9)	-	-
	B3	6.1 (0.2)	31.6 (1.4)	61.5 (6.1)	-	-
	C3	12.6 (1.6)	63.7 (28.4)	114.4 (54.7)	52 %	6 %
	D3	31.6 (5.7)	70.4 (7.4)	98 (20.4)	81 %	10 %
Ekebo	A3	2.6 (0.6)	26.6 (4.3)	79 (10.8)	-	-
	B3	6.2 (0.4)	66.3 (16.2)	150.9 (34.1)	-	-
	C3	11.1 (0.4)	72.0 (4.8)	161.1 (9.4)	44 %	3 %
	D3	16.9 (3.4)	106.4 (0.4)	235.6 (28.2)	63 %	3 %
Högåsa	A3	1.2 (0.5)	45.9 (6.4)	181.7 (1.3)	-	-
	B3	3.2 (0.7)	42.2 (0.3)	131 (2.5)	-	-
	C3	10.2 (0.8)	62.7 (4.0)	133.1 (11.4)	69 %	4 %
	D3	8.8 (0.1)	66.2 (11.7)	153.6 (40.1)	64 %	3 %
Vreta Kloster	A3	1.6 (0.5)	14.1 (3.9)	45.3 (11.1)	-	-
	B3	4.9 (1.0)	32.0 (0.1)	82.8 (11.9)	-	-
	C3	36.2 (10.3)	92.1 (20.4)	134.9 (24.6)	87 %	15 %
	D3	60.9 (1.5)	102.6 (3.7)	128.5 (5.2)	92 %	14 %
Kungsängen	A3	2.0 (0.4)	34.4 (0.4)	152.9 (21.4)	-	-
	B3	4.7 (1.6)	50.2 (13.5)	164.9 (32.3)	-	-
	C3	19.8 (1.3)	102.5 (0.9)	214.7 (6.4)	76 %	7 %
	D3	24.3 (8.8)	105.6 (18.9)	205.6 (14.7)	81 %	7 %
Fors	A3	1.8 (0.7)	9.7 (1.0)	30.8 (2.1)	-	-
	B3	7.1 (3.4)	20.1 (1.0)	35.2 (6.8)	-	-
	C3	29.0 (1.0)	41.7 (5.4)	49.9 (8.0)	75 %	15 %
	D3	29.8 (7.7)	44.8 (6.1)	55.0 (4.1)	76 %	15 %

5.2 Desorption experiments (Paper III)

The ability of the soils to desorb P in the presence of an ‘infinite’ sink was studied for a period of 20 days, and the results were used to fit the two-compartment model of Lookman *et al.* (1995a). In all six soils, the total amount of P removed by Fh papers during the desorption experiments (P-Fh) exceeded P-Olsen, but was smaller than P-AL. However, P-Olsen showed a very strong linear relationship ($r^2=0.96$) with the pool of fast-desorbing P (Q_1) (Figure 4a). These pools were also similar in size, with the values of P-Olsen ranging between 0.5 and 1.6 times Q_1. The relationship between Q_1 and P-AL was also significant ($r^2=0.63$) (Figure 4b), and the value for P-AL ranged between 2.1 to 24.1 times Q_1.

The desorption rate k_1 for the fast-desorbing pool was consistently much higher than the desorption rate k_2 for the slow-desorbing pool. In addition, k_1 was positively related to the C-org/(Al-ox + Fe-ox) ratio (linear, $r^2=0.72$, $p<0.001$), and negatively related to Al-ox + Fe-ox (exponential, $r^2=0.64$, $p<0.01$). This means that a soil with a larger amount of Al-ox and Fe-ox had a slower rate of desorption from the fast-desorbing P pool. However, the positive effect of a higher C-org/(Al-ox + Fe-ox) ratio indicates that competition from organic acids for the Al and Fe (hydr)oxide binding sites increased the P desorption rate from the fast pool. There was also a negative relationship between k_1 and the P-Olsen/P-$CaCl_2$ ratio (exponential, $r^2=0.67$, $p<0.01$), showing that a larger fraction of P in solution was connected to faster desorption rates. The desorption rate of the slow-desorbing pool (k_2) was related to the net mass P balance (linear, $r^2=0.86$, $p<0.001$), and inversely related to the ratio of P-ox to P-Olsen (linear, $r^2=0.91$, $p<0.001$).

There were significant relationships between the parameters of the Lookman model and the parameters of the IEK model. The fast-desorbing P pool, Q_1, displayed positive exponential relationships with both E_{1min} ($r^2=0.87$, $p<0.001$) and $E_{1\,day}$-$E_{1\,min}$ ($r^2=0.75$, $p<0.001$). The slow-desorbing P pool (Q_2) was significantly related to the $E_{1\,day} - E_{1\,min}$ and $E_{3\,months} - E_{1day}$ pools ($r^2=0.65$ and 0.57, $p<0.01$). There were also relationships between the rates of mass transfer, with both k_1 and k_2 showing a negative linear relationship to the IEK parameter *n*.

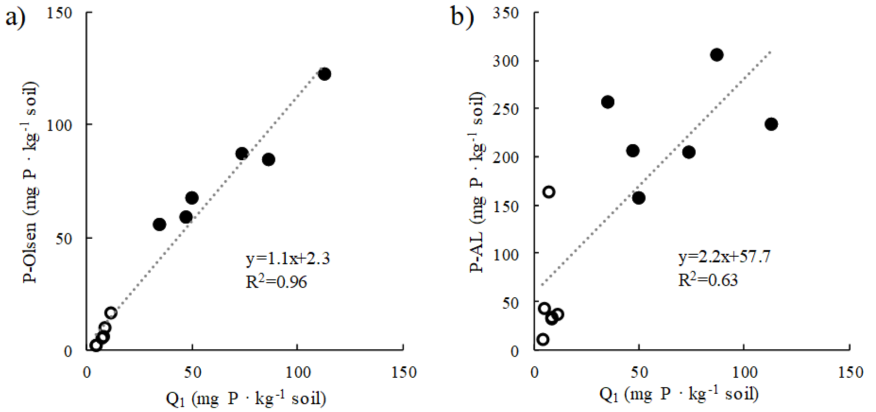

Figure 4. Amount of readily desorbable phosphorus, Q_1, derived from the Lookman model, versus a) P-Olsen and b) P-AL. Filled circles represent treatments that received phosphorus (P) fertiliser (D3), unfilled circles represent treatments with no P fertiliser (A3).

5.3 Changes in extractable P pools over time (Paper III)

Long-term cropping with various levels of P fertiliser addition has led to different concentrations of P-$CaCl_2$, P-Olsen, P-AL, P-ox and total P in the top 0-20 cm in the different treatments within locations (Table 6). In the unfertilised treatments, the P-Olsen, P-AL and P-ox values decreased between the start of the field experiments and 2017 at all locations (Table 7). Relative to the values at the beginning of the experiment, the decline was greatest in P-Olsen, for which the 2017 values were 13-47% of the start values. In relative terms, the change in P-ox was the smallest, with the 2017 values being 74-93% of the start values. In the mass P balance displayed in Table 7, the removal of P by harvest in the A3 plots always exceeded the decrease in P-ox over time, showing P uptake from more stable P forms and/or from the subsoil.

In the B3 treatment, P-Olsen, P-AL and P-ox also decreased at almost all locations. The only exceptions were observed at Kungsängen B3, where P-ox increased, and at Vreta Kloster B3, where P-AL increased slightly. As seen for the unfertilised plots, the change relative to the start values was largest for P-Olsen and smallest for P-ox. In 2017, all B3 plots except at Högåsa were still in P-AL class III or higher, where a P replacement strategy is recommended (Kvarmo, 2019). There is no Swedish P application guidelines based on the P-Olsen value, but according to the Danish guidelines all B3 plots except at Ekebo would be considered low in P (P-Olsen<20 mg P kg^{-1} soil) (Jordan-Meille *et al.*, 2012).

In the plots receiving more P than was removed by harvest (treatments C3 and D3), P-Olsen, P-AL and P-ox increased at all locations, with a larger increase in D3 than in C3. In the D3 treatment, the largest increase in P-Olsen and P-AL relative to the start value was found at Vreta Kloster, and the largest relative increase in P-ox at Fjärdingslöv. For all three extractions, the smallest relative increase was found at Ekebo. The increase in P-ox in the D3 treatment corresponds to 30-53% of the P balance, showing that some of the added excess P had been transformed to more stable forms, transferred to the subsoil or lost by leaching or erosion.

For P-Olsen, P-AL and P-ox, the change over time showed a significant ($p<0.05$) positive linear relationship with the soil surface P balance, with the strongest relationship observed concerning the change in P-ox ($r^2=0.94$, $p<0.001$) (Figure 5). Inclusion of exchangeable Ca^{2+} together with the P balance in a multiple linear regression model gave moderately higher R^2 values for both the model describing the change in P-Olsen ($R^2=0.83$, $p<0.05$) and for the model describing the change in P-ox ($R^2=0.95$, $p<0.01$). A higher concentration of Ca^{2+} gave a larger change in P-Olsen and P-ox at a given P balance.

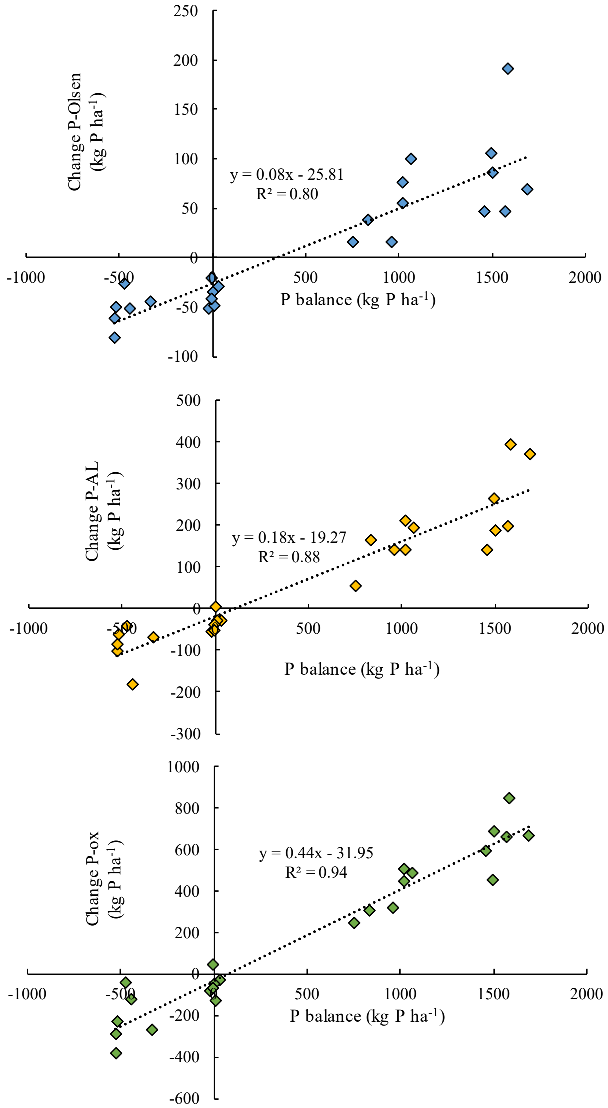

Figure 5. Change in P-Olsen, P-AL and P-ox plotted against the soil surface phosphorus (P) balance.

Table 6. *Soil concentration of extractable phosphorus (P) at the start and in 2017 at the six sites in the Swedish long-term soil fertility trials studied in this thesis. Standard deviation in brackets. See Table 1 for explanation of treatments A3, B3, C3 and D3. P-CaCl$_2$ is P extracted with CaCl$_2$, P-Olsen is P extracted with the Olsen method, P-AL is P extracted with ammonium acetate lactate, P-ox is P extracted with oxalate buffer. See Table 3 for extraction methods.*

Location		P-CaCl$_2$ 2017	P-Olsen start	P-Olsen 2017	P-AL start	P-AL 2017	P-ox start	P-ox 2017	P-inorg† 2017	P-org‡ 2017	Total P§ 2017
		mg P kg^{-1} air-dried soil									
Ekebo	A3	0.16 (0.05)	30.7 (4.7)	9.4 (1.1)	63 (1)	27 (1)	518 (68)	385 (13)	212 (48)	383 (3)	595 (51)
	B3	0.51 (0.06)	40.3 (3.9)	22.2 (1.3)	76 (6)	57 (5)	532 (28)	505 (25)	232 (13)	463 (10)	696 (23)
	C3	1.48 (0.03)	39.4 (3.4)	44.9 (1.9)	88 (11)	107 (2)	549 (3)	636 (61)	448 (20)	405 (25)	853 (45)
	D3	2.87 (1.22)	52.1 (4.0)	68.7 (2.6)	124 (20)	194 (23)	553 (17)	784 (66)	638 (52)	378 (14)	1015 (38)
Fjärdingslöv	A3	0.16 (0.04)	15.5 (4.3)	7.3 (0.5)	35 (8)	22 (3)	197 (4)	184 (24)	145 (9)	199 (16)	344 (26)
	B3	0.39 (0.13)	21.8 (4.9)	12.9 (0.5)	48 (10)	39 (0)	221 (1)	213 (26)	167 (23)	222 (17)	389 (39)
	C3	2.01 (0.46)	24.0 (5.7)	35.7 (2.6)	57 (21)	106 (12)	227 (23)	320 (9)	282 (20)	213 (21)	496 (1)
	D3	12.32 (9.12)	41.9 (5.8)	62.7 (1.5)	74 (14)	185 (10)	246 (7)	447 (20)	447 (3)	210 (25)	657 (22)
Vreta Kloster	A3	0.08 (0.03)	20.5 (0.7)	3.2 (0.2)	46 (4)	24 (9)	433 (14)	355 (20)	309 (28)	351 (41)	660 (13)
	B3	0.39 (0.29)	22.6 (1.3)	10.7 (2.9)	46 (8)	47 (9)	422 (16)	405 (24)	411 (93)	313 (98)	724 (5)
	C3	7.61 (2.87)	29.0 (1.4)	63.8 (17.4)	57 (28)	124 (27)	437 (12)	606 (95)	614 (85)	325 (21)	939 (64.)
	D3	15.73 (5.08)	35.3 (3.0)	102 (9.5)	47 (5)	184 (20)	458 (45)	752 (7)	761 (27)	360 (21)	1121 (6.)
Högåsa	A3	0.06 (0.07)	23.5 (5.6)	7.3 (3.6)	43 (16)	18 (8)	469 (55)	372 (77)	233 (105)	286 (33)	520 (72)
	B3	0.45 (0.18)	32.0 (4.8)	14.2 (0.7)	45 (2)	35 (2)	510 (3)	464 (2)	271 (52)	361 (31)	632 (21)
	C3	1.79 (1.01)	33.6 (4.2)	39.2 (6.2)	39 (17)	90 (14)	507 (13)	623 (93)	474 (140)	319 (66)	793 (73)
	D3	2.31 (0.55)	29.3 (1.6)	46.1 (2.6)	56 (1)	107 (5)	411 (26)	626 (36)	526 (37)	284 (6)	810 (43)
Kungsängen	A3	0.09 (0.08)	35.3 (11.5)	4.5 (0.5)	51 (15)	19 (0)	624 (21)	514 (17)	462 (21)	301 (5)	763 (16)
	B3	0.38 (0.19)	32.1 (4.0)	16.0 (6.3)	49 (7)	34 (7)	625 (24)	642 (89)	571 (35)	287 (21)	858 (13)
	C3	3.28 (0.33)	30.9 (0.5)	52.0 (2.3)	49 (7)	102 (16)	620 (32)	813 (48)	788 (76)	292 (15)	1080 (60)
	D3	5.32 (2.47)	31.0 (1.0)	63.7 (7.1)	48 (5)	119 (7)	595 (37)	857 (31)	843 (76)	293 (9)	1136 (67)
Fors	A3	0.29 (0.02)	21.5 (3.4)	4.2 (1.1)	138 (78)	76 (35)	517 (64)	476 (42)	680 (64)	346 (13)	1026 (77)
	B3	2.26 (0.81)	22.3 (2.0)	15.4 (4.4)	135 (30)	117 (31)	528 (40)	505 (34)	812 (72)	248 (36)	1060 (35)
	C3	14.84 (4.94)	26.0 (4.1)	51.5 (9.8)	110 (59)	180 (16)	452 (79)	602 (46)	980 (76)	226 (39)	1206 (37)
	D3	14.28 (4.02)	25.1 (2.8)	60.8 (10.5)	105 (52)	194 (57)	459 (77)	611 (105)	925 (76)	288 (6)	1214 (82)

†Extraction with 0.5 mol L^{-1} H$_2$SO$_4$.

‡Total P minus P-inorg.

§Extraction with 0.5 mol·L^{-1} H$_2$SO$_4$ after combustion.

Table 7. *Soil surface phosphorus (P) balance (kg P ha^{-1}), residual P (kg P ha^{-1}), change in P-Olsen, P-Al and P-ox, and P-Olsen (kg P ha^{-1}), P-Al and P-ox as a percentage of the start value at the six sites in the Swedish long-term soil fertility trials studied in this thesis. Atmospheric deposition was estimated to be 0.16 kg P ha^{-1} yr^{-1}, residual P was calculated as total P(treatment) – total P(B3). See Table 1 for explanation of A3, B3, C3 and D3.*

Location		Fertiliser P	Atm. dep.	Harvested P	P balance	Residual P	Change P-Olsen	Change P-AL	Change P-ox	P-Olsen 2017	P-AL 2017	P-ox 2017
		kg P ha^{-1}								% of start value		
Fjärdingslöv	A3	0	9	482	−473	-	−27	-42	−45	47%	52%	93%
1961-2017	B3	896	"	874	31	-	−29	-30	−27	60%	92%	96%
	C3	1811	"	984	836	353	39	164	308	149%	187%	141%
	D3	2685	"	1004	1690	888	69	369	666	150%	260%	181%
Ekebo	A3	0	9	535	−526	-	−61	-103	−380	31%	29%	74%
1961-2017	B3	615	"	645	−21	-	−52	-54	−79	55%	63%	95%
	C3	1594	"	847	757	449	16	56	247	114%	120%	116%
	D3	2529	"	970	1568	914	47	199	660	132%	157%	142%
Högåsa	A3	0	8	335	−327	-	−45	-69	−269	31%	29%	79%
1966-2017	B3	512	"	509	10	-	−49	-28	−126	44%	66%	91%
	C3	1552	"	596	964	445	16	142	319	117%	226%	123%
	D3	2140	"	687	1461	491	46	142	594	157%	193%	152%
Vreta Kloster	A3	0	8	526	−518	-	−50	-61	−226	15%	46%	82%
1966-2017	B3	710	"	715	3	-	−34	3	−49	47%	97%	96%
	C3	1870	"	815	1062	618	100	193	488	220%	220%	139%
	D3	2388	"	810	1586	1141	191	395	846	288%	409%	164%
Kungsängen	A3	0	9	530	−521	-	−81	-84	−288	13%	33%	82%
1963-2017	B3	653	"	669	−7	-	−42	-39	44	50%	63%	103%
	C3	1741	"	731	1019	582	55	140	506	168%	210%	131%
	D3	2241	"	744	1506	728	86	188	685	205%	250%	144%
Fors	A3	0	9	453	−444	-	−52	-183	−121	19%	60%	92%
1963-2017	B3	680	"	694	−4	-	−20	-51	−68	69%	95%	96%
	C3	1751	"	742	1018	435	76	210	447	199%	187%	133%
	D3	2280	"	794	1494	458	106	265	455	242%	210%	133%

5.4 Phosphorus mass balance (Paper III)

Assuming that the total P concentration in B3 has remained relatively stable over the years, the difference in total P between A3 and B3 can provide information on how much of P removed by harvest derived from the top 0-20 cm of the soil. In the unfertilised plots at Ekebo and Kungsängen, the difference in total P corresponded to about half (48-55%) of the negative P balance. At Fors, Fjärdingslöv and Vreta Kloster, the difference in total P corresponded to only 23-36%, while at Högåsa it corresponded to 95% of the negative P balance. This suggests that a significant part of plant P uptake could have occurred from deeper soil layers, with the exception of Högåsa.

The residual P in the C3 and D3 treatments corresponded to between 31 and 72% of the positive balance, with the lowest fraction of fertiliser P retained at Fors D3 and the highest at Vreta Kloster D3 (Table 7). The amount of residual P (equation 9) in the soil was positively correlated to the P balance, but only about half of the variation could be explained by P balance alone ($r^2=0.53$, $p<0.01$). None of the soil properties measured in this thesis was related to the amount of residual P. Regarding the fraction of the positive P balance retained in the soil, no relationship with soil properties could be found.

5.5 Phosphorus speciation (Paper III)

The soil P speciation in the 2017 samples was assessed by linear combination fitting of XANES spectra (Figure 6). For five of the six soils, long-term P fertiliser addition increased the amount of P bound to Fe and Al. At Fjärdingslöv, a large increase in calcium phosphates (CaP) was detected, while a small increase in CaP was found at Vreta Kloster and Fors.

According to both the XANES results and the results obtained using the Walker and Adams (1958) method (Table 6), the amount of organic P in the soils has not changed much as a result of fertilisation. However, the amounts of organic P were consistently higher when estimated by the Walker and Adams (1958)method compared with the XANES results, although the two methods were significantly linearly related ($r^2=0.45$, $p<0.001$). Moreover, the amount of organic P in the XANES results for the Kungsängen plots was unrealistically low compared with values reported by Ahlgren *et al.* (2013) and Eriksson *et al.* (2016). This was possibly because of an E_0 calibration error during sample collection. When the Kungsängen soils were removed from the regression analysis, the relationship between XANES and Walker-Adams organic P was stronger ($r^2=0.61$).

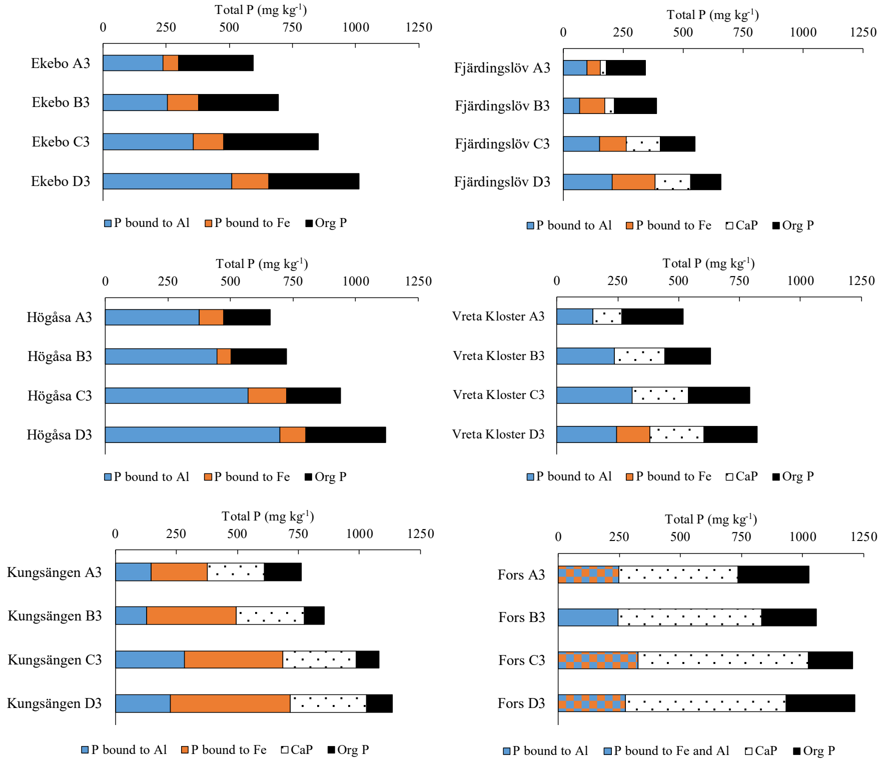

Figure 6. Phosphorus speciation in 2017 according to linear combination fitting of K-edge XANES spectra for the six sites in the Swedish long-term soil fertility trials studied in this thesis. See Table 1 for explanation about treatment levels A3, B3, C3, and D3.

5.6 Wheat, barley and oat grain yield (Paper III)

Grain yields of wheat, barley, and oats varied greatly between years in response to temperature, rainfall, and pests. However, for most of the years the grain yield in D3, the treatment with the highest level of NPK addition, is close to or higher than the regional average for the year for all locations. This indicates that no site specific factors were limiting production. However, the crop response to the various levels of P and K fertiliser addition over time varied between locations.

Winter wheat and spring barley were part of the crop rotation at all locations, and oats were part of the crop rotation at the central sites (Högåsa, Vreta Kloster, Kungsängen, and Fors). Significant ($p<0.05$) changes in winter wheat grain yield over the 50-60 years of the field trials were found only at Ekebo, Fjärdingslöv and Fors. At Ekebo and Fjärdingslöv, wheat yield increased over time in all treatments, including in the unfertilised A3. At Fors, was there a significant decrease in wheat yield over time in treatment A3. However, the average winter wheat yield level in A3 was always lower than the average yield in B3, and the difference was significant (p<0.05) at three of the six locations (Högåsa, Kungsängen and Fors) (Table 8). Only Högåsa showed a significant difference in average wheat yield between the B3 and D3, and between C3 and D3.

Over the course of the field trials, spring barley grain yields increased significantly (p<0.05) at Fjärdingslöv (C3 and D3) and Kungsängen (C3 and D3). Barley yield declined significantly over time in the A3 treatment at Fors, and the average barley yield was significantly lower in A3 compared with B3 at Fjärdingslöv, Högåsa and Fors. The average barley grain yield in the B3 treatment was not significantly lower than in C3 at any site. Högåsa was also the only location with a significant difference between B3 and D3 (Table 8).

Only Vreta Kloster had a significant increase in oat grain yield over time, in all treatments, and only Fors had a significant decline in oat yield over time in the A3 treatment. At all locations the average oat yield were lower in A3, but Högåsa alone had a significant (p<0.05) difference between A3 and B3 (Table 8). Like for wheat and barley, Högåsa was the only location with a significant difference in average oat yield between B3 and D3.

Table 8. Average yields of winter wheat, spring barley, and oats (kg ha^{-1}, 15% water content) calculated from yield data from all years when the crop was cultivated, and yield levels in the unfertilised treatment (A3) and the P-fertilised treatments (C3, D3) relative to the replacement treatment (B3=100%) at the six sites in the Swedish long-term soil fertility trials studied in this thesis. Different letters denote a significant (p<0.05) difference between treatments at the same location. See table 1 for explanation about treatment levels A3, B3, C3, and D3.

		Wheat yield (kg ha^{-1})	Relative yield	Barley yield (kg ha^{-1})	Relative yield	Oat yield (kg ha^{-1})	Relative yield
Fjärdingslöv	A3	5788a	86%	4142a	76%	n/a	n/a
	B3	6702a	100%	5437b	100%	n/a	n/a
	C3	6735a	100%	5665b	104%	n/a	n/a
	D3	6628a	99%	5624b	103%	n/a	n/a
Ekebo	A3	5279a	97%	4071a	90%	n/a	n/a
	B3	5416a	100%	4509ab	100%	n/a	n/a
	C3	5596a	103%	4919b	109%	n/a	n/a
	D3	5431a	100%	4709ab	104%	n/a	n/a
Högåsa	A3	2733a	70%	2879a	75%	2662a	78%
	B3	3890b	100%	3838b	100%	3414b	100%
	C3	4238b	109%	4423bc	115%	3386b	99%
	D3	4949c	127%	4783c	125%	4373c	128%
Vreta Kloster	A3	5474a	91%	4297a	93%	4214a	95%
	B3	5996ab	100%	4623a	100%	4428a	100%
	C3	6193b	103%	4751a	103%	4557a	103%
	D3	6123ab	102%	4471a	97%	4440a	100%
Kungsängen	A3	5182a	87%	3561a	89%	3911a	89%
	B3	5952b	100%	3988a	100%	4407a	100%
	C3	6125b	103%	4011a	101%	4507a	102%
	D3	6140b	103%	4049a	102%	4313a	98%
Fors	A3	4372a	75%	3045a	81%	3105a	77%
	B3	5849b	100%	3762b	100%	4009ab	100%
	C3	5678b	97%	3834b	102%	4375b	109%
	D3	5783b	99%	3830b	102%	4295b	107%

6 Discussion

6.1 Ability of AL and Olsen to quantify fast-desorbing phosphorus

The Olsen method was shown to be superior to the AL method for assessing the amount of soil P available for short-term desorption. This can be concluded from: i) the low relative specific activity (SA) in the AL extract; and ii) the strong linear relationship and the similarity in size between P-Olsen and the fast-desorbing pool Q_1.

When a soil suspension is in steady-state, the soil solution P is in equilibrium with the fast-desorbing P pool (consisting of P in direct contact with the soil solution). When radioactive ^{33}P is added to the soil suspension, it will be removed from solution by ionic exchange with the fast-desorbing P pool (Fardeau, 1996). This means that the fast-desorbing P pool will have the same SA ($^{33}P/^{31}P$) as the soil solution. In this work, the SA in the $CaCl_2$ extract was used as a proxy for SA in the soil solution. If an extraction has similar SA to $CaCl_2$, it can be assumed to extract mainly from the fast-desorbing P pool. If SA is lower than $CaCl_2$, the extraction can be assumed to extract more stable P forms. The latter was the case for the AL extraction, which had an average relative SA of 29%, showing dissolution of more stable P forms.

The size of the fast-desorbing P pool was estimated by the Q_1 parameter in the Lookman *et al.* (1995a) model. In comparison with P-Olsen, which had a close to 1:1 relation with Q_1, the relationship between P-AL and the fast-desorbing pool was weak. There was also a strong relationship between P-Olsen and $E_{1\ day} - E_{1\ min}$, further confirming that Olsen extraction is suitable for assessing the fast-desorbing pool.

The high P-AL values obtained for the calcareous Fors site indicate that some of the extracted 'stable' P originates from dissolution of CaP with low plant availability. However, both Högåsa and Ekebo had no CaP according to the

XANES analysis, but still showed dissolution of non-exchangeable P species in the AL extract according to the relative SA. This non-exchangeable P could be P that has penetrated deeper into particles, more stable forms of Al-P or Fe-P solid phases, or organic P forms. The AL extraction process is known to perform poorly for calcareous soils (Eriksson *et al.*, 2013; Zbíral, 2000), but the results in this thesis show that the amount of fast-desorbing soil P can also be overestimated by the AL method for non-calcareous soils.

6.2 Dynamics of the fast-desorbing phosphorus pool

The Olsen test seems to be a good estimate of the size of the readily desorbing P pool, but by itself it gives little information about the rate of transfer of P to solution. However, both $E_{1\ \mathrm{min,\ rf}}$ and the fraction of residual P in the pool of free ions, $E_{1\ \mathrm{min}}$, were strongly correlated with the P-Olsen/P-$CaCl_2$ ratio. This ratio also displayed a strong relationship with the desorption rate for the fast-desorbing P pool Q_1. It appears that the distribution of the fast-desorbing P pool between the soil solution and the solid phase is closely connected to the availability of the fast-desorbing P pool to desorption, and to the availability of the residual P. This is in agreement with Fick's law, according to which the diffusion rate is proportional to the dissolved P concentration.

One of the soil properties with the largest influence on the dynamics of the fast-desorbing P pool was exchangeable Ca^{2+}, which increased the size of the $E_{1\ \mathrm{min}}$ pool at a given P-Olsen level. Surface complexation of Ca^{2+} to Fe and Al (hydr)oxides facilitates adsorption of the negatively charged PO_4^{3-} ions, by increasing the surface net charge (Barrow *et al.*, 1980; Rietra *et al.*, 2001). Another soil property identified as important for the dynamics of the fast-desorbing P pool was the C-org/(Al-ox + Fe-ox) ratio, which was positively related to the desorption rate from the Q_1 pool (k_1). This ratio considers the competition from organic acids on the binding sites on Al and Fe hydr(oxides), with a larger ratio indicating higher competition, which would lead to more P in solution. The k_1 values were also inversely related to Al-ox + Fe-ox, which was shown by Börling *et al.* (2001) to be important for the P-sorbing capacity of Swedish soils. It is likely that a higher concentration of Al-ox + Fe-ox is associated with less P in the soil solution and a slower rate of desorption from the fast-desorbing pool.

6.3 Size of the slow-desorbing phosphorus pool

The size of the slow-desorbing P pool depends on the time scale of interest, since all soil P could be considered available for desorption in an infinite time frame. In the desorption model by Lookman *et al.* (1995), the size of the fast- and slow-desorbing pools together was set equal to P-ox. This means that the value of Q_2 is arbitrary, and would be significantly higher if *e.g.* total P were used instead of P-ox as the upper limit. However, over the period of the long-term field experiments, the difference in P-ox between treatments corresponded well with the difference in total P between treatments ($r^2=0.98$, $p<0.001$). This indicates that the majority of plant P uptake in the topsoil occurred from oxalate-extractable P forms, and that P-ox is an appropriate upper limit for the Lookman model in this time frame.

The size of the slowly exchanging P pool was also assessed by IEK. The difference in the $E_{3\ \mathrm{month}} - E_{1\ \mathrm{day}}$ pool relative to B3 corresponded to only a small fraction of the negative and positive P balance, and the relationship between the size of this pool and the P balance was very weak. The size of this pool was clearly controlled by factors other than the P balance. This was further supported by multiple regression modelling, according to which a lower pH and a higher concentration of Al-ox + Fe-ox were both found to increase the size of the $E_{3\ \mathrm{month}} - E_{1\ \mathrm{day}}$ pool and the $E_{1\ \mathrm{day}} - E_{1\ \mathrm{min}}$ pool at a given P-Olsen value. One possible explanation for this is that lower pH makes variable-charged surfaces more positive, which increases sorption of added fertiliser P (Devau *et al.*, 2011; Essington, 2004; Morel *et al.*, 1994b; Sen Tran *et al.*, 1988).

6.4 Dynamics of the slow-desorbing phosphorus pool

In the compartmental concept of soil P availability described by Frossard and Sinaj (1997) (Figure 2), the different compartments are in equilibrium with each other. When the equilibrium is disturbed by plant P uptake from the soil solution, the pool of free ions is partly or fully replenished from the fast- and slow-desorbing P pools, and the fast-desorbing P pool is partly or fully replenished by the slow-desorbing pool. Therefore, the transfer rate of P between the fast- and slow-desorbing pools, and to the soil solution, is a very important factor for long-term plant P uptake, and for the size of the pools.

Chemical extraction alone does not provide any information on the rate of transfer between the fast- and slow-desorbing P pools, or on the transfer between the slow-desorbing pool and the soil solution. However, the rate of desorption from the slow-desorbing P pool, k_2, was strongly related to the P-Olsen/P-ox ratio and to the P balance. This shows that a long-term positive P balance will not only increase the size of the slow-desorbing pool, but also increase the rate of desorption from this pool.

This can be explained by the decrease in the net charge of the adsorbing soil particles that results from diffusive penetration of P ions into the particle, lowering the ability of the soil to adsorb added P (Barrow & Debnath, 2014; Barrow, 1983b; Barrow, 2015). After long-term addition of high amounts of fertiliser P, the sorption by net diffusive penetration of P into particles declines (Barrow & Debnath, 2014). Therefore, a soil with a history of high P fertiliser addition is more likely to have a larger fraction of soil P in solution and to release P quickly. This suggestion is supported by the higher recovery of the added ^{33}P in the fertilised soils in this thesis.

6.5 Relationship between IEK and desorption

The Fh paper method and the IEK method are both minimally invasive and address the kinetics soil P transfer to solution. However, the Fh paper method assesses the P desorption kinetics and the IEK method the P exchange kinetics. Despite this, the IEK method, which is faster and easier, can be used to estimate the size of the fast-desorbing P pool based on the observed significant relationship between Q_1 and $E_{1\ min}$ and $E_{1\ day} - E_{1min}$. The results also indicates that a soil with a lower value of the IEK parameter *n* is likely to have a faster rate of desorption from both the fast- and slow-desorbing P pools.

6.6 Changes in extractable phosphorus pools

As expected, the changes in P-Olsen, P-AL and P-ox between the start of the experiment and 2017 were strongly related to the P balance. Further, when the decline in P-Olsen in the unfertilised plots was recalculated to kg P ha^{-1}, it only represented a fraction of the P removed by harvest, showing clearly that the fast-desorbing P-Olsen pool was continually replenished from the slow-desorbing P pool.

For both P-Olsen and P-ox, the change over time also seemed to be somewhat related to the soil concentration of exchangeable Ca^{2+}. Dissolved Ca^{2+} and PO_4^{3-} ions may form secondary CaP minerals (Essington, 2004; Haynes, 1984). This is likely to have occurred in some of the six soils studied in this thesis, according to the results of the XANES speciation. In addition, surface complexation of Ca^{2+} can increase the surface net charge, as discussed in section 6.2 of this thesis.

6.7 Phosphorus mass balance

This thesis investigated the mass balance for the top 0-20 cm of the six selected soils. In an earlier study of these soils, Börling *et al.* (2004) found significant differences in P-Olsen and P-AL between the A3 and D3 treatments down to a depth of 0.40 m from the soil surface. Downward transport of P in agricultural soils has also been reported by Rubæk *et al.* (2013) and van der Bom *et al.* (2019). Similar results were obtained in this thesis, where a large fraction of the positive P balance could not be accounted for in the residual P in the top 20 cm. This can be partly explained by the ploughing depth being >20 cm, mixing fertiliser P into deeper soil layers, but it is also possible that bioturbation by earthworms, leaching of dissolved P and internal erosion has removed P from the uppermost soil layer of soils in the long-term Swedish trials. In the A3 treatment with no P fertiliser addition, the decrease in the upper 0-20 cm for both P-ox and total P was also only a fraction of the negative P balance, indicating plant P uptake from deeper soil layers.

6.8 Phosphorus speciation

The change in XANES speciation with fertilisation was mostly in the P bound to Al and Fe fraction, confirming previous findings (Eriksson *et al.*, 2016). This is also reflected in the positive impact of Al-ox + Fe-ox on the size of the $E_{1\ \mathrm{day}} - E_{1\ \mathrm{min}}$ and $E_{3\ \mathrm{months}} - E_{1\ \mathrm{day}}$ pools. The only soil without a change in Al- and Fe-bound P with the different levels of P fertilisation was Fors. This soil also had the smallest change in total P in the top 0-20 cm, in both the unfertilised and fertilised treatments. In the Fors A3 treatment, only 23% of the negative P balance could be accounted for in the decrease of total P, while in the Fors D3 treatment only 31% of the positive P balance was reflected in the increase in total P. The low ability of this soil to both supply P (as evidenced by the declining yields in A3) and retain P may be connected to the small fraction of P bound to Al and Fe and the dominance of CaP.

In all soils containing CaP, and especially Fjärdingslöv, the amount seemed to increase with fertilisation. This is consistent with findings by Eriksson *et al.* (2016). There was also an influence of exchangeable Ca^{2+} on the change in extractable and exchangeable P with fertilisation in this thesis. This influence might be connected to the formation of CaP, but can also be due to the Ca^{2+} increasing the net charge of soil particles and therefore promoting adsorption. These results suggest that the formation of CaP can be an important mechanism regulating the fate of added fertiliser P even in some non-calcareous soils.

The small change in the organic P fraction confirms previous findings in a study on the organic P fraction in soils from the Swedish long-term soil fertility experiments using NMR spectroscopy (Ahlgren *et al.*, 2013). It also corresponds to the lack of difference in organic P between the treatments estimated by the Walker and Adams (1958) method (Table 6).

6.9 Impact of long-term cropping on grain yield

Despite the decline in extractable P in the A3 treatment at all sites during the 50-60 years of cropping without any P fertiliser, only two of the six experimental sites (Högåsa and Fors) showed a significant decline in grain yield over time. At the other four locations, the ability of the soil to deliver P for plant uptake seemed to be constant over the trial period, leading to no decrease in yield over time. However, without any P fertiliser addition the average yield was <100% of the fertilised (B3) yield at all locations, for both wheat and barley, although not always significantly lower. This indicates that P supply can be a yield-limiting factor in all the unfertilised A3 plots.

The decrease in yield over time in Fors A3 did not show any oblivious connection with the size of the fast-desorbing P pool. The Q_1, P-Olsen and E_{1min} values for Fors A3 were relatively similar to the values at other sites with no decline in yield or significant difference between treatments A3 and B3, such as Vreta Kloster A3. However, Fors A3 displayed a relatively small decrease in both P-ox and total P during the field trials and had the smallest $E_{1day} - E_{1min}$ and $E_{3months} - E_{1day}$ pools of all soils tested. This indicates that the Fors soil has lower availability of the slow-desorbing P pool to plant uptake than the other sites, explaining the decrease in grain yield over time.

For Högåsa, there was again no clear relationship between the P-Olsen value and the decline in yield levels. The P-Olsen value in Högåsa A3 was twice as high as in Vreta Kloster A3 and it had larger $E_{1day} - E_{1min}$ and $E_{3months} - E_{1day}$ pools, but half the average grain yield of Vreta Kloster A3. These two sites are located less than five kilometres from each other and have the same experimental plan, but the yield response to different levels of P fertilisation differs greatly. One explanation for this difference could be the partitioning of the P-Olsen pool between solid and solution phases, as estimated by the ratio of P-Olsen/P-$CaCl_2$. The analyses in this thesis showed that Vreta Kloster has a larger fraction of this pool in the solution phase in all treatments, with the greatest difference for A3. It is thus possible that the P-Olsen/P-$CaCl_2$ ratio can be useful to identify soils with low plant availability of soil P. Another factor to consider is that the soil structure at Vreta Kloster is more favourable for root growth, since the subsoil has shrinking clay minerals causing cracks (Kirchmann *et al.*, 2005). Högåsa has a very compact subsoil with high penetration resistance and few macropores (Kirchmann *et al*., 2005). Thus, physical properties might hinder root development and P uptake from deeper soil layers. Another important aspect is the design of the field experiment, with P and K levels connected in the same treatments. Högåsa A3 and B3 have low K-AL values, which can be part of the explanation for the low yields. It could also explain why Högåsa had significantly higher average yields in the treatments receiving additional P and K (C3 and D3) compared with the average yield in B3.

The wheat yield at the southern sites Ekebo and Fjärdingslöv increased significantly over time in all treatments, including those with no P or K fertilisation. These locations had a different crop rotation and received on average more N fertiliser than the central Swedish locations. However, the N application rate to wheat and barley does not differ greatly between the south and central trial sites. One possibility is that new, higher-yielding cultivars, technical development, and better plant protection, paired with a warmer climate in the south, are responsible for this increase (Fogelfors, 2001; Holmer, 2008; SMHI, 2012). This is reflected in an over-all increase of Swedish grain yields over the last 50 years.

In the B3 plots, which received fertiliser P to replace the P removed by harvest, the levels of P-Olsen and P-AL decreased with time. This decline in extractable P was not reflected in a decline in yield over time, and excessive P fertiliser addition in the C3 and D3 plots gave a higher average grain yield at only one location, Högåsa. This shows that replacement P addition can be a useful strategy to lower soil P concentration without wheat and barley yield loss in most soils. Similarly, Verloop *et al.* (2010) found that a P replacement strategy maintained maize and ley yields over 27 years of cropping on a Dutch experimental dairy farm.

It is known from previous studies that a build-up of soil P levels resulting from earlier applications of P fertilisers leads to a reduction in the P inputs required to obtain desired yields (Sattari *et al*., 2012). In a soil deprived of P, the application of more P than is utilised by the crop can be needed to obtain satisfactory yields, but after a certain point of soil P build-up crop yields may stay constant or even increase with lower or no P fertiliser additions (Mishima *et al*., 2010; Sattari *et al*., 2012). This effect was attributed by Barrow and Debnath (2014) to a decrease in net charge of adsorbing soil particles and a decrease in penetration of P into particles after long-term P fertilisation, as discussed in section 6.4 of this thesis. The soils studied in this thesis all had a long history of cropping with P fertilisers before the start of the long-term trials and initially had what would be considered good P-AL status according to current guidelines (Kvarmo *et al*., 2019). At the start of the trials, all B3 plots were in P-AL class III, where fertilisation to replace P is recommended for wheat and barley, except those at Fors, which were in class IVB (Kvarmo *et al*., 2019). After 50-60 years of cropping with replacement P addition, only Högåsa B3 had a significantly lower grain yield in B3 compared with D3, suggesting that the P-AL class III guideline is appropriate for most soils. However, the lack of significant difference in average yield between the A3 and B3 plots at some of the locations raises the question of whether the soil P status at which only replacement P is necessary could be even lower for some soils. It is also clear from the decline in yield at Fors A3, which had what would be considered high P status in 2017 according to the P-AL value, that the use of the AL method on this calcareous soil is inappropriate to estimate yield response to P fertilisation.

7 Agronomic implications and future perspectives

> *"Unless the quantity of P in the soil P reserves is known together with its rate of release, it is not possible to predict how long the reserves will last"*
> Syers *et al.* (2008)

There was a shift in concept in the late 1900s regarding the behaviour and dynamics of P in agricultural soils, from considering that soil P exists in discrete fractions (most irreversibly 'fixed') to viewing soil P as reversibly sorbed and available for plant uptake over long-term. Nevertheless, the idea of measuring 'plant-available P' by a single soil extraction persists. With current knowledge about the dynamics of soil P, a more appropriate assessment would be to estimate: i) the size of the P pool in direct contact with the soil solution, and ii) the rate of replenishment of this pool (Jordan-Meille *et al.*, 2012; Syers *et al.*, 2008). In this thesis, P-Olsen extraction was shown to provide a good estimate of the P pool in direct contact with the soil solution, while the ratios of P-Olsen/P-$CaCl_2$ and P-ox/P-Olsen provided estimates of the replenishment rates from the fast- and slow-desorbing P pools, respectively. All three of these extractions are simple to perform and can be done routinely. However, the added value of the use of multiple P tests needs to be assessed in future studies.

The change in P-Olsen, P-AL and P-ox after long-term cropping with four different levels of P addition revealed that the soil P balance was most strongly related to the change in P-ox over time and more weakly, but still significantly, related to the change in the other fractions. According to multiple linear regression modelling, the most important soil property for the change in P-Olsen and P-ox in response to long-term fertilization was exchangeable Ca^{2+}. Soils with a higher concentration of exchangeable Ca^{2+} also had a larger pool of free P ions, estimated by $E_{1\ min}$, at a given P-Olsen value, and a larger contribution of residual fertiliser P to the $E_{1\ min}$ pool. The importance of exchangeable Ca^{2+}

might be connected to the increase in CaP with fertilisation demonstrated by XANES speciation, but can also be due to Ca^{2+} promoting sorption of the negative P ions by increasing the net charge of soil particles. The size of the $E_{1\ day} - E_{1\ min}$, and $E_{3\ months} - E_{1\ day}$ pools at a given P-Olsen value were larger at lower soil pH or at higher concentration of Al-ox + Fe-ox. Using XANES, an increase in P bound to Al and Fe with fertilisation was found in five of the six soils studied, confirming the importance of Al and Fe minerals for the long-term changes in soil P pools. In conclusion, the most important properties governing the studied soils ability to retain fertiliser P in forms likely to be available for plant uptake were the concentration of exchangeable Ca^{2+}, the concentration of oxalate extractable Al and Fe, and the soil pH.

The differences in yield response to P fertilisation between the sites cannot be solely explained by differences in the size or availability of the various P pools. This highlights the fact that chemical availability is only a part of the full picture regarding plant P uptake, and raises questions about the possible integration of soil P test and biological or physical measures. In the mass P balances calculated in this thesis, the possible role of the subsoil was highlighted. According to the P balances, considerable amounts of P are transferred to and from the subsoil over time, a process that needs to be taken into account in soil P management strategies. Finding ways to identify soils such as Högåsa where high P fertilisation is needed to obtain good yields in spite of relatively high P-Olsen values, possibly due to a compact subsoil, is essential for sustainable P management. Future research should seek to determine when the correct response to low yields is to increase P fertilisation, or when other measures such as improving soil structure may be more important.

At only one of the six studied locations, grain yields of winter wheat, barley, and oat declined over time in the treatments with no P addition. The average yield in the no P treatments were lower than in the treatments receiving P fertiliser, but the difference were not always significant. This shows that the soils ability to deliver P for plant uptake stayed relatively constant during the experimental time, even if the amount of P delivered was not always enough to obtain optimal grain yields. Additionally, we found that for most of the studied soils, all with a long history of cultivation and fertiliser addition before the start of the experiments, a management practice where P removed by harvest is replaced the following rotation decreased the P-Olsen and P-AL values without any substantial grain yield loss. This, combined with the consistent yields in the unfertilized treatments, even with low P-Olsen and P-AL values, suggests that a “P in balance” approach to grain production could be beneficial even at lower than recommended P-Olsen and P-AL values.

References

Ahlgren, J., Djodjic, F., Börjesson, G. & Mattsson, L. (2013). Identification and quantification of organic phosphorus forms in soils from fertility experiments. *Soil Use and Management* 29, 24-35.

Aigner, M., Fardeau, J.C. & Zapata, F. (2002). Does the Pi strip method allow assessment of the available soil P?: Comparison against the reference isotope method*. Nutrient cycling in agroecosystems* 63, 49-58.

Andersen, J.H., Carstensen, J., Conley, D.J., Dromph, K., Fleming-Lehtinen, V., Gustafsson, B.G., Josefson, A.B., Norkko, A., Villnäs, A. & Murray, C.J.B.R. (2017). Long-term temporal and spatial trends in eutrophication status of the Baltic Sea. *Biological Reviews* 92, 135-149.

Andersson, K.O., Tighe, M.K., Guppy, C.N., Milham, P.J. & McLaren, T.I.J.G. (2016). The release of phosphorus in alkaline vertic soils as influenced by pH and by anion and cation sinks. *Geoderma* 264, 17-27.

Audi, G., Kondev, F., Wang, M., Huang, W. & Naimi, S. (2017). The NUBASE2016 evaluation of nuclear properties. *Chinese physics* C 41, 030001.

Azeez, M.O., Rubæk, G.H., Pedersen, I.F. & Christensen, B.T. (2020). Depletion, accumulation and availability of soil phosphorus in the Askov long-term field experiment. *Soil Research* 58, 117-124.

Bache, B. & Williams, E. (1971). A phosphate sorption index for soils. *Journal of Soil Science* 22, 289-301.

Baligar, V. & Bennett, O. (1986). Outlook on fertilizer use efficiency in the tropics. *Fertilizer Research* 10, 83-96.

Barrow, N. (1980). Evaluation and utilization of residual phosphorus in soils*. The role of phosphorus in agriculture*, 333-359.

Barrow, N. (2020). Comparing two theories about the nature of soil phosphate. *European Journal of Soil Science* 1-7.

Barrow, N., Bowden, J., Posner, A. & Quirk, J. (1980). Describing the effects of electrolyte on adsorption of phosphate by a variable charge surface. *Soil Research* 18, 395-404.

Barrow, N. & Debnath, A. (2014). Effect of phosphate status on the sorption and desorption properties of some soils of northern India. *Plant and soil* 378, 383-395.

Barrow, N. & Shaw, T. (1976). Sodium bicarbonate as an extractant for soil phosphate, I. Separation of the factors affecting the amount of phosphate displaced from soil from those affecting secondary adsorption. *Geoderma* 16, 91-107.

Barrow, N. J. (1983a). A mechanistic model for describing the sorption and desorption of phosphate by soil. *Journal of soil science*, 34, 733-750.

Barrow, N.J. (1983b). On the reversibility of phosphate sorption by soils. *European Journal of Soil Science* 34, 751-758.

Barrow, N.J. (2015). Soil phosphate chemistry and the P-sparing effect of previous phosphate applications. *Plant and Soil* 397, 401-409.

Bationo, A., Baethgen, W.E., Christianson, C.B. & Mokwunye, A.U. (1991). Comparison of five soil testing methods to establish phosphorus sufficiency levels in soil fertilized with water-soluble and sparingly soluble-P sources. *Fertilizer Research* 28, 271-279.

Beegle, D. (2005). Assessing Soil Phosphorus for Crop Production by Soil Testing. In: J.T. Sims, A.N. Sharpley (Eds.), *Phosphorus: Agriculture and the Environment*. Agronomy Monograph. American Society of Agronomy, Crop Science Society of America, and Soil Science Society of America, Madison, WI, pp. 123-143.

Bell, L. & Black, C. (1970). Crystalline phosphates produced by interaction of orthophosphate fertilizers with slightly acid and alkaline soils. *Soil Science Society of America Journal* 34, 735-740.

Blake, L., Johnston, A., Poulton, P. & Goulding, K. (2003). Changes in soil phosphorus fractions following positive and negative phosphorus balances for long periods. *Plant and Soil* 254, 245-261.

Brock, W.H. (2002). Justus von Liebig: the chemical gatekeeper. Cambridge University Press.

Börling, K., Barberis, E., Otabbong, E. (2004). Impact of long-term inorganic phosphorus fertilization on accumulation, sorption and release of phosphorus in five Swedish soil profiles. *Nutrient Cycling in Agroecosystems* 69, 11-21.

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

Carlgren, K. & Mattsson, L. (2001). Swedish Soil Fertility Experiments. *Acta Agriculturae Scandinavica, Section B - Soil & Plant Science* 51, 49-76.

Chang, S. & Jackson, M. (1957). Fractionation of soil phosphorus. *Soil Science* 84, 133-144.

Chardon, W.J., Menon, R.G. & Chien, S.H. (1996). Iron oxide impregnated filter paper (Pi test): a review of its development and methodological research. *Nutrient Cycling in Agroecosystems* 46, 41-51.

Condron, L.M. & Newman, S. (2011). Revisiting the fundamentals of phosphorus fractionation of sediments and soils. *Journal of Soils and Sediments* 11, 830-840.

Condron, L.M., Turner, B.L. & Cade-Menun, B.J. (2005). Chemistry and dynamics of soil organic phosphorus. *Phosphorus: Agriculture and the environment* 46, 87-121.

Cordell, D., Drangert, J.-O. & White, S. (2009). The story of phosphorus: global food security and food for thought. *Global environmental change* 19, 292-305.

Cross, A.F. & Schlesinger, W.H. (1995). A literature review and evaluation of the. Hedley fractionation: Applications to the biogeochemical cycle of soil phosphorus in natural ecosystems. *Geoderma* 64, 197-214.

Daubeny, C. (1845). Memoir on the Rotation of Crops, and on the Quantity of Inorganic Matters Abstracted from the Soil by Various Plants under Different Circumstances. *Philosophical Transactions of the Royal Society of London* 135 (1845).

de Ridder, M., de Jong, S., Polchar, J. & Lingemann, S. (2012). Risks and Opportunities in the Global Phosphate. *The Hague Centre for Strategic Studies*.

Dean, L., Nelson, W., MacKenzie, A., Armiger, W. & Hill, W. (1948). Application of radioactive tracer technique to studies of phosphatic fertilizer utilization by crops. *Soil Science Society of America Journal* 12(C), 107-112.

Demaria, P., Flisch, R., Frossard, E. & Sinaj, S. (2005). Exchangeability of phosphate extracted by four chemical methods. *Journal of Plant Nutrition and Soil Science* 168, 89-93.

Devau, N., Hinsinger, P., Le Cadre, E., Colomb, B. & Gérard, F. (2011). Fertilization and pH effects on processes and mechanisms controlling dissolved inorganic phosphorus in soils. *Geochimica et Cosmochimica Acta* 75, 2980-2996.

Djodjic, F., Börling, K. & Bergström, L. (2004). Phosphorus leaching in relation to soil type and soil phosphorus content. *Journal of environmental quality* 33, 678-684.

do Horta, M., Roboredo, M., Coutinho, J. & Torrent, J. (2010). Relationship between Olsen P and Ammonium Lactate–Extractable P in Portuguese Acid Soils. *Communications in Soil Science and Plant Analysis* 41, 2358-2370.

Doherty, J. (2010). PEST. Model-independent parameter estimation. User manual, 5th edition. . Watermark Numerical Computing, Bethesda, MD, USA.

Dyer, B. (1894). XV.—On the analytical determination of probably available "mineral" plant food in soils. *Journal of the Chemical Society*, Transactions 65, 115-167.

Dyer, B. (1902). Results of investigations on the Rothamsted soils. Bulletin (United States. Office of Experiment Stations); no. 106.

Egnér, H., Riehm, H. & Domingo, W. (1960). Untersuchungen über die chemische Bodenanalyse als Grundlage für die Beurteilung des Nährstoffzustandes der Böden. II. Chemische Extraktionsmethoden zur Phosphor-und Kaliumbestimmung. *Kungliga Lantbrukshögskolans Annaler* 26, 199-215.

Eriksson, A., Hesterberg, D., Klysubun, W. & Gustafsson, J. (2016). Phosphorus dynamics in Swedish agricultural soils as influenced by fertilization and mineralogical properties: Insights gained from batch experiments and XANES spectroscopy. *Science of the Total Environment* 566, 1410-1419.

Eriksson, A.K., Ulén, B., Berzina, L., Iital, A., Janssons, V., Sileika, A. & Toomsoo, A. (2013). Phosphorus in agricultural soils around the Baltic Sea–comparison of laboratory methods as indices for phosphorus leaching to waters. *Soil Use and Management* 29, 5-14.

Eriksson, J., Mattsson, L. & Söderström, M. (2010). Current status of Swedish arable soils and cereal crops. Data from the period 2001-2007, *Naturvårdsverket*, Sweden

Essington, M.E. (2004). Soil and Water Chemistry: An Integrative Approach, Second Edition.

FAO, 2019. World Fertilizer Trends and Outlook to 2022. *Food and Agriculture Organization of the United Nations* Rome, Italy.

Fardeau, J.-C., Morel, C. & Boniface, R. (1988). Pourquoi choisir la methode Olsen pour estimer le phosphore" assimilable" des sols? *Agronomie, EDP Sciences* 8, pp.577-584.

Fardeau, J. (1996). Dynamics of phosphate in soils. An isotopic outlook. *Fertilizer Research* 45, 91-100.

Fitter, A. & Sutton, C. (1975). The use of the Freundlich isotherm for soil phosphate sorption data. *Journal of Soil Science* 26, 241-246.

Fixen, P. & Grove, J. (1990). Testing soils for phosphorus. Soil testing and plant analysis 3, 141-180.

Fixen, P., Ludwick, A. & Olsen, S. (1983). Phosphorus and potassium fertilization of irrigated alfalfa on calcareous soils: II. Soil phosphorus solubility relationships. *Soil Science Society of America Journal* 47, 112-117.

Fogelfors, H. (2001). Växtproduktion i jordbruket. Natur och Kultur/LTs förlag. Centraltryckeriet. Borås. Sweden.

Frossard, E., Achat, D.L., Bernasconi, S.M., Bünemann, E.K., Fardeau, J.-C., Jansa, J., Morel, C., Rabeharisoa, L., Randriamanantsoa, L., Sinaj, S., Tamburini, F. & Oberson, A. (2011). The Use of Tracers to Investigate Phosphate Cycling in Soil–Plant Systems. In: E. Bünemann, A. Oberson, E. Frossard (Eds.), *Phosphorus in Action: Biological Processes in Soil Phosphorus Cycling.* Springer Berlin Heidelberg, Berlin, Heidelberg, pp. 59-91.

Frossard, E., Demaria, P., Sinaj, S. & Schärer, M. (2014). A flow-through reactor to assess potential phosphate release from agricultural soils. *Geoderma* 219, 125-135.

Frossard, E., Morel, J.L., Fardeau, J.C. & Brossard, M. (1994). Soil Isotopically Exchangeable Phosphorus: A Comparison between E and L Values. *Soil Science Society of America Journal* 58, 846.

Frossard, E. & Sinaj, S. (1997). The Isotope Exchange Kinetic Technique: A Method to Describe the Availability of Inorganic Nutrients. Applications to K, P, S and Zn*. Isotopes in Environmental and Health Studies* 33, 61-77.

Goldberg, S. & Sposito, G. (1984). A chemical model of phosphate adsorption by soils: II. Noncalcareous soils. *Soil Science Society of America Journal* 48, 779-783.

Gustafsson, J.P., Braun, S., Tuyishime, J., Adediran, G.A., Warrinnier, R. & Hesterberg, D. (2020). A Probabilistic Approach to Phosphorus Speciation of Soils Using P K-edge XANES Spectroscopy with Linear Combination Fitting. *Soil Systems* 4, 26.

Haygarth, P.M., Jarvie, H.P., Powers, S.M., Sharpley, A.N., Elser, J.J., Shen, J., Peterson, H.M., Chan, N.-I., Howden & N.J. & Burt, T. (2014). Sustainable phosphorus management and the need for a long-term perspective: The legacy hypothesis. *Environ. Sci. Technol.* 48, 8417–8419

Haynes, R. (1984). Lime and phosphate in the soil-plant system, *Advances in agronomy*, 249-315. Elsevier.

Heckman, J.R., Jokela, W., Morris, T., Beegle, D.B., Sims, J.T., Coale, F.J., Herbert, S., Griffin, T., Hoskins, B., Jemison, J., Sullivan, W.M., Bhumbla, D., Estes, G. & Reid, W.S. (2006). Soil Test Calibration for Predicting Corn Response to Phosphorus in the Northeast USA. *Agronomy Journal* 98(2), 280.

Hedley, M. & McLaughlin, M. (2005). Reactions of phosphate fertilizers and by-products in soils. *Phosphorus: agriculture and the environment* 46, 181-252.

Hedley, M., Mortvedt, J., Bolan, N. & Syers, J. (1995). Phosphorus fertility management in agroecosystems. In: *Phosphorus in the global environment: transfers, cycles and management.*(Ed. H Tiessen) pp. 59–92. Wiley and Sons: London.

Hedley, M.J., Stewart, J. & Chauhan, B. (1982). Changes in inorganic and organic soil phosphorus fractions induced by cultivation practices and by laboratory incubations. *Soil Science Society of America Journal* 46, 970-976.

Holmer, B. (2008). Fluctuations of winter wheat yields in relation to length of winter in Sweden 1866 to 2006. *Climate Research* 36, 241-252.

Houba, V.J.G., Temminghoff, E.J.M., Gaikhorst, G.A. & Vark, V.W. (2000). Soil analysis procedures using 0.01 M calcium chloride as extraction reagent. *Communications in Soil Science & Plant Analysis* 31, 1299-1396.

Johnston, A. (1970). The value of residues from long-period manuring at Rothamsted and Woburn. II. A summary of the results of experiments started by Lawes and Gilbert. *Report of the Rothamsted Experimental Station, 1969* (Part 2), 7-21.

Johnston, A. & Poulton, P. (2019). Phosphorus in Agriculture: A Review of Results from 175 Years of Research at Rothamsted, UK. *Journal of environmental quality* 48(5), 1133-1144.

Jordan-Meille, L., Rubæk, G.H., Ehlert, P.A.I., Genot, V., Hofman, G., Goulding, K., Recknagel, J., Provolo, G. & Barraclough, P. (2012). An overview of fertilizer-P recommendations in Europe: soil testing, calibration and fertilizer recommendations. *Soil Use and Management* 28, 419-435.

Karlsson, P. & Pihl Karlsson, G. (2018). Deposition av fosfor till Östersjön-Kunskapsläge och möjligheter till löpande mätningar. *SMED Rapport* (18).

Kirchmann, H., Eriksson, J., & Snäll, S. (1999). Properties and classification of soils of the Swedish long-term fertility experiments: IV. Sites at Ekebo and Fjärdingslöv. *Acta Agriculturae Scandinavica, Section B- Soil & Plant Science*, 49, 25-38.

Kirchmann, H., Snäll, S., Eriksson, J., & Mattsson, L. (2005). Properties and classification of soils of the Swedish long-term fertility experiments: V. Sites at Vreta Kloster and Högåsa. *Acta Agriculturae Scandinavica, Section B-Soil & Plant Science,* 55, 98-110.

Kirchmann, H. (1991). Properties and classification of soils of the Swedish long-term fertility experiments: I. Sites at Fors and Kungsängen. *Acta Agriculturae Scandinavica*, 41, 227-242.

Kleinman, P., Sharpley, A., Buda, A., McDowell, R., Allen, A. (2011). Soil controls of phosphorus in runoff: Management barriers and opportunities. *Canadian Journal of Soil Science* 91, 329-338.

Klysubun, W., Sombunchoo, P., Deenan, W. & Kongmark, C. (2012). Performance and status of beamline BL8 at SLRI for X-ray absorption spectroscopy. *Journal of Synchrotron Radiation* 19, 930-936.

Kruse, J., Abraham, M., Amelung, W., Baum, C., Bol, R., Kühn, O., Lewandowski, H., Niederberger, J., Oelmann, Y. & Rüger, C. (2015). Innovative methods in soil phosphorus research: A review. *Journal of plant nutrition and soil science* 178, 43-88.

Kurtz, L. (1953). Inorganic phosphorus in acid and neutral soils. In WH Pierre and AG Norman eds., *Soil and fertilizer phosphorus in crop nutrition.* American Society of Agronomy, Volume IV., 59-85.

Kvarmo, P., Andersson, E., Börling, K., Hjelm, E., Jonsson, P., Listh, U. & Malgeryd, J. (2019). Rekommendationer för gödsling och kalkning 2020, Jordbruksverket.

Larsen, S. (1952). The use of P 32 in studies on the uptake of phosphorus by plants. *Plant and soil* 4, 1-10.

Larsen, S. (1967). Soil phosphorus, *Advances in Agronomy*. Elsevier, pp. 151-210.

Lemming, C., Oberson, A., Magid, J., Bruun, S., Scheutz, C., Frossard, E., Jensen, L.S. (2019). Residual phosphorus availability after long-term soil application of organic waste. *Agriculture, Ecosystems & Environment* 270, 65-75.

Li, B., Bicknell, K. & Renwick, A. (2019). Peak phosphorus, demand trends and implications for the sustainable management of phosphorus in China. *Resources, Conservation and Recycling* 146, 316-328.

Lončarić, Z., Popović, B., Teklić, T., Engler, M. & Karalić, K. (2006). Comparison of Two Soil Phosphorus Analytical Methods in Croatia. *Communications in Soil Science and Plant Analysis* 37, 2867-2881.

Lookman, R., Freese, D., Merckx, R., Vlassak, K., van Riemsdijk, W.H. (1995a). Long-term kinetics of phosphate release from soil. *Environmental science & technology* 29, 1569-1575.

Lookman, R., Vandeweert, N., Merckx, R., Vlassak, K. (1995b). Geostatistical assessment of the regional distribution of phosphate sorption capacity parameters (Feox and Alox) in northern Belgium. *Geoderma* 66, 285-296.

Maguire, R.O., Chardon, W.J. & Simard, R.R. (2005). Assessing potential environmental impacts of soil phosphorus by soil testing. *Phosphorus: agriculture and the environment* 46, 145-180.

Mason, S.D., McLaughlin, M.J., Johnston, C., McNeill, A. (2013). Soil test measures of available P (Colwell, resin and DGT) compared with plant P uptake using isotope dilution. *Plant and Soil* 373, 711-722.

Mattingly, G. & Widdowson, F. (1958). Uptake of phosphorus from P^{32}-labelled superphosphate by field crops: part. II. Comparison of placed and broadcast applications to barley. *Plant and Soil*, 161-175.

McAuliffe, C., Hall, N., Dean, L. & Hendricks, S.B. (1948). Exchange Reactions Between Phosphates and Soils: Hydroxylic Surfaces of Soil Minerals 1. *Soil Science Society of America Journal* 12C, 119-123.

McBeath, T., McLaughlin, M., Kirby, J. & Armstrong, R. (2012). The effect of soil water status on fertiliser, topsoil and subsoil phosphorus utilisation by wheat. *Plant and Soil* 358, 337-348.

McLaren, T.I., Guppy, C.N., Tighe, M.K., Moody, P. & Bell, M. (2014). Dilute acid extraction is a useful indicator of the supply of slowly available phosphorus in Vertisols. *Soil Science Society of America Journal* 78, 139-146.

McLaren, T.I., McLaughlin, M.J., McBeath, T.M., Simpson, R.J., Smernik, R.J., Guppy, C.N. & Richardson, A.E. (2016). The fate of fertiliser P in soil under pasture and uptake by subterraneum clover–a field study using 33 P-labelled single superphosphate. *Plant and Soil* 401, 23-38.

McLaughlin, M.J., Alston, A. & Martin, J. (1988). Phosphorus cycling in wheat pasture rotations. I. The source of phosphorus taken up by wheat. *Soil Research* 26, 323-331.

McLaughlin, M.J., McBeath, T.M., Smernik, R., Stacey, S.P., Ajiboye, B. & Guppy, C. (2011). The chemical nature of P accumulation in agricultural soils—implications for fertiliser management and design: an Australian perspective. *Plant and Soil* 349, 69-87.

Mishima, S., Endo, A., Kohyama, K. (2010). Recent trends in phosphate balance nationally and by region in Japan. *Nutrient Cycling in Agroecosystems* 86, 69-77.

Moody, P.W., Speirs, S.D., Scott, B.J. & Mason, S.D. (2013). Soil phosphorus tests I: What soil phosphorus pools and processes do they measure? *Crop and Pasture Science* 64, 461-468.

Morel, C., & Plenchette, C. (1994a). Is the isotopically exchangeable phosphate of a loamy soil the plant-available P?. *Plant and Soil* 158, 287-297.

Morel, C., Tiessen, H., Moir, J. O., & Stewart, J. W. B. (1994b). Phosphorus transformations and availability under cropping and fertilization assessed by isotopic exchange. *Soil Science Society of America Journal* 58, 1439-1445.

Murray, J. (1841). Advice to Farmers, London.

Mårald, E. (1998). I mötet mellan jordbruk och kemi: agrikulturkemins framväxt på Lantbruksakademiens experimentalfält, 1850-1907. *Kungl. Skogs-och lantbruksakademien*.

Nawara, S., Dael, V.T., Merckx, R., Amery, F., Elsen, A., Odeurs, W., Vandendriessche, H., McGrath, S., Roisin, C., Jouany, C., Pellerin, S., Denoroy, P., Eichler-Löbermann, B., Börjesson, G., Goos, P., Akkermans, W. & Smolders, E. (2017). A comparison of soil tests for available phosphorus in long-term field experiments in Europe. *European Journal of Soil Science* 68, 873-885.

Neyroud, J.A. & Lischer, P. (2003). Do different methods used to estimate soil phosphorus availability across Europe give comparable results? *Journal of Plant Nutrition and Soil Science* 166, 422-431.

Olsen, S.R. (1954). Estimation of available phosphorus in soils by extraction with sodium bicarbonate. *United States Department Of Agriculture*; Washington.

Otabbong, E., Börling, K., Kätterer, T., Mattsson, L. (2009). Compatibility of the ammonium lactate (AL) and sodium bicarbonate (Olsen) methods for determining available phosphorus in Swedish soils. *Acta Agriculturae Scandinavica, Section B - Plant Soil Science* 59, 373-378.

Parfitt, R., Hume, L. & Sparling, G. (1989). Loss of availability of phosphate in New Zealand soils. *Journal of Soil Science* 40, 371-382.

Penn, C. J., & Camberato, J. J. (2019). A critical review on soil chemical processes that control how soil pH affects phosphorus availability to plants. *Agriculture* 9, 120.

Pierzynski, G. M., Logan, T. J., Traina, S. J., & Bigham, J. M. (1990). Phosphorus chemistry and mineralogy in excessively fertilized soils: Quantitative analysis of phosphorus-rich particles. *Soil Science Society of America Journal*, 54, 1576-1583.

Pierzynski, G., McDowell, R., Sims, T., 2005. Chemistry, Cycling, and Potential Movement of Inorganic Phosphorus in Soils. In: T. Sims, A. Sharpley (Eds.), *Phosphorus: Agriculture and the Envirionment,* Madison, Wisconsin, USA, pp. 53-86.

Posner, A. & Barrow, N. (1982). Simplification of a model for ion adsorption on oxide surfaces. *Journal of Soil Science* 33, 211-217.

Ravel, B. & Newville, M. (2005). ATHENA, ARTEMIS, HEPHAESTUS: data analysis for X-ray absorption spectroscopy using IFEFFIT. *Journal of synchrotron radiation* 12, 537-541.

Rietra, R.P., Hiemstra, T. & van Riemsdijk, W.H. (2001). Interaction between calcium and phosphate adsorption on goethite. *Environmental science & technology* 35, 3369-3374.

Roy, R.N., Finck, A., Blair, G.J. & Tandon, H.L.S. (2006). Plant nutrition for food security: A guide for integrated nutrient management, *Food and Agriculture Organization of the United Nations*, Rome.

R Core Team (2016). RStudio: Integrated Development for R. RStudio, Inc., Boston, MA.

Rubæk, G.H., Kristensen, K., Olesen, S.E., Østergaard, H.S. & Heckrath, G. (2013). Phosphorus accumulation and spatial distribution in agricultural soils in Denmark. *Geoderma* 209, 241-250.

Sample, E., Soper, R. & Racz, G. (1980). Reactions of phosphate fertilizers in soils. *The role of phosphorus in agriculture*, 263-310.

Sattari, S.Z., Bouwman, A.F., Giller, K.E. & van Ittersum, M.K. (2012). Residual soil phosphorus as the missing piece in the global phosphorus crisis puzzle. *Proceedings of the National Academy of Sciences* 109, 6348-6353.

Schindler, D. (1977). Evolution of phosphorus limitation in lakes. *Science* 195, 260-262.

Sen Tran, T., Giroux, M. & Fardeau, J. (1988). Effects of soil properties on plant-available phosphorus determined by the isotopic dilution phosphorus-32 method. *Soil Science Society of America Journal* 52, 1383-1390.

Sharpley, A. (1986). Disposition of fertilizer phosphorus applied to winter wheat. *Soil Science Society of America Journal* 50, 953-958.

Sharpley, A., Ahuja, L., Yamamoto, M. & Menzel, R. (1981). The kinetics of phosphorus desorption from soil. *Soil Science Society of America Journal* 45, 493-496.

Sharpley, A., Jarvie, H.P., Buda, A., May, L., Spears, B. & Kleinman, P. (2013). Phosphorus legacy: overcoming the effects of past management practices to mitigate future water quality impairment. *Journal of environmental quality* 42, 1308-1326.

Six, L., Pypers, P., Degryse, F., Smolders, E. & Merckx, R. (2012). The performance of DGT versus conventional soil phosphorus tests in tropical soils - An isotope dilution study. *Plant and Soil* 359, 267-279.

Smeck, N.E. (1985). Phosphorus dynamics in soils and landscapes. *Geoderma* 36, 185-199.

SMHI (2012). Medeltemperatur för Sverige. Accessed at: https://www.smhi.se/kunskapsbanken/klimat/sveriges-klimat/sverigemedeltemperatur-1.21151

Smil, V. (2000). Phosphorus in the environment: natural flows and human interferences. *Annual review of energy and the environment* 25, 53-88.

Sparks, D. L. (2003). Sorption Phenomena on Soils. Editor(s): Donald L. Sparks, Environmental Soil Chemistry (Second Edition), Academic Press. Pages 133-186.

Speirs, S.D., Scott, B.J., Moody, P.W., Mason, S.D. (2013). Soil phosphorus tests II: A comparison of soil test–crop response relationships for different soil tests and wheat. *Crop and Pasture Science* 64, 469-479.

Stewart, W.M., Hammond, L.L. & van Kauwenbergh, S.J. (2005). Phosphorus as a natural resource. *Phosphorus: agriculture and the environment* 46, 1-22.

Stutter, M.I., Shand, C.A., George, T.S., Blackwell, M.S., Dixon, L., Bol, R., MacKay, R.L., Richardson, A.E., Condron, L.M. & Haygarth, P.M. (2015). Land use and soil factors affecting accumulation of phosphorus species in temperate soils. *Geoderma* 257, 29-39.

Syers, J., Johnston, A., Curtin, D. (2008). Efficiency of soil and fertilizer phosphorus use. *FAO Fertilizer and plant nutrition bulletin* 18.

Tiessen, H. & Moir, J. (1993). Characterization of available P by sequential extraction. *Soil sampling and methods of analysis* 7, 5-229.

Walan, P., Davidsson, S., Johansson, S. & Höök, M. (2014). Phosphate rock production and depletion: Regional disaggregated modeling and global implications. *Resources, conservation and recycling* 93, 178-187.

Walker, T. & Adams, A. (1958). Studies on soil organic matter: I. Influence of phosphorus content of parent materials on accumulations of carbon, nitrogen, sulfur, and organic phosphorus in grassland soils. *Soil science* 85, 307-318.

Walker, T. & Syers, J.K. (1976). The fate of phosphorus during pedogenesis. *Geoderma* 15, 1-19.

van der Bom, F.J., McLaren, T.I., Doolette, A.L., Magid, J., Frossard, E., Oberson, A. & Jensen, L. (2019). Influence of long-term phosphorus fertilisation history on the availability and chemical nature of soil phosphorus. *Geoderma* 355, 113909.

van Reeuwijk, L. (1995). Procedures for soil analysis. *Int. Soil Ref. Inf. Centre*, Wageningen, Netherlands.

van Rotterdam, A., Temminghoff, E.J.M., Schenkeveld, W.D.L., Hiemstra, T. & van Riemsdijk, W.H. (2009). Phosphorus removal from soil using Fe oxide-impregnated paper: Processes and applications. *Geoderma* 151, 282-289.

Verloop, J., Oenema, J., Burgers, S., Aarts, H., Van Keulen, H. (2010). P-equilibrium fertilization in an intensive dairy farming system: effects on soil-P status, crop yield and P leaching. *Nutrient Cycling in Agroecosystems* 87, 369-382.

Wiklander, L. (1950). Kinetics of phosphate exchange in soils. *Kungliga Lantbrukshogskolans Annaler* 17, 407-424.

Wild, A. (1950). The retention of phosphate by soil. A review. *Journal of Soil Science* 1, 221-238.

Wuenscher, R., Unterfrauner, H., Peticzka, R. & Zehetner, F. (2016). A comparison of 14 soil phosphorus extraction methods applied to 50 agricultural soils from Central Europe. *Plant, Soil and Environment 61*, 86-96.

Yuan, G. & Lavkulich, L. (1994). Phosphate sorption in relation to extractable iron and aluminum in Spodosols. *Soil Science Society of America Journal* 58, 343-346.

Zbíral, J. (2000). Determination of phosphorus in calcareous soils by mehlich 3, mehlich 2, cal, and egner extractants. *Communications in Soil Science and Plant Analysis* 31, 3037-3048.

Popular science summary

In 1669, the German alchemist Henning Brandt accidentally discovered the elemental form of phosphorus (P), during a search for the ‘philosopher’s stone’. The curiously glowing material he found disappointed by neither giving immortality nor turning metals into gold. For some time, the only usage of this new substance was to entertain the upper classes in popular ‘science shows’, a dangerous game with an element that can spontaneously combust when exposed to air. It would take until the late 18th century before the importance of Brandt’s discovery was clear, and later uses of P in industry, warfare and agriculture have had an immense impact on the development of human society.

The use of manure, human excreta, guano (droppings from birds and bats) and other organic materials to promote plant growth has been common practice for more than 5000 years, but the use of inorganic P fertilisers is quite recent. Commercial production of inorganic P fertilisers started in the mid-1800s, and such fertilisers became affordable and widely accessible after the Second World War. The improved access to P fertilisers, together with other developments during the ‘Green Revolution’, is partly responsible for global agriculture now being able to feed four times as many people as in the early 1900s.

As a result of the increase in P fertiliser use, many agricultural soils now have high soil P concentrations. This accumulated soil P can be a resource for farmers, especially since some scientists have warned that the finite global deposits of good-quality, P-rich rock used for P fertiliser production are being depleted. However, high soil P concentrations have also been linked to environmental issues, since P can leach to freshwater and oceans, causing algae blooms and destroying ecosystems. Therefore, a sustainable P management strategy is to decrease high soil P concentrations, and increase low soil P concentrations, to a level where only replacement of P removed by crop harvest is needed (P in balance).

In Sweden, the P fertilisation recommendations are based on P content determined by acidic soil extraction with ammonium acetate lactate (P-AL). The results from this extraction are used to divide soils into different classes, with class III being a common goal for the P in balance strategy. However, this extraction can sometimes overestimate the amount of 'plant-available' P, placing the soil in too high a P class. In addition, this extraction only gives information on the size of the extractable P pool, and not about how fast a soil can replenish the soil solution P after plant P uptake.

In this thesis, the Swedish long-term soil fertility trials, which were started in the 1950s and 1960s in response to the increased use of inorganic fertilisers, were used to investigate how more than half a century of cropping with different levels of P addition has affected soil P status and crop yield. The focus was on comparing methods to quantify the soil P pools that are available at fast and slow rates to the soil solution, and to investigate the dynamics of these pools.

The main finding in this thesis was that long-term P fertilisation with a surplus of P led to larger pools of fast and slowly available P, with a larger proportion of the total P present in the fast P pool compared with an unfertilised soil. After long-term fertilisation, the rate of transport of P from solid phases to the soil solution had increased. However, not all of the added fertiliser P which was not removed by harvest had stayed in the topsoil. Between 30-70% of the extra P could not be accounted for by increased total P in topsoil.

When cropping was performed with no P fertiliser for ~50-60 years, the size of both the fast and slow P pools decreased. In these plots receiving no fertiliser, the average grain yield of wheat and barley tended to be lower (but not always statistically significantly lower), but the yield declined over time at only two of the six locations studied. Thus for most of the soils, the ability to supply P to plant uptake stayed constant, even when the soil was in a low P-AL class (class I). For many of the soils studied, there appeared to have been considerable plant P uptake from the subsoil.

When P was in balance and the amount of P fertiliser added was calculated from the amount of P removed by harvest, the P-AL and P-Olsen values decreased. However, there were no differences in winter wheat and spring barley grain yield between these plots in balance and the plots receiving a surplus of P, except on one soil. This soil had a very compact subsoil, which can have limited rooting depth and thus P uptake by roots. The P in balance strategy can possibly be useful to decrease the P level in a soil without yield loss, but it is important to find ways to identify soils for which this approach is not appropriate.

Lastly, the AL and Olsen methods was assessed to see if they could quantify the size of the fast available P pool. Based on results from isotopic and desorption experiments, the AL method was concluded to dissolve more stable P forms than Olsen, especially but not exclusively in calcareous soils.

Populärvetenskaplig sammanfattning

År 1669 upptäckte den tyska alkemisten Henning Brandt av misstag grundämnet fosfor (P), i sökandet efter den vises sten. Det mystiskt lysande materialet gjorde honom dock besviken genom att vare sig ge evigt liv eller förvandla någonting till guld. Under en tid var den enda användningen av denna nya substans underhållande vetenskapliga uppvisningar för överklassen, en farlig lek med ett ämne som kan självantända i kontakt med syre. Det skulle ta ända till sent 1700-tal innan storheten i Brandts upptäckt stod klar, och den senare användningen av fosfor i industri, krigsföring, och jordbruk har haft en oerhörd inverkan på det samhälle vi lever i idag.

Användningen av stallgödsel, mänskliga exkrement, guano (avföring från fåglar och fladdermöss), och annat organiskt material har använts för att höja skördar i mer än femtusen år, men användandet av oorganiska P gödselmedel, även kallat mineralgödsel, är ganska nytt. Kommersiell produktion av oorganiskt P gödselmedel startade i mitten av 1800-talet, och de blev allmänt tillgängliga i stor mängd efter andra världskriget. Den förbättrade tillgången av P gödningsmedel, tillsammans med annan utveckling under den ”gröna revolutionen”, är delvis ansvarig för att världens jordbruk nu kan försörja fyra gånger så många människor som under tidigt 1900-tal.

Som ett resultat av den ökande användningen av P gödselmedel, har många jordbruksjordar nu höga koncentrationer av P i jorden. Denna anrikning av mark-P kan vara en resurs för lantbrukarna, särskilt eftersom vissa forskare har varnat för att reserverna av hög-kvalitativa P-rika mineral som används för tillverkning av mineralgödsel minskar. Dock så har dessa höga mark-P koncentrationer även kopplats till miljöproblem, då P kan läcka till sötvatten och hav vilket leder till algblomningar och stör de naturliga ekosystemen. Därför är en hållbar strategi för P användning att försöka minska de höga P koncentrationerna, och öka de låga, så att man hamnar på en nivå där enbart den P som förts bord med skörd behöver återföras till fält (fosfor i balans).

I Sverige baseras P gödslingsrekommendationerna på en sur extraktion med ammoniumacetat-laktat, P-AL. Resultaten från denna extraktion används för att dela upp jordar i olika klasser, där klass III är ett vanligt mål för ”fosfor i balans”-strategin. Denna extraktion kan dock ibland överskatta mängden ”växttillgängligt P”, vilket placerar jorden i en för hög P-AL klass. Dessutom ger denna extraktion bara information om storleken på den extraherbara P poolen, och ingen information om hur snabbt en jord kan fylla på marklösningen efter växt upptag av P därifrån.

I denna studie användes de svenska bördighetsförsöken, vilka startades på 50- och 60-talet i respons till den ökade användningen av mineralgödsel, för att undersöka hur över ett halvt århundrande av växtodling med olika nivåer av P tillförsel har påverkat markens P status samt skördenivåer. Fokus var på att jämföra metoder som kan kvantifiera markens pool av P som är snabbt och långsamt tillgängligt till marklösningen, och att studera dessa poolers dynamik.

De huvudsakliga fynden från denna studie var att en lång period av P gödsling med ett överskott av P har lett till större pooler av både snabbt och långsamt tillgängligt P, med en större fraktion av total P i den snabba poolen jämfört med ogödslad jord. Efter långvarig gödsling ökade också hastigheten av transporten av P från den fasta fasen till marklösningen. Dock så har inte allt P som inte tagits upp av växter stannat i det översta jordlagret. Mellan 30-70 % av P överflödet kunde inte hittas i ökningen av total P i matjorden.

När odling skedde utan P-gödsel under ~ 50-60 år minskade storleken på både den snabba och långsamma P-poolen. I ogödslade leden tenderade genomsnittsavkastningen att vara lägre (men inte alltid statistiskt signifikant lägre), men på bara två av sex platser minskade avkastningen över tiden. Detta visar att för de flesta jordarna var förmågan att leverera P till växtupptag konstant, även när marken var i P-AL-klass I. Dessutom har det förekommit ett betydande P-upptaget från alven i många av jordarna.

När P var i balans, och mängden P-gödselmedel som tillsattes beräknades från mängden P som avlägsnades genom skörd, minskade P-AL- och P-Olsen-värdena. Emellertid fanns det ingen skillnad i skördenivån av höstvete och vårkorn mellan behandlingarna i balans och behandlingarna som fick ett överskott av P, förutom för en jord. Denna jord hade en mycket kompakt alv som kan ha begränsat P-upptag. Det är möjligt att ”P i balans”-strategin kan vara användbar för att sänka en jords P-nivå utan skördeförluster, men det är viktigt att hitta sätt att identifiera jordar där detta tillvägagångssätt inte är lämpligt. Slutligen bedömdes AL- och Olsen-metoderna för att se om de kunde kvantifiera storleken på den snabbt tillgängliga P-poolen. Genom användning av isotop- och desorptionsexperiment visades det att AL-metoden löser upp mer stabila P-former än Olsen, särskilt men inte uteslutande i kalkhaltiga jordar.

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The size and dynamics of the fast- and slow-desorbing soil P pools were investigated in six long-term Swedish field experiments. The Olsen extraction was shown to provide a good estimate of the size of the fast-desorbing P pool. Soils higher in exchangeable calcium and/or aluminium and iron (hydr)oxides retained more fertiliser P in the fast-desorbing pool. A P replacement fertilisation strategy decreased the size of the P pools, but maintained optimal grain yields for more than 50 years.

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