# Phosphorus speciation in Swedish agricultural clay soils

## Influence of fertilisation and mineralogy

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Doctoral Thesis
Swedish University of Agricultural Sciences
Uppsala 2016

Cover: Soil after plowing. The word cloud contains the words most frequently occurring in the abstract of this thesis. Also shown are the bulk soil XRD patterns of the Fors soil.

(photo: A.K. Eriksson)

# Phosphorus speciation in Swedish agricultural clay soils. Influence of fertilisation and mineralogy

## Abstract

Phosphorus (P) is an important element for crop production, but build-up of excess soil P can promote P leaching and eutrophication of surface waters. To better understand the dynamics of P release from soil to waters, more knowledge is needed about sorption patterns and P speciation in agricultural soils.

   Two new indices were developed to assess the importance of P sorption to hydroxy-interlayered clay minerals, and to evaluate the amount of hydroxy-interlayering and hydroxy-interlayer stability. A strong relationship was found between oxalate-extractable aluminium (Al) and the amount of hydroxy-interlayering in soil, suggesting a common source. This makes it difficult to analytically distinguish between phosphate ($PO_4$) adsorbed to hydroxy-interlayers from $PO_4$ adsorbed to Al hydroxide-type precipitates.

   Application of X-ray absorption near-edge structure (XANES) spectroscopy to evaluate P speciation in soil profiles and the effects of P depletion and fertilisation revealed a distinct change in P speciation with increasing soil depth in an agricultural clay soil profile. The results indicated that the subsoil P predominantly occurred as apatite, whereas $PO_4$ adsorbed with Al-hydroxides or hydroxy-interlayers dominated in the topsoil. Organic P and $PO_4$ adsorbed to iron (Fe)-(hydr)oxides were observed only in the topsoil. This can be explained by long-term weathering of apatite and silicates, particularly ferromagnesian forms such as amphibole, in the upper soil horizons, causing an association of the released $PO_4$ with secondary metal (hydr)oxides.

   Collectively, the XANES results showed that the most important phases governing P retention and release in agricultural clay soils are adsorption of $PO_4$ to Al and to Fe in (hydr)oxide minerals or interlayers. After fertilisation, P was adsorbed to Al hydroxide phases in six different soil types studied, but in two of the soils there was also an increase in calcium phosphate. Moreover, P solubility was shown to be lowest at pH values ranging from 4.5 to 7.5 and increased with decreasing pH, probably as a result of the dissolution of apatite and $PO_4$-bearing hydroxy-Al precipitates at low pH.

*Keywords:* Soils, XANES spectroscopy, phosphorus, phosphate, clays, apatite, secondary iron and aluminium (hydr)oxides, clay mineralogy, hydroxy-interlayered minerals, X-ray diffraction

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# Dedication

To my grandmother, Hildur

*"Environments are not just containers, but are processes that change the content totally"*
    Marshall McLuhan

so…

*"What we plant in the soil of contemplation, we shall reap in the harvest of action"*
    Meister Eckhart

# 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   Eriksson, A.K., Hillier, S., Simonsson, M. and Gustafsson J.P. X-ray diffraction using *in situ* heating to characterise hydroxy-interlayering in clay minerals: A new method evaluated on Swedish agricultural soils (manuscript).

II  Eriksson, A.K., Hesterberg, D. and Gustafsson, J.P. (2015). Phosphorus speciation of clay fractions from long-term fertility experiments in Sweden. *Geoderma* 241-242, 68-74. doi:10.1016/j.geoderma.2014.10.023

III Eriksson, A.K., Hillier, S., Hesterberg, D., Klysubun, W., Ulén, B. and Gustafsson J.P. Evolution of phosphorus speciation with depth in an agricultural soil profile (submitted to *Geoderma*).

IV  Eriksson, A.K., Hesterberg, D., Klysubun, W. and Gustafsson, J.P. Phosphorus dynamics in Swedish agricultural soils as influenced by fertilisation and mineralogical properties: insights gained from batch experiments and XANES spectroscopy (manuscript).

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My contribution to paper I-IV included in this thesis was as follows:

Planned the experimental work together with the co-authors. Performed the practical laboratory work with assistance from co-authors. Performed data analysis and writing, with assistance from the co-authors.

# Abbreviations

| | |
|---|---|
| Al | Aluminium |
| BNL | Brookhaven National Laboratory |
| BL | Beamline |
| Ca | Calcium |
| COG | Centre of gravity |
| DOM | Dissolved organic matter |
| e.s.d. | Equivalent spherical diameter |
| Fe | Iron |
| Ha | Hectare |
| HIV | Hydroxy-interlayered vermiculite |
| K | Potassium |
| LCF | Linear Combination Fitting |
| Mg | Magnesium |
| N | Nitrogen |
| $NH_4$ | Ammonium |
| NMR | Nuclear Magnetic Resonance spectroscopy |
| NSLS | National Synchrotron Light Source |
| P | Phosphorus |
| P-HCl | Phosphorus digested in HCl |
| P-AL | Phosphorus extracted in ammonium lactate and acetic acid |
| PCA | Principal Component Analysis |
| $PO_4$ | Orthophosphate |
| $PO_4$-P | Orthophosphate phosphorus |
| PsTotP | Pseudo-total phosphorus |
| RIR | Reference Intensity Ratio |
| SLRI | Synchrotron Light Research Institute |
| XANES | X-ray Adsorption Near-edge Structure |
| XRD | X-ray Diffraction |
| Yr | Year |

# 1 Introduction

Phosphorus (P) is a macronutrient and an important element for crop production. Too little P may limit crop yield, whereas too much may promote P leaching and contribute to eutrophication of surface waters. Chemical fertilisers are a primary source of P in agricultural soils, but application of animal wastes to soil also contributes to build-up of P in soils. Apatite is commonly mined for use in fertiliser, but it is a non-renewable resource. Current reserves may be depleted in 50-100 years (Cordell *et al.*, 2009). In general, soil P management in crop production must be responsive both to crop needs and water quality protection.

The largest terrestrial source of P entering surface waters from Sweden is agricultural fields (Boesch *et al.*, 2006). Phosphorus in soil water occurs as inorganic orthophosphate ($PO_4$) ions (*e.g.* $H_2PO_4^-$, $HPO_4^{2-}$), as dissolved organic P or as inorganic or organic P bound to suspended colloids. Leachate from clay soils commonly contains a larger fraction of particulate P than leachate from coarse-textured soils (*e.g.* Djodjic *et al.*, 2004).

The plant availability of P is generally related to soil P solubility. The processes affecting soil P availability to the crop are not all fully understood. According to the established paradigm of soil P availability, P is most available to plants at neutral pH (Brady & Weil, 1999). However, many recent studies have shown that this paradigm does not hold for clay-rich soils and that in fact the P solubility in laboratory experiments is *lowest* at neutral pH (*e.g.* Gustafsson *et al.*, 2012; Devau *et al.*, 2011; Weng *et al.*, 2011). It has been suggested that this solubility behaviour may be due to the instability of hydroxy-aluminium (Al) polymers of clay mineral interlayers at low pH (Gustafsson *et al*., 2012), but this has not been confirmed. Furthermore, the roles of particle size distribution and fertilisation history in P availability are not clear (Gustafsson *et al.*, 2012).

Different sequential chemical extraction methods have commonly been used for P speciation (*e.g.* Hedley *et al.*, 1982; Williams *et al.*, 1967; Chang & Jackson, 1957). The current limited knowledge of P speciation in soils (despite many years of research on the topic) can be attributed to the lack of methods that permit direct identification of the various P-containing phases. However, in recent years Nuclear Magnetic Resonance (NMR) spectroscopy and X-ray Adsorption Near-edge Structure (XANES) spectroscopy have emerged as powerful techniques that allow more specific information regarding P speciation to be obtained (McLaughlin *et al.*, 2011). Correct characterisation of P speciation in soils is a challenge, not least due to the presence of many different P phases, such as organic P, calcium (Ca) and Al phosphates, and $PO_4$ adsorbed to iron (Fe) and Al (hydr)oxides. Nevertheless, for process-oriented modelling of $PO_4$ sorption/desorption in soils, it is essential to know which processes dominate. Another prerequisite for successful modelling is that the P dynamics of each individual P-containing phase must be sufficiently well known (*e.g.* Devau *et al.*, 2011; Weng *et al.*, 2011), and any interactions between phases in these multi-phase systems must be understood.

Clay mineralogy is important for studies of soil P chemistry for at least two reasons: (i) There may be a direct role of hydroxy-interlayered minerals in P sorption (as suggested by Gustafsson *et al.,* 2012); and (ii) variations in clay mineralogy in a pedon or among soils may be linked to a number of soil-forming processes that affect P chemistry (*e.g.* pH, weathering, formation of secondary solid phases *etc.*). However, clay mineral identification and quantification are subject to a number of analytical difficulties. One property that is particularly difficult to determine accurately and consistently from one soil to another is the amount of hydroxy-Al-interlayering.

# 2   Aims and hypotheses

The overall aim of this thesis was to investigate the sorption patterns and speciation of P in agricultural clay soils, in order to better understand the dynamics of P release from soils to waters (see review in Figure 1).

Specific objectives of the work were to:

1. Develop a new method to characterise hydroxy-interlayered clay minerals semi-quantitatively with regard to the amount and stability of interlayers.
2. Investigate P speciation in a clay-rich soil profile as influenced by mineralogical composition and soil-forming processes.
3. Evaluate changes in P speciation caused by long-term P fertilisation for a range of typical Swedish agricultural soils.
4. Study the pH dependence of sorption/desorption patterns (for the same soils).

The hypotheses tested were:

1. Soils with a large proportion of hydroxy-Al-interlayered clay minerals have higher P sorption capacity than those with a small proportion.
2. a) In clay soils with low P status, P is mainly sorbed to Al hydroxide phases;
b) In clay soils with high P status, P is bound to both Al and Fe (hydr)oxide phases;
c) Ca-bound P as apatite is only reactive in calcareous soils.
3. Apatite increases with depth in the soil profile as a result of its dissolution in the upper horizons during pedogenic weathering.

4.     The solubility of phosphate ($PO_4$) in Swedish agricultural clay soils is lowest at near neutral pH and increases with both increasing and decreasing pH.
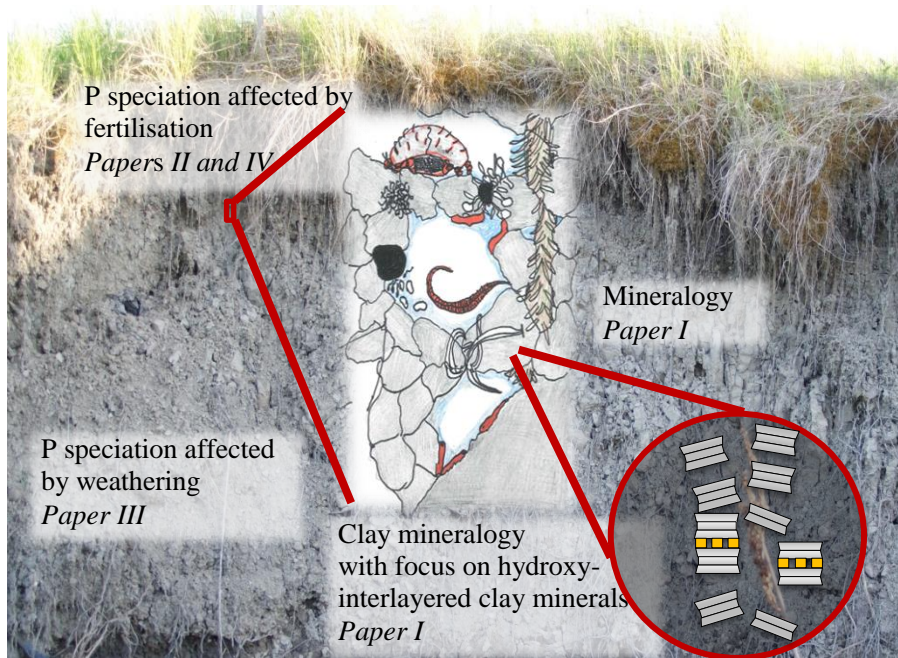


*Figure 1*. Illustration of how the different studies described in Papers I-IV in this thesis relate to each other (photo and drawing by A.K. Eriksson).

# 3 Background

## 3.1 Phosphorus in soils

Phosphorus in soils is present both in the solid phase of the soil matrix and in the soil solution. In the solid phase, P can be present as: (1) a constituent of primary and secondary minerals; (2) surface complexes on oxides [mainly Al- and Fe (hydr)oxides] and on clay minerals; and (3) organic forms. Adsorption/desorption is considered the single most important process controlling soil P solubilisation during the season. However, precipitation/dissolution of minerals and immobilisation/mineralisation of organic forms are also important (Pierzynski *et al.*, 2005). According to the conventional paradigm (*e.g.* Brady & Weil, 1999), at low soil pH $PO_4$ is adsorbed to Al- and Fe (hydr)oxides or precipitated as Al and/or Fe phosphates, whereas at higher pH $PO_4$ is mostly fixed as Ca phosphates. This paradigm states that $PO_4$ has its greatest solubility at neutral soil pH (pH 6-7), where solubility is defined as the concentration of soluble P after a given time. An overview of the different P forms and reactions in soils is provided in Figure 2.

### 3.1.1 Phosphorus in minerals

Phosphorus is present in both primary and secondary minerals. The weathering of primary minerals, and subsequent release of P, is usually a very slow process. Some examples of P-containing primary minerals are variscite, strengite and apatite. Secondary minerals occur predominantly as poorly crystalline precipitates, for example less crystalline Al, Fe and Ca phosphate minerals. The secondary mineral phases usually have a larger surface area than the primary minerals, and hence they are more reactive and more easily dissolved (Pierzynski *et al.*, 2005).
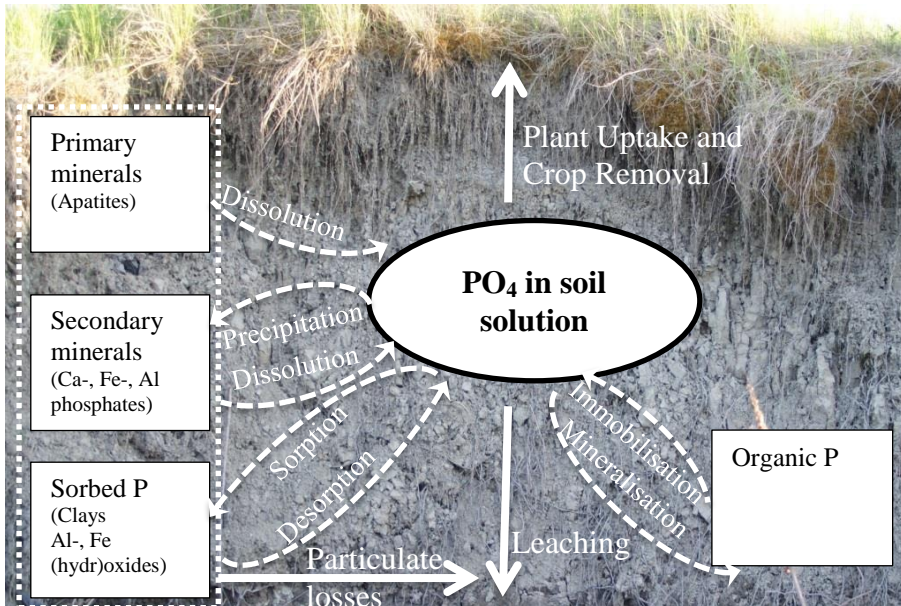
*Figure 2.* Pools and reactions of P in the soil system (modified from Pierzynski *et al.*, 2005; photo A.K. Eriksson).

### 3.1.2 Adsorbed phosphate

Phosphate is commonly adsorbed to Al and Fe (hydr)oxides, *e.g.* goethite, ferrihydrite, gibbsite and boehmite (Pierzynski *et al.*, 2005). Previous research indicates that amorphous Al-hydroxide and aluminosilicate phases are among the most important P-bearing particles (Pierzynski *et al.*, 1990) and may also control the solubility of inorganic P in soils (*e.g.* Cui & Weng, 2013).

A number of factors affect $PO_4$ adsorption, for example; (1) the variable charge properties of adsorption sites, which cause decreased $PO_4$ adsorption when the pH is increased (*e.g.* Antelo *et al.*, 2010; Hansen *et al.*, 1999); (2) the reaction time, as a prolonged reaction time will increase the quantity of adsorbed $PO_4$ (Hansen *et al.*, 1999); (3) competition for adsorption sites by *e.g.* organic acids (Oburger *et al.*, 2011), carbonate (Sø *et al.*, 2011) and, arsenate (Gustafsson *et al.*, 2012); and (4) the ionic strength, with increased ionic strength decreasing $PO_4$ adsorption at low pH, but increasing adsorption at high pH (Barrow, 2008; Barrow *et al.*, 1980).

The adsorption process is usually divided into two different types of reactions, one fast and one slow. Fast reactions dominate in the early stage (during the first minute) and are reversible. Slow reactions dominate in the later stages and are partly reversible (depending on the time scale for desorption). The slow reactions are probably due to slow diffusion of $PO_4$ into

the interior of Fe and Al (hydr)oxide precipitates (Strauss *et al.*, 1997; Willett *et al.*, 1988), but the mechanisms are not yet completely understood.

### 3.1.3 Organic P forms

Between 15 and 80 % of the P in the surface horizon of soils is usually present in organic forms, mainly originating from plant residues. Inositol phosphates (phytates), sugar phosphates, phospholipids and nucleic acids are the most frequently found organic P species. However, less than 50 % of the organic P in soil can be characterised into known compounds. Organic P is mainly found in the topsoil and decreases with soil depth (Stevenson, 1994).

## 3.2 Speciation of P in soils

Traditional techniques for determining P speciation in soils involve various extraction procedures, *e.g.* sequential extractions (*e.g.* Hedley *et al.*, 1982; Williams *et al.*, 1967; Chang & Jackson, 1957). However, extraction results are only indicative (at best), as they provide only indirect information about soil P speciation. It is probably impossible to design extraction procedures that target specific P forms.

A number of challenges are involved in measuring P in soils and especially P speciation (McLaughlin *et al.*, 2011). The heterogeneity of the soil material, with many different surfaces and minerals, gives a high matrix complexity, resulting in many different P species. For example, it has been shown that a particular form of extraction can release different kinds of P species in different soils (Kar *et al.*, 2011).

More recently, NMR (Leinweber *et al.*, 1997) and XANES (*e.g.* Beauchemin *et al.*, 2003; Hesterberg *et al.*, 1999) spectroscopy have been used. These techniques potentially represent a vast improvement over extractions, as they permit more direct identification of the species involved. With the XANES technique, it is possible to estimate the dominant P species in the soil by means of linear combination fitting (LCF), in which the spectra of known standards are compared against the spectrum of a specific soil sample (Kelly *et al.*, 2008).

The principle employed in XANES spectroscopy is that a sample is exposed to an X-ray beam and scanned across an energy range corresponding to the binding energy of core electrons (*e.g.* K-shell electrons) in atoms of the element of interest. A synchrotron X-ray beam of high intensity is used in XANES spectroscopy of soils to increase the analytical sensitivity. The high X-ray intensity causes excitation of the core electrons into the continuum and a core hole is formed in the orbital that the electron occupied. However, this is

an unstable state for the atom, and therefore one electron from a higher energy level drops down to the core hole, releasing fluorescence X-rays (or secondary electrons). The emitted fluorescence can be measured by a sensitive fluorescence detector, and the intensity of this radiation is proportional to the amount of absorbed X-rays, *i.e.* the energy-dependent absorption coefficient. The energy level at which K-shell electrons are excited corresponds to the so-called K edge of the element. For phosphorus, the K edge ranges between 2145 eV for elemental P and 2153 eV for P(V).

In a typical K-edge XANES experiment on soil P, the soil sample is exposed to the X-ray beam, the energy of which is varied from a level below the edge (usually about 2100 eV) to an energy level above the edge (in this case usually 2320 eV). The amount of absorbed energy is measured continuously as the fluorescence signal. The exact binding energy of the electron and variations in signals due to back-scattering of the excited electrons by surrounding atoms above the edge are affected by the oxidation state and molecular coordination environments of P atoms. Average absorption coefficients vary depending on the local molecular structure of the P species present, and hence different combinations of species will give rise to different spectra (Kelly *et al.*, 2008).

Franke & Hormes (1995) identified the properties giving rise to the different features of the K-edge XANES spectra for P. They found that phosphate associated with transition metal cations (*e.g.* Mn or Fe) shows a pre-edge resonance, while alkaline, alkaline earth and condensed phosphates (P bound to Ca, K or Na) show a wider peak base. They also found a high intensity of the so-called white line (the main absorption edge) in samples that contained ionic and covalently bound phosphates and a less intense white line for metal-bound phosphates.

McLaughlin *et al.* (2011) rated XANES spectroscopy as one of the best methods for direct speciation of inorganic P. However, the method offers very limited information on organic P species due to lack of sensitivity. Negassa & Leinweber (2009) suggested a combination of NMR and XANES spectroscopy for full information about P speciation. Kruse *et al.* (2009) also suggested the use of $L_{2,3}$-edge XANES spectroscopy, which seems to give more information about organic P species.

## 3.3 The pH dependence of $PO_4$ sorption/desorption in soils

As mentioned above, $PO_4$ is usually considered to be most readily dissolved at around neutral pH. However, a number of recent studies (*e.g.* Gustafsson *et al.*, 2012; Devau *et al.*, 2011; Weng *et al.*, 2011) have shown the opposite trend for

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clay soils, with the lowest P solubility near neutral pH. There are different explanations for these observations, *e.g*. (1) instability of hydroxy-Al polymers of clay mineral interlayers at low pH (Gustafsson *et al*., 2012); (2) interaction between $Ca^{2+}$ and metal oxides leading to increased P sorption, especially at high pH (Weng *et al.,* 2011); (3) adsorption of $Al^{3+}$ to organic material at lower pH, which removes P-adsorbing Al hydroxides or hydroxy-Al-interlayers (Gustafsson *et al.,* 2012; Weng *et al.,* 2011); and (4) competition between phosphate and organic matter for sorption surfaces.

However, it seems that other factors also have an effect. After long-term fertilisation, Gustafsson *et al.* (2012) found that the soluble $PO_4$-P increased. They also found that the solubilisation behaviour differed depending on whether the P was freshly added in the laboratory or in long-term experiments in the field, as a result of occlusion processes. Moreover, the P solubility was found to increase with decreasing pH for soils with > 20 % clay and to decrease with increasing pH for soils with < 10 % clay (Gustafsson *et al.*, 2012).

## 3.4 Clay mineralogy and effect on P sorption

Previous research has indicated that clay mineralogy is rather uniform on regional scale in Sweden. Illite is commonly the dominant mineral phase in the clay fraction, followed by vermiculite and chlorite (Wiklander, 1950). However, the county of Skåne in southern Sweden is an exception, as smectite-rich and kaolinite-rich soils are also frequently found in this area (Ahlberg *et al.*, 2003). Most clay fractions present in Swedish agricultural soils also contain large amounts of primary minerals, *e.g*. quartz (Kirchmann *et al.*, 2005; Stevens & Bayard, 1994; Wiklander, 1950).

The following hypotheses have been forwarded to explain the observed similarities on regional scale (Stevens & Bayard, 1994): (1) most clay soils originate from glacial and postglacial deposits; (2) the landscape formed after the glacial period was not eroded down to the bedrock, and therefore there is a limiting effect of the underlying rock type as a parent material; (3) long-range transport of minerals (including clay minerals) took place with ice-melt water; (4) the ice milled down pre-glacial exposed bedrock further north from which fine-grained primary mineral particles were produced and transported.

Penn *et al.* (2005) found that soils containing hydroxy-interlayered vermiculite (HIV) also commonly showed stronger $PO_4$ sorption. Hydroxy-interlayered vermiculite can be considered an intermediate between pure vermiculite and aluminium chlorite. It is commonly formed by deposition of hydroxy-Al polymers in the interlayer area of vermiculite or as a weathering

product of Al chlorite (Barnhisel & Bertsch, 1989). However, the presence of carbonate inhibits the weathering of clay minerals and the formation of these hydroxy-interlayers (Stevens & Bayard, 1994).

## 3.5   Research questions

It has been suggested that sorption of $PO_4$ onto hydroxy-interlayered clay minerals can explain the observed lowest P solubility at near neutral pH (Gustafsson *et al.*, 2012). Moreover, Penn *et al.* (2005) observed that soils containing hydroxy-interlayered clay minerals commonly had higher P sorption capacity than other soils. In order to obtain more knowledge about the effect of mineralogy, more information is needed. In this thesis XRD was used for this purpose, in collaboration with the James Hutton Institute, which has a well-established method for quantifying mineralogy and clay mineralogy (Omotoso *et al.*, 2006; Hillier, 2003; Hillier, 1999).

To the best of my knowledge, there is no simple way to estimate the proportion and stability of hydroxy-interlayered minerals. Heating is one way to quantify the amount of interlayering (Harris *et al.*, 1992). In this approach, XRD is used with an *in situ* heating stage that also prevents rehydration, which has otherwise been observed to affect quantification (Sayegh *et al.*, 1965). To estimate the influence of these clay minerals on the $PO_4$ sorption properties of the whole soil, an index to characterise the hydroxy-interlayering of the whole soil is needed. For comparison, minerals with different amounts of interlayering need to be synthesised in the laboratory. The results can then be compared with those for the clay fraction of soils.

To understand the differences in the pH-dependent sorption/desorption patterns of P in agricultural clay soils (Gustafsson *et al.*, 2012), more knowledge is needed about the P speciation in these soils. The XANES method seems to be the most prominent approach used to date for such analyses of inorganic phosphates. Using information about P speciation and mineralogy, pH-dependent P solubility and $PO_4$ adsorption can be studied. Gustafsson *et al.* (2012) showed for one soil that fertilisation may affect the pH-dependent solubility behaviour, which is further investigated in the present thesis.

Higher P content has been reported in the subsoil of agricultural soil profiles, but the origin of this P and how it may affect P leaching is not explained (*e.g.* Andersson *et al.*, 2015; Andersson *et al.*, 2013). To investigate this issue, in this thesis the P speciation in a soil profile was determined by XANES spectroscopy and the influence of minerological composition on P speciation was analysed by XRD.

# 4 Materials and Methods

## 4.1 Site description

### 4.1.1 Long-term fertility experiments

The Swedish long-term soil fertility experiments were initiated in the period 1957-1969 and comprise different fertilisation treatments and crop rotations (Carlgren & Mattsson, 2001). The samples used in this thesis were from six sites in southern and central Sweden, namely Fors, Kungsängen, Vreta Kloster, Bjertorp, Ekebo and Fjärdingslöv (Table 1). Soil was sampled from three different P and potassium (K) fertiliser application treatments: 'A', where no P and K were added; 'C', where P and K were applied to replace the amounts removed with the previous year's harvest plus a surplus of 20 kg P and 50 kg K ha$^{-1}$ yr$^{-1}$ (except for the Ekebo and Fjärdingslöv sites, where the surplus was 15 kg P and 40 kg K ha$^{-1}$ yr$^{-1}$); and 'D', where P and K were applied to replace the amounts removed with the previous year's harvest plus a surplus of 30 kg P and 80 kg K ha$^{-1}$. All samples were taken from a non-livestock crop rotation with the highest N fertiliser application rate ('3'), 125 kg N ha$^{-1}$ yr$^{-1}$ (150 N ha$^{-1}$ yr$^{-1}$ at Ekebo and Fjärdingslöv). Selected treatments in the soil fertility experiments have been investigated previously in the context of P studies, *e.g.* regarding speciation of organic P (Ahlgren *et al.*, 2013) and P leaching (e.g. Djodjic *et al.*, 2004; Svanbäck *et al.*, 2013). Temporal changes in P status in these experiments have also been investigated (Bergström *et al.*, 2015).

### 4.1.2 Lanna

Lanna is an experimental farm on the largest agricultural plain (Vara plain) in south-western Sweden (Table 1). The experimental farm was started in 1929 and the location was chosen to represent the conditions usually found on the Vara plain (Johansson, 1944). The soil profile shows an increase in P content with depth (Andersson *et al.*, 2015; Andersson *et al.*, 2013;

Mattson *et al.*, 1950) and is silty clay in the topsoil and clay in the subsoil. Both horizons have a strong coarse subangular blocky structure (Bergström *et al.*, 1994). The samples used in this thesis were collected in conjunction with the studies by Andersson *et al.* (2013) and Andersson *et al.* (2015). Previous investigations on P at this site have addressed the effects of liming on soil P (Mattson *et al.*, 1950), the influence on P losses of different soil management practices and cropping systems (Aronsson *et al.*, 2011; Neumann *et al.*, 2011), and the effects on P leaching of the chemical composition of the subsoil (Andersson *et al.*, 2015; Andersson *et al.*, 2013).

### 4.1.3 Bornsjön

Bornsjön is an experimental field situated in central Sweden (Table 1), on a soil of marine origin (Ulén *et al.*, 2014). The field is situated in a catchment area where research concerning P losses and P chemistry is carried out. The field experiment was established in 2006 to study the effect of different mitigation options for nutrient (primarily P) and pesticide leaching (Svanbäck *et al.*, 2014). Soil samples used in this thesis were taken from the topsoil in four plots with conventional tillage and conventional P fertilisation. The P added by fertilisation corresponded to the expected crop requirement in the current year. Previous studies at the site have examined the importance of subsoil conditions for P losses (Andersson *et al.*, 2015; Andersson *et al.*, 2013) and P retention in constructed wetlands (Kynkäänniemi *et al.*, 2013).

### 4.1.4 Lilla Böslid

Lilla Böslid is an experimental farm situated in south-western Sweden (Table 1). It is divided into two areas with experimental leaching plots. The experimental activities were initiated in 2002 (Aronsson *et al.*, 2011). The area contains both sandy and clayey soils. The samples used in this thesis originated from a clay loam soil. The leaching experiments were started in 2010, when mineral fertiliser was applied (supplying 21 kg P ha$^{-1}$ yr$^{-1}$).

### 4.1.5 20E

The 20E field is included in the Swedish environmental monitoring programme of single observation fields (Table 1). It belongs to a farm with pig production situated in south-eastern Sweden. The soil is managed according to conventional practices by the commercial farmer (Ulén *et al.*, 2012).

Table 1. *Coordinates and soil classification of the field experiments at different sites in Sweden from which samples were taken for this thesis. n.d.= not classified*

| Site | Coordinates | Soil taxonomy | Soil type |
|---|---|---|---|
| Fors | 60°20´N, 17°29´E | Calcaric Phaeozem[1] | Silt loam |
| Kungsängen | 59°50´N, 17°40´E | Gleyic Cambisol[1] | Clay |
| Vreta Kloster | 58°30´N, 15°30´E | Haplic Phaeozem[2] | Silty clay |
| Bjertorp | 58°14´N, 13°08´E | *n.d.* | Silty clay loam |
| Ekebo | 55°59´N, 12°52´E | Haplic Phaeozem[3] | Loam |
| Fjärdingslöv | 55°24´N, 13°14´E | Haplic Phaeozem[3] | Sandy loam |
| Lanna | 58°21´N, 13°07´E | Udertic Haploboroll[4] | Silty clay / clay |
| Bornsjön | 59°14´N, 17°41´E | Eutric Cambisol[5] | Silty clay |
| Lilla Böslid | 56°35´N, 12°56´E | *n.d.* | Clay loam |
| 20E | *n.d.* | *n.d.* | Clay |

[1]Kirchmann (1991)
[2]Kirchmann *et al.* (2005)
[3]Kirchmann *et al.* (1999)
[4]Bergström *et al.* (1994)
[5]Ulén & Persson, (1999)

## 4.2   Soil sampling and preparation

Samples of topsoil (0-20 cm) were collected using a core sampler (approx. 2 cm diameter) within a circle of 1 m in diameter and combined into 1-2 kg bulk samples. At the long-term fertility experiment sites, all samples were taken at least 0.5 m from the edge of the plots. The samples from the Lanna soil profile were collected from five different depths (0-10, 10-30, 30-50, 50-70 and 70-100 cm) at five different points along a linear transect of approximately 10 m. The five samples from each depth were mixed to form one bulk sample with approximately the same amount of soil from each sampling point. The samples were air-dried (approx. 30 ºC), sieved (2 mm) and stored under dry conditions until analysis.

Clay fractions (< 2 μm in equivalent spherical diameter (e.s.d.)) were separated from the soil samples by sedimentation according to Stokes' law. In brief, subsamples of 20 g soil were mixed with 200 mL water and treated twice with ultrasonic dispersion for 5 minutes. The suspension was stirred thoroughly with a spatula between the ultrasound treatments. The suspension was then transferred to a 1-L cylinder, mixed thoroughly and left to sediment for 16 h before the top 20 cm was siphoned off. The water level was then refilled and the sedimentation was repeated. The clay fraction suspension was freeze-dried and stored under dry conditions. The clay fraction samples used for oxalate

extraction and for K and magnesium (Mg) saturation were separated in the same way, but dried at approx. 30-40 °C.

## 4.3   General soil characterisation

The particle size distribution of soil samples was analysed by sieving and sedimentation analysis according to ISO 11277 (2009). A summary of the soil chemical characterisation methods used is provided in Table 2. Soil pH was measured using a Radiometer PHM93 pH meter with a GK2401C combination pH electrode in a suspension containing 6 g air-dried soil and 18 mL de-ionised water (1:3 soil:water). Organic carbon (OrgC) content was determined after combustion using a LECO CNS-2000 analyser (LECO, St Joseph, MI). Aluminium, Fe and P were extracted in ammonium oxalate according to van Reeuwijk (1995). The extract was filtered through a 0.2 µm single-use filter and diluted 1:5 in ultra-pure $H_2O$. The concentrations of Al and Fe in the extracts were analysed using ICP-OES on an ICP Optima 7300 DV instrument. The extractant is assumed to dissolve Fe phases with low crystallinity and surface-reactive Al, such as Al in organic complexes, allophane, imogolite, Al hydroxide and other forms of non- and paracrystalline inorganic Al. In this thesis, no effort was made to differentiate non-crystalline $Al(OH)_3$ from non- and paracrystalline Al silicates, such as allophane and imogolite; all are referred to as 'Al hydroxide'. The Al and Fe were also extracted in pyrophosphate where the extract was filtered through a 0.2 µm single use filter and diluted 1:5 in $H_2O$. The pyrophosphate extract was analysed using ICP-OES on a Perkin Elmer 5300 DV instrument. The extraction is assumed to dissolve organically bound Fe and Al, although it may also to some extent dissolve non- and paracrystalline inorganic phases (Kizewski *et al.*, 2011; Kaiser & Zech, 1996). A summary of these methods is provided in Table 2.

## 4.4   Mineralogy

### 4.4.1  Bulk soil mineralogy

Air-dried soil samples (< 2 mm) were micronised in ethanol (10 mL ethanol to 3 g air-dried soil) in a McCrone mill. The suspension was formed into a random powder by spray-drying (Hillier, 1999). The powder was packed into a metal holder and diffraction patterns were recorded with a Philips Xpert Pro diffractometer using Ni-filtered Cu Kα radiation. The XRD patterns were recorded from $2\theta = 3°$ to 70° by scanning in steps of 0.0167° and counting for 300 s per step. The recorded patterns were quantitatively analysed by full pattern fitting, as described in Omotoso *et al.* (2006). The group of clay

Table 2. *Methods used for general soil characterisation in this thesis*

| Method | Element | Soil (mg) | Solution (mL) | Solution specification | Reaction time | Measure-ment | Reference |
|---|---|---|---|---|---|---|---|
| P-AL | P | 5 | 100 | 0.1 M $NH_4$ lactate, 0.4 M acetic acid (pH 3.75) | 1.5 h | ICP | Egnér *et al.* (1960) |
| P-HCl | P | 2 | 50 | 2 M HCl | 2 h | ICP | KLS (1965) |
| Oxalate | P, Al, Fe | 1 | 100 | 0.2 M $NH_4$ oxalate (pH 3.0) | 4 h[1] | ICP[2] | van Reeuwijk (1995) |
| Pyro-phosphate | Al, Fe | 1 | 100 | 0.1 M $Na_2P_2O_7 \cdot 10H_2O$ | 16 h | ICP | |
| Pseudo-total P | Al, Fe | 3 | 30 | *Aqua regia* 3.95 M $HNO_3$, 9 M HCl | 2 h | ICP | ISO 11466 (1995) |

[1] In darkness

[2] $PO_4$ analysed colorimetrically according to Wolf & Baker (1990)

minerals used in this method included vermiculite, hydrobiotite, chlorite, illite, kaolinite and various types of mica/smectite mixed-layer clay minerals.

### 4.4.2 Clay mineralogy

Mounts of orientated clay fractions (<2 μm e.s.d.; see section 4.2) were prepared on glass slides using the filter transfer method (Moore & Reynolds, 1997). The XRD patterns were recorded on a Siemens D5000 diffractometer using Fe-filtered Co Kα radiation after air-drying, glycolation (ethylene glycol vapour solvation at 60 ºC) and heating (300 ºC for 1 h on a hotplate). Diffraction patterns were recorded from $2\theta = 3º$ to 45º by scanning in steps of 0.02º and counting for 1 s per step. The XRD patterns were analysed semi-quantitatively using a peak area-based reference intensity ratio (RIR) method (see Table 3) (Hillier, 2003). All measurements were made using the EVA DIFFRAC[plus] software (Bruker, 2005) and calculations based on RIRs were calculated in NEWMOD© (Reynolds, 1985).

### 4.4.3 Characterisation of hydroxy-interlayered minerals

All methods used to characterise the amount of hydroxy-interlayering rely on measurements of the decrease of the *d*-spacing (Å) with different treatments at the laboratory. Two existing methods for determining the amount of hydroxy-interlayering were used as references; both involve K- and Mg-saturation (Esser, 1990; Matsue & Wada, 1988). In this thesis work, two new methods were developed. The first is a simple method ranking the COG values of the clay fractions after K-saturation and heating.

Table 3. *Reference intensity ratio (RIR) values used for semi-quantitative analysis of clay minerals*

| Clay mineral | Peak position  (Å) | Peak order | RIR | Used trace |
|---|---|---|---|---|
| Kaolinite | 7.10 | 001 | 2.45 | Air-dried |
| | 3.58 | 002 | 1.70 | |
| | 2.38 | 003 | 0.12 | |
| Chlorite | 14.20 | 001 | 0.59 | Air-dried |
| | 7.10 | 002 | 3.32 | |
| | 4.72 | 003 | 0.81 | |
| | 3.52 | 004 | 1.77 | |
| Illite | 10.00 | 001 | 1.00 | Glycolated |
| Expandable minerals | 10.00 | 001 | 1.00 | Heated |

Clay fractions from soils and synthesised hydroxy-interlayered minerals were investigated by all described methods. The synthesised hydroxy-interlayered minerals were used to verify the amount of hydroxy-interlayering. In the second method, an *in situ* heating stage was used to assess the amount and stability of the hydroxy-interlayers. To evaluate these methods both vermiculite with synthesised hydroxy-interlayers and clay fractions from soils were investigated.

*Preparation of synthetic hydroxy-interlayered vermiculite*

Hydroxy-interlayered vermiculite can be synthesised from pure vermiculite using one of three different approaches: (1) The Al hydroxide polymer is prepared in a separate solution, which is mixed with the clay mineral to incorporate the aluminium polymer into the interlayer space (*e.g*. Carstea, 1968; Slaughter & Milne, 1960). (2) The clay mineral is saturated with an easily exchangeable cation, followed by ion exchange of aluminium ions and titration with sodium hydroxide to form polymers in the interlayer space (*e.g*. Janssen *et al.*, 1997; Rich, 1960; Sawhney, 1960). (3) The clay mineral is artificially weathered (using *e.g*. acid in a reaction chamber), resulting in the formation of hydroxy-interlayers from weathered Al (Mareschal *et al.*, 2009).

The second method was used because it was deemed more likely that the $Al^{3+}$ ion is able to enter the interlayer space to form aluminium polymers than for the formed aluminium polymers to diffuse into the interlayer space, both because of charge and size. The third method may lead to the formation of hydroxy-interlayers that not only contain aluminium polymers.

Synthetic hydroxy-interlayered minerals were prepared from pure trioctahedral vermiculite (<20 µm e.s.d; sample KL2 in the paper by Marwa *et al.*, 2009). First, vermiculite was sodium-saturated, and afterwards it was

loaded with two different levels of hydroxy-interlayers (0.032 and 0.67 mol Al kg$^{-1}$ vermiculite, respectively) according to the titration method described by Janssen *et al.* (1997).

*K and Mg saturation*

To detect hydroxy-interlayering in a sample, different pre-treatment steps were performed before XRD analysis. The samples were K- and Mg-saturated by adding 20 mL 1 M KCl or MgCl$_2$ to approximately 100 mg clay and equilibrating overnight. In the morning, the suspension was filtered (0.45 µm) and rinsed twice with the same amount of the saturating solution. The sample was then washed three times with 20 mL deionised H$_2$O and the clay fraction was mounted and analysed as described in section 4.4.2.

*In situ heating treatment*

The XRD patterns were recorded upon *in situ* heating using an Anton Paar XRK900 reaction chamber from 25 to 300 ºC in 25 ºC steps and from 300 to 550 ºC in 50 ºC steps.

*Method 1: Change in COG upon K saturation (using the Mg-saturated sample as a reference)*

This method was developed by Esser (1990) and quantifies the shift in COG (x-scale, *d*-distance (Å)) after K-saturation compared with an Mg-saturated reference sample (measured at room temperature). Instead of RIR values, a value of 0 is set at 9.5 Å, increasing to 1 at 15.5 Å. The calculation is as follows:

$$\Delta \bar{x}_{Mg-K} = \bar{x}_{Mg} - \bar{x}_K \qquad (1)$$

where $\bar{x}_{Mg}$ is the COG of the Mg-saturated sample (Å), $\bar{x}_K$ is the COG of the K-saturated sample (Å), and $\Delta \bar{x}_{Mg-K}$ is the difference between these (Figure 3a).

*Method 2: Intensity ratios of Mg- and K-saturated samples*

This index was developed by Matsue and Wada (1988) and is defined as:

$$I_K/I_{Mg} = \frac{(I_{14}/(I_{14}+I_{10}))_K}{(I_{14}/(I_{14}+I_{10}))_{Mg}} \qquad (2)$$

where $I_{14}$ represents the height of the 14 Å peak, $I_{10}$ is the height of the 10 Å peak, and the subscripts K and Mg denote the K-saturated and Mg-saturated

samples measured at room temperature, respectively. The ratio $I_K/I_{Mg}$ describes the resistance of the 14 Å peak of an Mg-saturated sample to collapse upon saturation with K (Figure 3b).

*Method 3: COG after K saturation and heating (300 ºC)*

This is a newly developed index, which is defined as the COG between 9.5 and 15.5 Å measured after K-saturation and heating to 300 ℃ on a hot plate (Figure 3c). This method was developed as a simple and quick method to characterise the amount of hydroxy-interlayering without any special equipment.

*Method 4: Changes in COG upon in situ heating (250 to 450 ºC)*

This new method was developed to get more precise characterisation of the hydroxy-interlayers (both amount and stability).

This index was measured on the *in situ* heated samples. It is divided into two different parts, describing (4a) the amount of hydroxy-interlayering; and (4b) the thermal stability of the hydroxy-interlayers. The first part is defined as the COG between 8 Å (approx. 11º 2θ) and 25 Å (approx. 3.5º 2θ):

$$x_{amount} = \bar{x}_{450℃} - 10.2Å \qquad (3)$$

where $x_{amount}$ represents the amount of hydroxy-interlayering, $\bar{x}_{450℃}$ is the COG at 450 ℃ and 10.2 Å is the reference (COG) value for a completely collapsed 2:1 mineral.

The second part of the index describes the thermal stability of the hydroxy-interlayers and is defined as the change in COG, $\Delta\bar{x}_{temp.}$, when the sample is heated from 250 ℃ to 450 ℃ (Figure 3d):

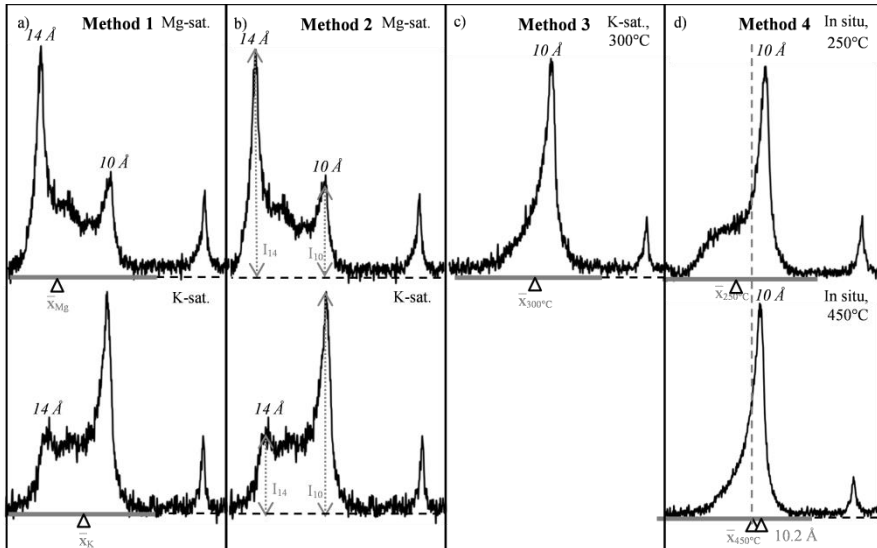$$\Delta\bar{x}_{temp.} = \bar{x}_{250℃} - \bar{x}_{450℃} \qquad (4)$$

*Figure 3.* Measurements to determine the amount of hydroxy-interlayered minerals in clay fractions according to: a) Esser (1990), comparing COG after K saturation with Mg saturation as a reference; b) Matsue & Wada (1988), using an intensity ratio comparing the intensities of the 14 Å peak ($I_{14}$) and 10 Å peak ($I_{10}$); c) a new index measuring centre of gravity after K saturation and heating and d) another new index measuring centre of gravity after *in situ* heating at 250 and 450 ºC. The horizontal (*x*) axis represents *d*-distance (Å), and the vertical axis the diffracted intensity.

## 4.5 Speciation of phosphorus

### 4.5.1 Clay fractions

Phosphorus K-edge XANES spectra of the clay fractions from the long-term fertility experiments were collected on Beamline X-15B at the National Synchrotron Light Source (NSLS), Brookhaven National Laboratory (BNL) in NY state, U.S. The data were collected using an Si(111) monochromator. Fluorescence signals were collected in a helium (He) atmosphere using a solid-state Ge-detector. To minimise the signal from silicon (Si) in the samples, the detector window was covered with an approx. 40 µm thick polypropylene film. A minimum of 13 and 9 scans was made for unfertilised and fertilised treatments, respectively. Baseline correction, normalisation and LCF analysis were carried out using the Athena Software (Athena v. 0.8.056 and Demeter v. 0.9.18; Ravel & Newville, 2005). Three sets of standards were used in the LCF analysis: (1) mineral samples from Ingall *et al.* (2011); (2) mineral standards, standards with adsorbed $PO_4$ and organic P standards from Hesterberg *et al.* (1999); and (3) mineral standards and standards with adsorbed phosphate from Eveborn *et al.* (2009). For the unfertilised treatments, a maximum of three

standards (selected as described in Paper II) was allowed in the fit. For the fertilised treatments, there was also a maximum of three standards, but the best-fit model spectrum generated for the unfertilised treatment was used as a mandatory standard which assumes that fertiliser may add new P species to the unfertilised soil P species.

### 4.5.2 Bulk soils

Phosphorus K-edge XANES spectra were collected at Beamline BL-8 at the Synchrotron Light Research Institute (SLRI) in Nakhon Ratchasima, Thailand, for the soil samples from the long-term soil fertility experiments and the bulk soil and clay fraction samples from the Lanna site. The data were collected using an InSb(111) crystal monochromator, and fluorescence signals were measured using a solid-state 13-element Ge detector. The sample was held in a He gas atmosphere. Baseline correction and normalisation were performed using the Athena software, version 0.9.020 (Ravel & Newville, 2005). LCF analysis was conducted using weighted combinations of 31 known standards (Figure 5), including amorphous calcium phosphate (ACP), octacalcium phosphate (OCP), three different natural apatites, synthetic hydroxyapatite, brushite, monetite, amorphous aluminium phosphate, phosphate adsorbed to aluminium hydroxide, phosphate adsorbed to gibbsite, variscite, amorphous iron phosphate, phosphate adsorbed to ferrihydrite, phosphate adsorbed to goethite, strengite, struvite, lecithin and phytate. In the topsoil sample of the unfertilized treatments, four standards were allowed in the fit, including lecithin and apatite (Taiba) as mandatory standards. For the fertilised treatments, a maximum of three standards was allowed, but the best-fit model spectrum generated for the unfertilised treatment was used as a mandatory standard to investigate the speciation of the P bound from added fertiliser.

The absolute fluorescence intensity, defined as the edge step in the XANES spectrum (Leri *et al.,* 2006), was compared to the amount of P as determined by different extractions (Figure 4). The most significant relationship ($r = 0.81$***) was found between P digestible in HCl (KLS, 1965) and the absolute fluorescence intensity. In principle, the X-ray fluorescence is directly related to the total concentration of sample P; however, a lower correlation was found for the fluorescence signal with pseudo-total P (measured as digestion with *aqua regia*; $r = 0.69$***) than with HCl digestion (Figure 4c).

a) b)

c) d)

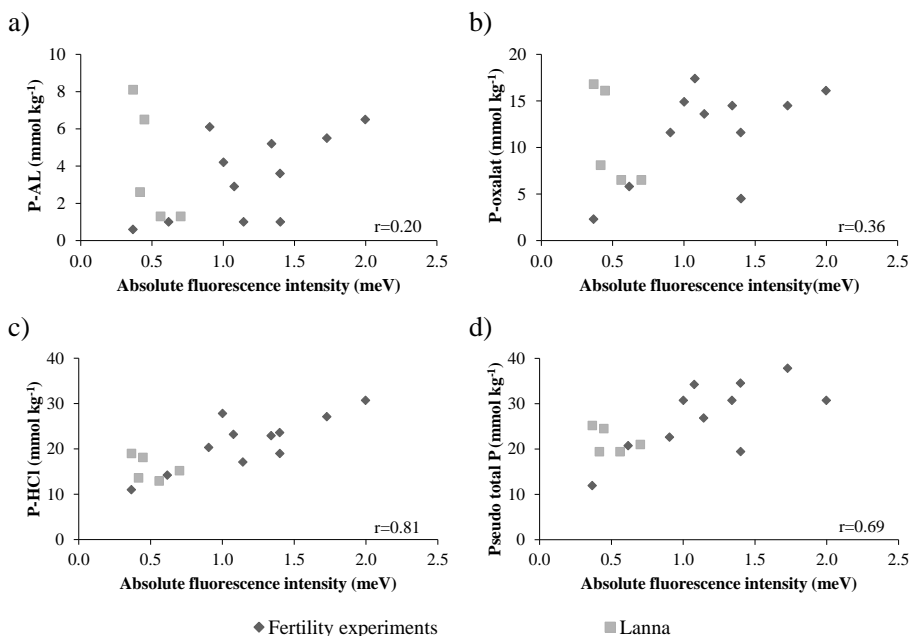◆ Fertility experiments     ■ Lanna

*Figure 4.* Scatter plots for correlations between absolute fluorescence intensity and a) P extracted with ammonium lactate, b) P extracted with oxalate, c) P solubilised by HCl digestion, and d) P solubilised by *aqua regia* digestion from samples included in the long-term fertility experiments (treatments A3 and D3) and the Lanna soil profile.

## 4.1 Solubility experiments

Batch experiments were carried out to determine pH-dependent P solubility from the soil samples by adding acid or base to soil samples at a rate ranging from 0.075 mol acid $kg^{-1}$ soil to 0.03 mol base $kg^{-1}$. The suspensions were equilibrated for 7 d in darkness on an end-over-end shaker. After centrifugation, the pH was measured in the supernatant, which was then filtered (0.2 µm) and analysed colorimetrically for molybdate reactive $PO_4$-P using a Tecator Aquatec 5400 spectrophotometer with flow injection analysis, based on the method by Murphy & Riley (1962). In addition, Ca, Al and Fe were determined using ICP-OES on an ICP Optima 7300 DV instrument.

To calculate the activity of free $Ca^{2+}$ and $PO_4^{3-}$, Visual MINTEQ ver. 3.1 software was used (Gustafsson, 2014). The solubility constants of various P-containing mineral phases used were those detailed by Gustafsson *et al.* (2012).

**Phosphorus-aluminium standards**
P adsorbed on Al hydroxide
P adsorbed on gibbsite
Amorphous Al-phosphate
Variscite AM5 US
Variscite US
Variscite UK
Wavellite

**Phosphorus-iron standards**
P adsorbed on ferrihydrite
P adsorbed on goethite
$FePO_4$
Amorphous Fe-phosphate
Vivianite
Strengite XL5
Strengite PXL
Strengite UK

**Calcium phosphates (except apatite)**
Octacalcium phosphate US
Octacalcium phosphate UK
Brushite
Monetite US
Monetite UK

**Apatites**
Apatite Taiba (carbonate apatite)
Hydroxyapatite
Apatite Templeton (hydroxyfluor apatite)
Apatite Gafsa (carbonate apatite)
Apatite UK

**Organic P standards**
Lecithin
Phytic Ca salt
Phytic Na salt
Phosphonate

**Other standards with NH$_4$, Mg and K**
K-taranakite
Struvite

*Figure 5.* XANES spectra for the standards used for LCF analysis.

2140  2145  2150  2155  2160  2165  2170  2175  2180  2185

## 4.2 Sorption experiments

Batch sorption isotherm experiments were also performed on the soil samples, to which $PO_4$ was added in a range from 0 to 0.0045 mol kg$^{-1}$. Equilibration and measurements were performed as described in section 4.6 at natural soil pH. Afterwards, pH was measured in the supernatant and $PO_4$-P was analysed colorimetrically (Seal Analytical AAS Autoanalyzer).

A Freundlich isotherm was fitted to the data:

$$n_{sorb} = K_F \cdot c^m - n_{init} \tag{5}$$

where $n_{sorb}$ represents the amount of $PO_4$ sorbed during the experiment, $n_{init}$ is the amount of $PO_4$ sorbed before the start of the experiment (mol kg$^{-1}$), $K_F$ and $m$ are coefficients that have to be optimised during the fitting process, and $c$ is the equilibrium concentration of total dissolved P (mol L$^{-1}$). Equation 5 can be logarithmically transformed to:

$$\log n = \log K_F + m \cdot \log c \tag{6}$$

where $n = n_{init} + n_{sorb}$. This equation is linear, where $m$ is the slope and $\log K_F$ the intercept. In this thesis, the value of $m$ was set to 0.33 as suggested by Tolner & Füleky (1995). This was shown to give values of $n_{init}$ comparable with isotopically exchanged P. Values of $\log K_F$ and $\log n$ were determined after adjusting $n_{init}$ to the best fit as judged by the R$^2$ value.

# 5 Results

## 5.1 Mineralogy (Paper I)

### 5.1.1 Bulk soil mineralogy

The results of the quantitative bulk mineralogical analysis are shown in Table 4. A finding in common for all soil samples was that more than 40 % of the mineral soil consisted of quartz, plagioclase and K-feldspar. Quartz was the single most common mineral in all soils. Only one of the soils, Fors, had a substantial amount of calcite.

Table 4. *Bulk fine earth(<2 mm) topsoil mineralogy in soil samples (% of bulk soil) of Swedish field experiments, analysed by full XRD pattern fitting after micronising and spray drying*

|  | Quartz | Plagioclase | K-feldspar | Calcite | Amphibole | Iron oxides | Clay minerals[1] |
|---|---|---|---|---|---|---|---|
|  | | | | *(% of bulk soil)* | | | |
| Fors | 30 | 18 | 14 | 6.4 | 3.4 | 2.0 | 15 |
| Kungsängen | 17 | 14 | 11 | n.d.[2] | 2.9 | 3.8 | 34 |
| Vreta Kloster | 32 | 14 | 12 | n.d.[2] | 2.2 | 2.6 | 23 |
| Bjertorp | 33 | 18 | 16 | n.d.[2] | 2.6 | 2.7 | 15 |
| Ekebo | 48 | 14 | 14 | n.d.[2] | 1.7 | 1.1 | 11 |
| Bornsjön | 18 | 15 | 12 | n.d.[2] | 2.9 | 3.7 | 32 |
| Lilla Böslid | 24 | 21 | 17 | n.d.[2] | 3.2 | 2.6 | 17 |
| 20E | 21 | 13 | 11 | n.d.[2] | 2.4 | 3.6 | 31 |

[1] Including chlorite, muscovite, biotite, hydrobiotite, vermiculite, illite, mixed layer minerals with illite/smectite and kaolinite.
[2] Not detected.

## 5.1.2  Clay mineralogy

All soils had a high content of expandable minerals (> 50 %), especially the soil from Fjärdingslöv, for which a high content of smectite was observed. The clays also commonly had a high content of mica/illite (> 20 %), except for the sample from Fjärdingslöv. The soils had a low content of kaolinite (< 5 %) with the exception of Ekebo, which had a content of 20 % (Table 5).

Most of the samples showed an increase in d-spacing of the 14 Å peak after ethylene glycol solvation, which is an indication of low layer charge (Brindley & Brown, 1980). However, the d-spacing did not increase in Ekebo, Bjertorp and Lilla Böslid, soils that contained obvious hydroxy-interlayers.

## 5.1.3  A new index to characterise hydroxy-interlayered minerals

*Clay mineral response to increased heating*

As a starting point for evaluation of the heating effects, the response of synthetic hydroxy-interlayered vermiculite was investigated. Below 100 ºC, the pure vermiculite had a d-spacing of 14.4 Å, consistent with two layers of water molecules in the interlayer. Between 100 and 200 ºC this decreased to a d-spacing of 11.8 Å, corresponding to one layer of water molecules. Above 200 ºC the peak collapsed to 10 Å, consistent with a completely dehydrated interlayer.

Table 5. *Semi-quantitative XRD analysis of parallel oriented clay mineral specimens prepared by the filter transfer method (% of clay fraction, <2 μm) from topsoil samples*

|  | Kaolinite | Chlorite | Mica | Expandable minerals[1] |
|---|---|---|---|---|
|  |  | *(% of clay fraction)* |  |  |
| Fors | 2 | 3 | 44 | 51 |
| Kungsängen | 1 | 3 | 40 | 56 |
| Vreta Kloster | 4 | 1 | 23 | 73 |
| Bjertorp | 4 | *n.d.*[2] | 27 | 69 |
| Ekebo | 20 | *n.d.*[2] | 23 | 57 |
| Fjärdingslöv | 6 | *n.d.*[2] | 8 | 86 |
| Bornsjön | 1 | 2 | 25 | 71 |
| Lilla Böslid | 4 | 3 | 36 | 60 |
| 20E | 3 | 2 | 41 | 54 |

[1]Including minerals that contract from 14 to 10 Å upon heating, *e.g.* smectite, vermiculite, hydroxy-interlayered minerals and mixed layer illite-smectite minerals.

[2]Not detected.

In contrast to the stepwise contraction of synthetic HIV, in natural clay fractions with hydroxy-interlayers there was a progressive movement of the peak towards 10 Å with increasing temperature. The collapse to 10.3-10.4 Å was not achieved until heating to 500 ℃. In the remainder of this thesis, the resistance to collapse is described by the term 'stability'. As discussed by Tolpeshta *et al.* (2010), there is no single definition of the term stability, as it has been used to describe the response to a multitude of treatments, such as displacement by cations, added dissolving reagents, heating or ageing. Here, the term relates to thermal stability, and a certain degree of stability (*i.e.* resistance to collapse upon heating) was observed in all soils, indicating some hydroxy-interlayering.

There are different ways to describe the amount of hydroxy-interlayering in the soil: (1) Determining the amount of hydroxy-interlayers in a specific clay mineral; (2) determining the amount of hydroxy-interlayered mineral in the clay fraction (<2 μm e.s.d.); and (3) determining the amount of hydroxy-interlayering in the bulk soil. However, the mixture of minerals makes it impossible to identify the amount of hydroxy-interlayers in each specific mineral. In this thesis the amount of hydroxy-interlayering in the clay fraction (2) was estimated.

*Methods 1 and 2: Prior indices based on Mg and K saturation*

Methods 1 and 2 showed similarities when ranking the amount of hydroxy-interlayering. Both methods identified the Ekebo sample as that with the highest amount of hydroxy-interlayering, followed by Lilla Böslid and Bjertorp. The Vreta Kloster sample had the lowest amount of hydroxy-interlayering. The samples from Fors and Kungsängen also had low amount of hydroxy-interlayering. For the samples from Fjärdingslöv and 20E, the results differed depending on the method. A summary of the results obtained is presented in Table 6.

*Method 3: COG after K saturation and heating*

Method 3 was clearly correlated with Method 1 ($r = 0.81**$), but not with Method 2. An even better match ($r = 0.96*$) was found with Method 1 when only the samples containing obvious amounts of hydroxy-interlayers were considered (Ekebo, Lilla Böslid, Bjertorp and Fjärdingslöv).

*Method 4: Change in COG upon in situ heating*

This new method based on measurement of COG at 450 ℃ *in situ* heating showed a clear correlation with Method 3 ($r = 0.94***$ for clay samples originating from soil). There was also a strong correlation with Method 1

($r = -0.78*$) and Method 2 ($r = 0.84***$). According to Method 4, all clay fractions had a higher amount of hydroxy-interlayering than the pure vermiculite. The samples were therefore grouped into: (1) clay fractions containing obvious amounts of hydroxy-interlayers (Ekebo, Lilla Böslid, Bjertorp and Fjärdingslöv); and (2) clay fractions with only small amounts of hydroxy-interlayers (Vreta Kloster, Fors, Kungsängen, 20E and Bornsjön) (Figure 6). A relationship between the amount of hydroxy-interlayering and soil pH was also found, with more hydroxy-interlayering at lower pH ($r = -0.75*$ with the calcareous Fors soil with pH>7.7 excluded). Thermostability was defined as the difference between the COG at 450 and 250 ºC. For the clay fractions originating from the soil samples, a strong correlation was found between the stability and the amount of hydroxy-interlayering ($r = 0.97***$). For synthetic samples with different amount of hydroxy-interlayering, there were no clear differences in stability between the samples. However, some soils with a lower amount of hydroxy-interlayering also had higher stability, which may be related to the proportions of hydroxy-interlayers that contract rather than to the properties of the hydroxy-polymers.

Table 6. *Determination of the amount of hydroxy-interlayering with different methods*

| | Method 1: Esser (1990)[1] | Method 2: Matsue & Wada (1988)[2] | Method 3: COG as K-sat and heated to 300 °C (Å) | Method 4a: Amount as COG at 450 °C[3] (Å) | Method 4b: Stability as change in COG[4] (Å) |
|---|---|---|---|---|---|
| HIV + 0 mol Al kg$^{-1}$ | | | 11.24 | 0.15 | 0.15 |
| HIV + 0.032 mol Al kg$^{-1}$ | | | 11.43 | 0.93 | 0.59 |
| HIV + 0.67 mol Al kg$^{-1}$ | | | 11.93 | 1.52 | 0.67 |
| Fors | 22.9 | 0.35 | 10.51 | 0.23 | 0.09 |
| Kungsängen | 24.5 | 0.30 | 10.48 | 0.16 | 0.07 |
| Vreta Kloster | 35.1 | 0.12 | 10.54 | 0.37 | 0.17 |
| Bjertorp | 21.6 | 0.52 | 10.47 | 0.65 | 0.41 |
| Ekebo | 9.9 | 0.91 | 11.26 | 1.97 | 0.88 |
| Fjärdingslöv | 25.7 | 0.67 | 10.63 | 0.63 | 0.46 |
| Bornsjön | 27.7 | 0.29 | 10.45 | 0.10 | 0.04 |
| Lilla Böslid | 15.6 | 0.54 | 10.60 | 0.90 | 0.48 |
| 20E | 21.4 | 0.15 | 10.41 | 0.37 | 0.27 |

[1]See equation 1: A low value of the Esser index indicates a large amount of hydroxy-interlayering, whereas for the other methods, low values indicate a small amount of hydroxy-interlayering
[2]See equation 2
[3]See equation 3.
[4]See equation 4: A low value of the change in stability indicates a large termostability of the hydroxy-interlayers.
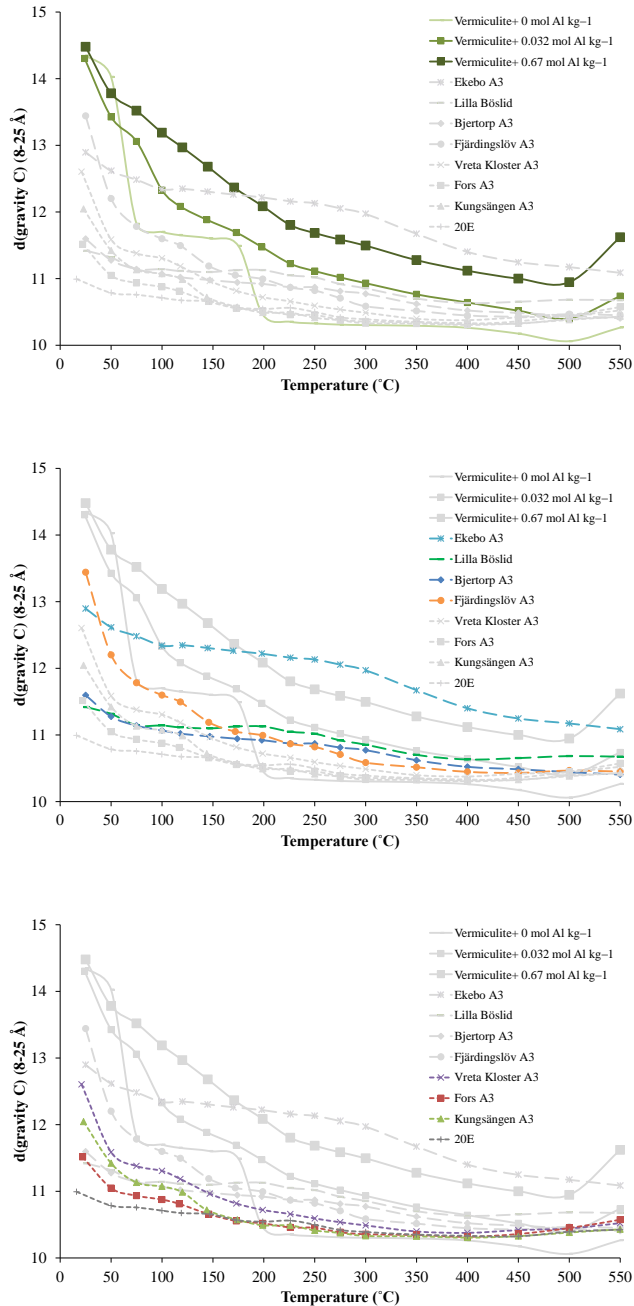
*Figure 6.* Hydroxy-interlayered vermiculite (HIV) index (Method 4) for pure vermiculite, synthetic HIV and clay fractions from soil samples.

Oxalate extraction of the clay fractions from the soils originating from the unfertilised treatments in the long-term fertility experiments was used as a complementary method for determining the amount of hydroxy-interlayering. A strong correlation ($r = 0.95$***) was found between the amount of hydroxy-interlayering (Method 4a) and oxalate-extractable Al (ranging between 2.18 to 7.49 mg kg$^{-1}$ clay fraction). However, the extraction did not affect the samples to an extent that was visible by XRD.

## 5.2 The effect of weathering and soil development, an example from Lanna (Paper III)

### 5.2.1 Mineralogy affected by weathering

The Lanna soil consisted of 60 – 70 % quartz, plagioclase and K-feldspar, and the mineral composition was largely consistent throughout the profile (Table 7). There was also a significant proportion of clay minerals (between 21 and 33 %). The profile had a higher content of amphibole and iron oxides in the subsoil than the topsoil. The clay content and pH also increased with depth.

When evaluating the clay fraction, the topsoil was found to contain a relatively large proportion of mica/illite, whereas enrichment of expandable minerals was observed in the subsoil. Kaolinite was found in small amounts in the profile, and no chlorite was detected. The minerals in the topsoil showed somewhat higher resistance to collapse upon heating, which is an indication of more extensive hydroxy-interlayering (Table 8). However, the clay fraction of the topsoil was also rich in quartz and feldspar.

Table 7. *Bulk soil mineralogy of the Lanna soil as determined by XRD after spray drying*

| Depth | Quartz | Plagioclase | K-feldspar | Amphibole | Iron oxides | Clay minerals[1] |
|---|---|---|---|---|---|---|
| | | | *(% of bulk soil)* | | | |
| 0-10 cm | 31 | 22 | 20 | 1.9 | 2.3 | 23 |
| 10-30 cm | 30 | 22 | 20 | 1.8 | 2.4 | 24 |
| 30-50 cm | 21 | 22 | 19 | 1.9 | 3.0 | 33 |
| 50-70 cm | 21 | 23 | 20 | 2.3 | 3.1 | 31 |
| 70-100 cm | 22 | 23 | 19 | 2.5 | 2.7 | 31 |

[1]The value in this column includes patterns of chlorite, muscovite, biotite, hydrobiotite, vermiculite, illite, mixed layer minerals with illite/smectite and kaolinite

Table 8. *Clay mineralogy and index for the amount of hydroxy-interlayering (Method 3) in samples from the Lanna soil profile*

| Depth | Kaolinite | Chlorite | Mica/illite | Expandable minerals | COG K-sat 300°C |
|---|---|---|---|---|---|
| | | *(% of clay fraction)* | | | *(Å)* |
| 0-10 cm | 2 | *n.d.* | 23 | 75 | 10.5 |
| 10-30 cm | 3 | *n.d.* | 21 | 76 | 10.4 |
| 30-50 cm | 2 | *n.d.* | 17 | 81 | 10.2 |
| 50-70 cm | 3 | *n.d.* | 14 | 83 | 10.2 |
| 70-100 cm | 3 | *n.d.* | 16 | 81 | 10.2 |

### 5.2.2 Phosphorus speciation affected by soil development

The P speciation was determined by LCF analysis of the XANES spectra. The results shown in Figure 7 present the best fits for each sample. There was a clear trend for increasing amount of apatite with increasing depth in the soil profile, from 15 % in the topsoil to 86 % in the 70-100 cm layer. By contrast, a decreasing percentage of $PO_4$ adsorbed to Al hydroxides was found, with 55 % and 14 % of the P in the topsoil and 70-100 cm layer, respectively.

Organically bound P was found in the topsoil. The standard that best described organic P was lecithin, a diester organic P. The P speciation fitting results for the clay fraction indicated that the topsoil was enriched in Al-hydroxide-bound P and organic P relative to the bulk soil. In contrast, fits for the subsoil showed relative depletion of apatite in the clay fraction compared with the bulk soil, which may indicate preferential weathering of apatite from the finer fractions.
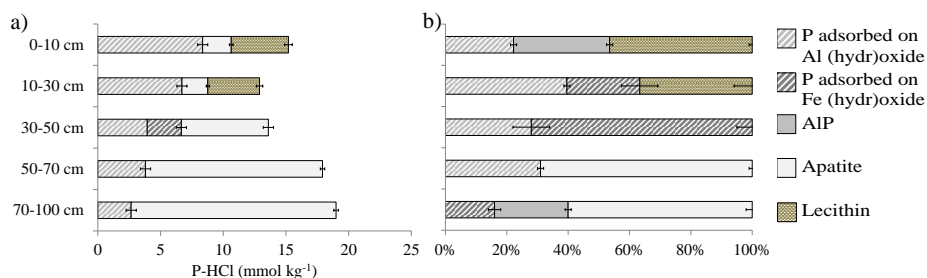


*Figure 7.* Phosphorus speciation in: a) the bulk soil (mg P kg^{-1} HCl-digestible P) and b) the clay fraction (% of total P) in the Lanna soil profile.

### 5.2.3 Phosphorus solubility patterns affected by soil development

The batch experiments showed that the solubility of $PO_4$ in the Lanna soil increased with decreasing pH in samples from all horizons. The lowest dissolved $PO_4$ concentrations were observed between pH 5.5 and pH 7, depending on the horizon. The topsoil had a higher $PO_4$ solubility and a relatively low pH at which the minimum P solubility was observed (Figure 8).

Furthermore, the solubility of Ca, Al and Fe increased with decreasing pH, but for the topsoil the solubility of Fe and Al increased above pH 5 and 6, respectively. This may be explained by an increase in dissolved organic matter (DOM) containing dissolved Fe(III)- and Al-organic complexes at higher pH (Gustafsson & van Schaik, 2003). Using the Visual MINTEQ software (Gustafsson, 2014), it was shown that the samples from the 50-70 and 70-100 cm horizons were supersaturated with respect to hydroxyapatite at natural pH (no acid or base added) and also at higher pH, whereas the samples from the surface horizons were undersaturated (Figure 9). This suggests that the apatite in the surface horizons is thermodynamically unstable and likely to dissolve.
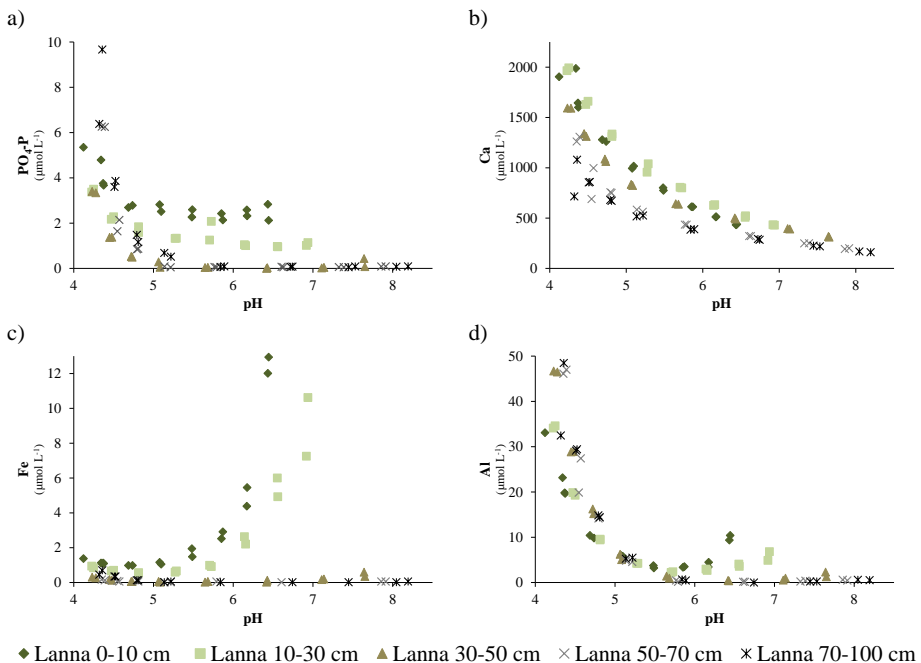


◆ Lanna 0-10 cm ■ Lanna 10-30 cm ▲ Lanna 30-50 cm ✕ Lanna 50-70 cm ✷ Lanna 70-100 cm

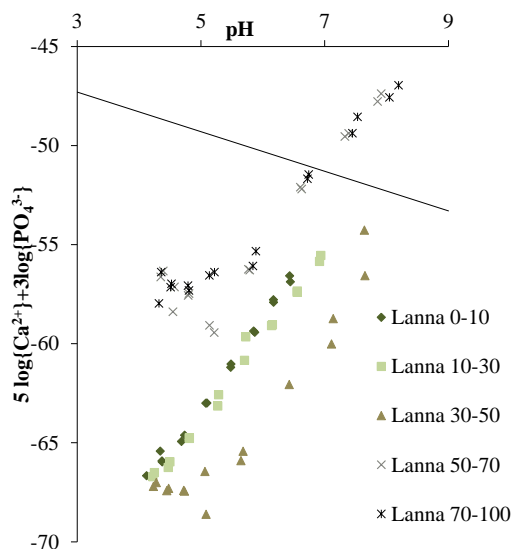*Figure 8.* Solubility patterns of: a) $PO_4$, b) Ca c) Fe and d) Al as influenced by pH for the Lanna soil.

*Figure 9.* Stability diagram for the equilibrated suspensions of the pH-dependent sorption experiment. The points represent the calculated solution activities in Visual MINTEQ. The solubility line for hydroxyapatite was calculated from the solubility constant given in Visual MINTEQ (log $*K_s$ = -44.3 at 25$^o$C). Data points above the line indicate supersaturation.

## 5.3 Phosphorus speciation affected by long-term fertilisation (Papers II and IV)

The overall XANES signal was found to be most closely related to the HCl-extractable P in the soil (`P-HCl´; Paper IV). Therefore Figure 10a and 11a present the different P species relative to this fraction.

### 5.3.1 Phosphorus speciation in soils and clay fractions with no added phosphorus

The LCF analysis of the unfertilised samples showed that the P speciation differed between soil samples from different field sites (Figure 10). All bulk soils contained organic P, but only three of the clay fractions indicated appreciable amounts of organic P and no significant correlation was found between organic carbon and organic P ($r$=0.77 n.s.). However, the three soils that were relatively high in organic C also had organic P in the clay fraction. All bulk soils except the sample from Ekebo contained apatite or some other form of calcium phosphate. For the former, a strong positive relationship was observed between the fitted proportions of calcium phosphates (including apatite) and pH ($r$=0.97***). With LCF, calcium phosphates were identified also in the clay fractions except for Fjärdingslöv. Aluminium or Fe phosphate

mineral phases were not detected by LCF in any of the samples. In the bulk soils, most of the $PO_4$ adsorbed to metal oxides had been adsorbed to Al hydroxides, and a minor part to Fe (hydr)oxides. It was more difficult to differentiate between adsorbed P to the different metal (hydr)oxides in the clay fractions, which may be a result of the noisier data obtained at NSLS. In the clay fractions from Kungsängen, Bjertorp and Ekebo, fitting indicated P adsorbed to Fe oxides. In soils with more than 35 mmol kg$^{-1}$ oxalate-extractable Fe, a major proportion of P was adsorbed to Fe (hydr)oxides in the clay fraction. A strong correlation was observed between the ratio of oxalate-extractable Al to Fe and the amount of P adsorbed to Al hydroxides in the clay fraction ($r$=0.92**). For all bulk soils except Ekebo, there was a significant contribution of P adsorbed to Fe oxides. A correlation was found between the amount of P adsorbed to Al- and Fe (hydr)oxides and the suggested index for hydroxy-interlayering (Method 1a, clay content; r=0.84*). For the clay fractions, there was also a correlation between PsTotP and the amount of calcium phosphates ($r$=0.89*).

### 5.3.2 Phosphorus speciation in soils and clay fractions after long-term fertilisation

In both bulk soil and clay fractions, K-edge XANES fitting results indicated that Al-bound P was important for sorption of P added by fertilisation (Figure 11). However, in two of the soils (Vreta Kloster and Fjärdingslöv), part of the added P appeared to be precipitated as apatite, and in three soils (Kungsängen, Vreta Kloster and Bjertorp) adsorption to iron oxides was also important.
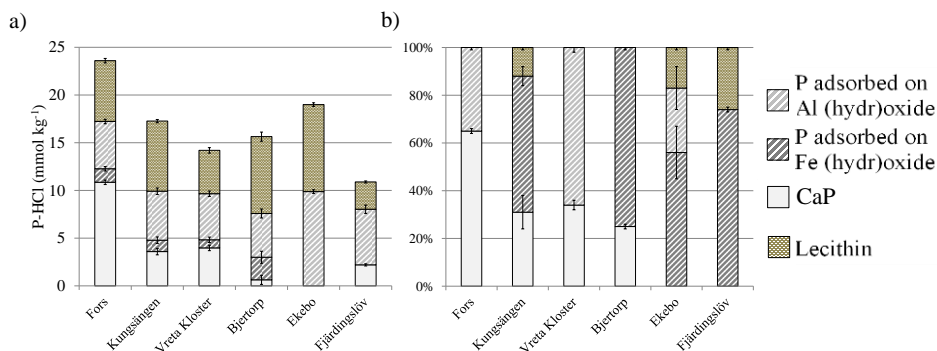


*Figure 10.* Speciation of P in: a) bulk soils (mg P kg$^{-1}$ HCl-digestible P) and b) clay fractions (%) from the unfertilised treatment (A3) of the six long-term fertility experiment sites.

## 5.4 Dissolved phosphate as affected by long-term fertilisation (Paper IV)

The pH dependence of the $PO_4$ solubility was different for P-depleted and P-fertilised soils (Figures 12-14). In the unfertilised soils, there was a clear increase in the $PO_4$ solubility with decreasing pH (Figure 13). In the fertilised soils, a greater dissolved P concentration was found. In some cases (Bjertorp, Kungsängen, Ekebo), the effect of pH on $PO_4$ solubility was small and/or inconsistent. The inconsistency agrees with observations by Gustafsson *et al.* (2012), who attributed it to different pH-dependent behaviour for desorption of native soil $PO_4$ (increasing with decreasing pH) and desorption of recently added $PO_4$ (decreasing with decreasing pH).

However, in the Fjärdingslöv and Vreta Kloster soils, a similar or stronger trend of dissolved P increasing with decreasing pH after fertilisation was found, with minimum dissolved P occurring at pH ~7 (Figure 14). At neutral soil pH, most of the soils were undersaturated with respect to hydroxyapatite. The exception was Fors, for which both the unfertilised and fertilised soils were supersaturated (Figure 12). For the fertilised soils from Vreta Kloster and Fjärdingslöv, the degree of undersaturation was relatively small, which may indicate apatite dissolution.
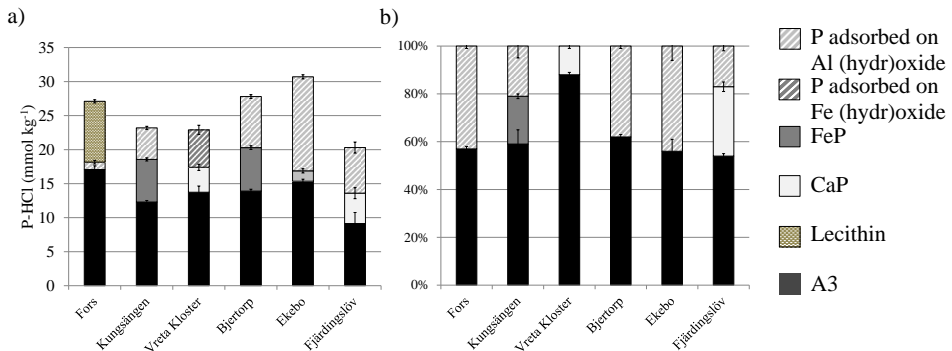


*Figure 11*. Speciation of P in: a) bulk soils (mg P kg$^{-1}$ HCl-digestible P) and b) clay fractions (%) from the fertilised treatment (D3) of the six long-term fertility experiment sites. A3 is the P content from the unfertilised treatment.
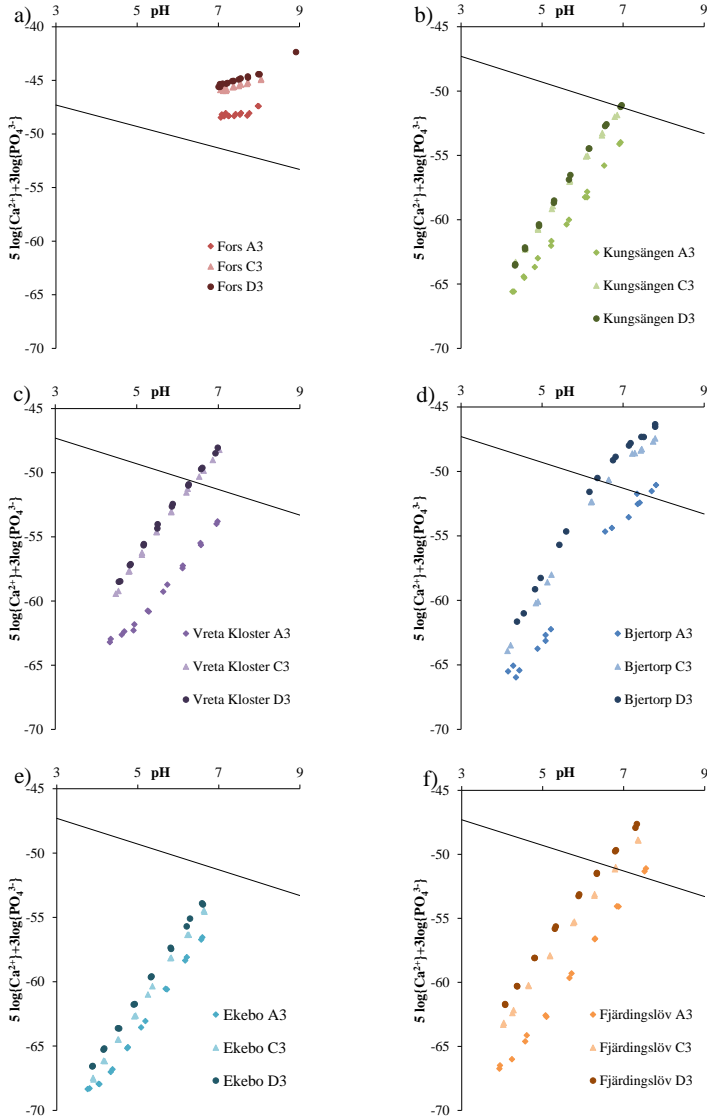
*Figure 12.* Stability diagrams for the equilibrated suspensions of the pH-dependence experiment for a) Fors, b) Kungsängen, c) Vreta Kloster, d) Bjertorp, e) Ekebo and f) Fjärdingslöv. `A3´ represents the unfertilised treatment, `C3´ and `D3´ fertilised treatments with addition of surplus P + 15/20 kg and 30 kg, respectively. The points represent the calculated solution activities in Visual MINTEQ. The solubility line for hydroxyapatite was calculated from the solubility constant given in Visual MINTEQ (log $*K_s$ = -44.3 at 25°C). Data points above the line indicate supersaturation.

The XANES results (Figure 11) also showed that apatite had accumulated in these two soils as a result of fertilisation. In other words, the increased solubility of the Vreta Kloster and Fjärdingslöv soils could result from apatite formation in response to high P fertilisation (Figures 13 and 14). As the apatite formed is unstable at low pH, it may have dissolved (although not at equilibrium), creating the pH-dependent solubility behaviour shown in Figure 15. However, the possibility cannot be entirely excluded that the results are attributable to weathering of apatite originally present in the P-depleted (unfertilised) treatment, whereas the apatite was more resistant to solubility in the fertilised treatment.
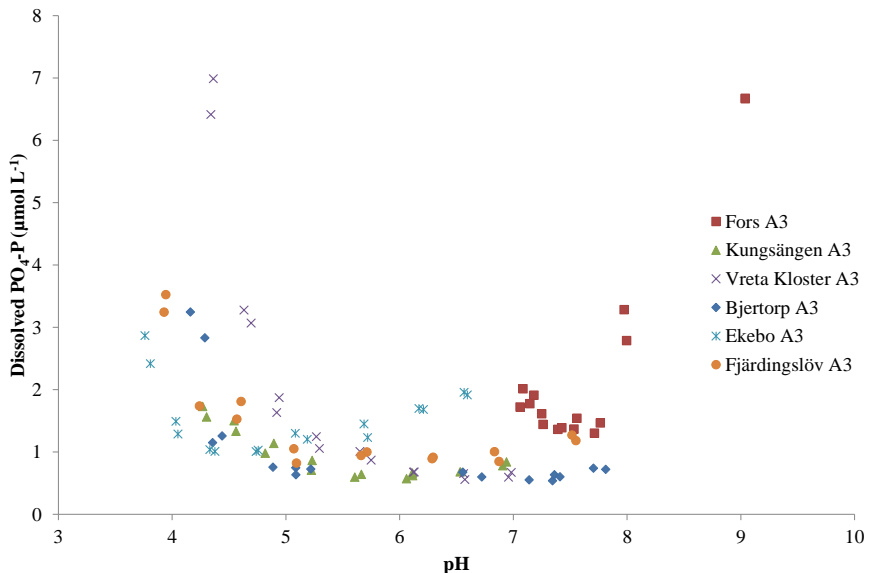


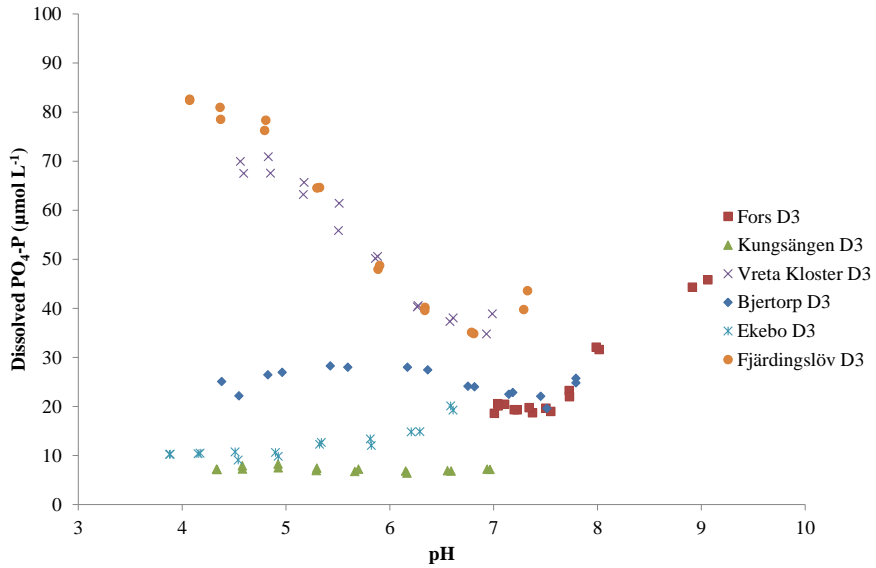*Figure 13.* pH-dependent solubility of PO$_4$-P in the unfertilised soils from the long-term fertility experiments.

*Figure 14.* pH dependent-solubility of PO$_4$-P in the fertilised soils from the long-term fertility experiments.
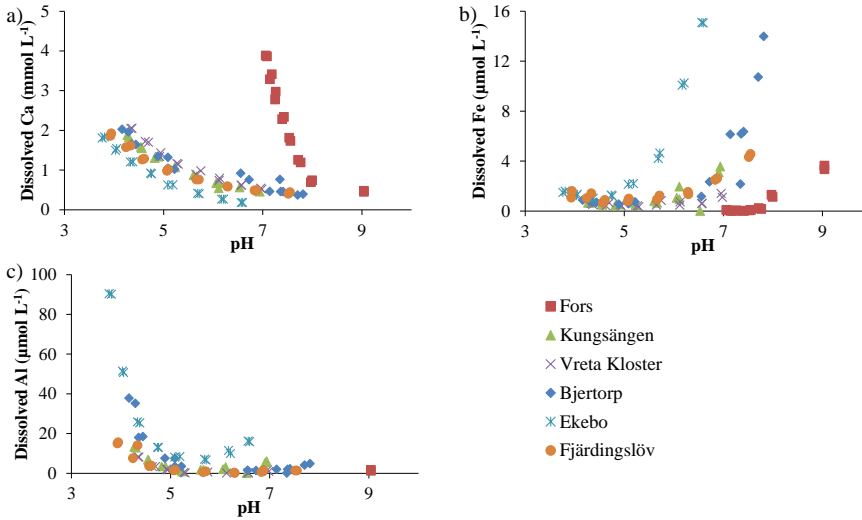


*Figure 15.* pH-dependent solubility of: a) Ca, b) Fe and c) Al in soils from the unfertilized treatments of the long-term fertility experiments.

## 5.5 Phosphate sorption affected by long-term fertilisation (Paper IV)

The $PO_4$ sorption varied between different soils (see Table 9). In most cases there was stronger $PO_4$ sorption in the unfertilised soil than in the fertilised counterpart. If the Freundlich exponent $m$ is kept constant, the Freundlich coefficient $K_F$ can be seen as an estimate of the sorption strength. By stepwise regression, a multivariate linear relationship between $K_F$ and oxalate-extractable Al and Fe was found (adjusted $R^2 = 70$ %):

$$K_F = 0.0529 + 0.000918 \times Al_{ox} + 0.000239 \times Fe_{ox} \qquad (7)$$

where $Al_{ox}$ and $Fe_{ox}$ denote oxalate-extractable Al and Fe, respectively (in mmol $kg^{-1}$). For fertilised soils, an even stronger relationship was found when competition from organic acids (using soil organic C as a surrogate) was considered in addition to oxalate-extractable Al (adjusted $R^2 = 79$ %)

$$K_F = 0.120 + 0.000809 \times Al_{ox} - 0.00280 \times \frac{OrgC}{Al_{ox} + Fe_{ox}} \qquad (8)$$

where OrgC is the soil organic C content (%). Moreover, there was a correlation between the sorption of P (as indicated by $K_F$) and the amount of hydroxy-interlayering in the clay fraction ($r = 0.95*$).

The initial adsorbed $PO_4$ ($n_{init}$) was related to the P extracted by the P-AL extraction ($r = 0.72***$). However, it is clear that P-AL overestimated adsorbed $PO_4$ in the soils with reactive apatite, as the acid ammonium lactate solution is likely to cause partial dissolution of the calcium phosphate minerals (Figure 16). A relationship was also found between the amount of adsorbed $PO_4$ in the XANES analysis of the sorption experiments and the hydroxy-interlayering index (Method 4a $\times$ Clay content; $r = 0.97***$).
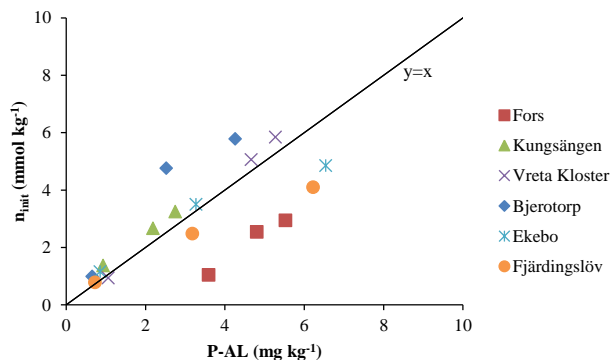
*Figure 16.* Relationship between the initial adsorbed $PO_4$ $n_{init}$, determined from the sorption equations and the extracted P in ammonium lactate.

Table 9. *pH range, $K_F$, $n_{init}$ and coefficient of determination ($R^2$) for the Freundlich equation calculated for each sample from the long-term fertility experiments*

| Soil | Range of pH values after equilibration | $K_F$ | $n_{init}$ | $R^2$ |
|---|---|---|---|---|
| Fors A3 | 7.55-7.77 | 0.085 | 1.05 | 0.989 |
| Fors C3 | 7.50-7.67 | 0.091 | 2.54 | 0.989 |
| Fors D3 | 7.49-7.64 | 0.090 | 2.94 | 0.994 |
| Kungsängen A3 | 6.01-6.11 | 0.165 | 1.37 | 0.992 |
| Kungsängen C3 | 6.06-6.12 | 0.148 | 2.67 | 0.987 |
| Kungsängen D3 | 6.13-6.16 | 0.165 | 3.25 | 0.992 |
| Vreta Kloster A3 | 6.12-6.17 | 0.092 | 0.94 | 0.994 |
| Vreta Kloster C3 | 6.22-6.31 | 0.131 | 5.06 | 0.976 |
| Vreta Kloster D3 | 6.20-6.27 | 0.142 | 5.84 | 0.990 |
| Bjertorp A3 | 6.07-6.12 | 0.094 | 0.99 | 0.990 |
| Bjertorp C3 | 6.22-6.31 | 0.105 | 4.76 | 0.978 |
| Bjertorp D3 | 6.20-6.28 | 0.140 | 5.78 | 0.988 |
| Ekebo A3 | 6.07-6.12 | 0.135 | 1.15 | 0.999 |
| Ekebo C3 | 6.17-6.23 | 0.140 | 3.50 | 0.993 |
| Ekebo D3 | 6.23-6.41 | 0.154 | 4.85 | 0.987 |
| Fjärdingslöv A3 | 6.29-6.38 | 0.088 | 0.78 | 0.997 |
| Fjärdingslöv C3 | 6.27-6.34 | 0.089 | 2.48 | 0.996 |
| Fjärdingslöv D3 | 6.31-6.40 | 0.097 | 4.10 | 0.991 |

# 6    Discussion

## 6.1    Characterising hydroxy-interlayering in clay fractions and soils (Paper I)

There are different ways in which the amount of hydroxy-interlayering can be defined: (1) The amount of hydroxy-interlayers in a specific mineral; (2) the amount of hydroxy-interlayering in the clay fraction; and (3) the amount of hydroxy-interlayering of the whole soil. There is also a difference between the *amount* of hydroxy-interlayers in the samples and the *degree* of hydroxy-interlayering. The amount of hydroxy-interlayers describes the total content of hydroxy-interlayers in the sample, whereas the degree refers to the fraction of the interlayer space that consists of hydroxy-interlayers. The methods used in this thesis estimate the amount of hydroxy-interlayering in the clay fraction. All methods investigated consistently identified the same soils as having the highest amount of hydroxy-interlayering.

A feature in common for all methods is that they involve the term *stability*. In general, stability can be conceptualised as the resistance to collapse caused by the displacement of cations, dissolving reagents, heating or ageing. The methods suggested by Esser (1990) and Matsue & Wada (1988) involve collapse of the interlayer space caused by K-saturation, using the Mg-saturated sample as a reference. However, this method does not provide a direct measure of the amount of hydroxy-interlayering, but instead it describes a property that is dependent on the amount of hydroxy-interlayering. Another issue with this type of method is the risk of incomplete collapse as a result of K-saturation (Sayegh *et al.*, 1965), especially of expandable minerals. In Method 3 the samples were heated to 300 ℃ before measurement to decrease rehydration and re-expansion. This procedure seems to result in total collapse for samples low in hydroxy-interlayers, but overestimates the collapse for samples with a higher amount of hydroxy-interlayering. A general impression of all methods

outlined is that they all seem to work well for ranking soils with high amounts of interlayering, but for soils that are low in hydroxy-interlayers, the measurements seem more inconsistent.

The new method (Method 4) quantifies the resistance to collapse upon *in situ* heating. This method involves a more direct measurement of the amount of hydroxy-interlayering than the methods of Esser (1990) and Matsue and Wada (1988). At 250 ºC there is complete dehydration of the interlayers of hydroxy-interlayered vermiculite, causing a decrease in the *d*-spacing (*i.e.* contraction) of the mineral. Further increases in the temperature result in dehydroxylation of the hydroxy-Al or hydroxy-Fe polymers in the interlayer, which causes a further decrease of the d-spacing (Harris *et al.*, 1992). Hence this method includes contributions from both dehydration and dehydroxylation processes, but only the latter are directly related to the amount of hydroxy-interlayering.

The idea behind the new method (referred to here as Method 4b) is to obtain a more specific estimate of the thermostability of the hydroxy-interlayers, by quantifying the change in the *d*-spacing (as indicated by COG) between 250 and 450 ºC. Ideally, this would reflect only the dehydroxylation of the hydroxy-interlayers, and thereby the amount of hydroxy-Al-interlayering.

For the set of soils studied, it was found that the soils with the highest amount of hydroxy-interlayers also had the lowest stability. Soils with low pH commonly also had higher amount of hydroxy-interlayers in the clay fraction, but at the same time they had lower clay content. This probably reflects the fact that the weathering process tends to slow up at higher pH and consequently there is less formation of these hydroxy-interlayers (Stevens & Bayard, 1994).

At present, the new method cannot be claimed to work 'better' than any of the existing methods. However, it can be claimed that it represents a step forward in the determination of hydroxy-interlayering, as it is based on fundamental properties of hydroxy-interlayered minerals.


## 6.2 How does soil development affect P speciation? (Papers I and III)

### 6.2.1 Formation of hydroxy-interlayers and (hydr)oxides

Hydroxy-interlayers are commonly found in dioctahedral minerals as a weathering product of dioctahedral mica (Farmer *et al.*, 1988; Brown, 1953). However, trioctahedral minerals with hydroxy-interlayers can also be found, as a result of weathering of biotite (Wilson, 1999). Hydroxy-interlayered minerals are commonly formed by weathering of the edges, forming hydroxy-Al or hydroxy-Fe polymers. Weathering also produces secondary Al and Fe(III) oxide-type phases, which may adsorb $PO_4$ (Prietzel *et al.*, 2013). For the Lanna

soil, amphiboles were suggested as sources of Al and Fe in secondary oxides, as indicated by the parallelism of the gradients of the decreasing amount of $PO_4$ adsorbed to Al hydroxides and the increasing amount of amphiboles with increasing depth. The high amount of expandable minerals may also be a result of vermiculitisation, which may be a further source of Fe for forming Fe oxide-type phases (Farmer *et al.*, 1971) and of Al.

For the clay fraction samples from the long-term fertility experiments, XRD patterns suggest that hydroxy-interlayer material is apparently unaffected oxalate extraction. There was, however, a clear relationship between the amount of extracted Al and the amount of hydroxy-interlayers in the clay fraction. These observations can be interpreted in two different ways: (1) a large part of the oxalate-extracted Al consists of interlayer Al, but the latter is only a small fraction of the amount of hydroxy-interlayers (small enough not to be seen by XRD), and/or (2) the correlation between oxalate-extractable Al and hydroxy-interlayered Al represent two different pools that both have a common source of formation. With our data, it is not possible to tell which of these interpretations that is the most likely one. As a consequence, it is uncertain to what extent the P-adsorbing Al-hydroxide represents a precipitated mineral phase (such as Al hydroxide, gibbsite or allophane), or a hydroxy-Al-interlayer with similar P binding properties

### 6.2.2  Weathering of apatite

For the Lanna soil, it was observed that the amount of apatite increased with depth. According to Walker & Syers (1976), during soil weathering, total P and apatite contents can be expected to decrease, whereas the relative amount of other P species increases. For the Lanna soil, depletion of apatite was observed in the clay fraction compared with the bulk soil. This is probably because fine-grained apatite dissolves faster due to its higher surface area. This assumption was supported by the observation that apatite was thermodynamically unstable in the upper 50 cm of the pedon. The low content of apatite in the topsoil may be caused by long-term weathering, plant uptake of cations and accumulation of organic material, all of which would contribute to lower pH and increasing dissolution of apatite.

In the fertilised samples from Fjärdingslöv and Vreta Kloster, the apatite content was higher than in the unfertilised samples. There are at least two possible reasons for this: (1) The unfertilised samples may have had a higher apatite dissolution rate due to the P-depleted conditions; or (2) Ca phosphates may have formed after fertilisation. The results available do not allow an assessment of which, if either, of these explanations may be correct.

### 6.2.3 Organic P and PO₄ adsorbed to Fe (hydr)oxides in the topsoil

In the Lanna soil, the XANES speciation results only indicated the presence of organic P in the topsoil, along with $PO_4$ adsorbed to Fe (hydr)oxides. It has been pointed out in several reviews (*e.g.* Colombo *et al.*, 2014; Zhu *et al.*, 2014; Borch *et al.*, 2010) that there is a strong relationship between the C and Fe cycles. One of the reasons for this relationship is that plants produce organic ligands, *e.g.* oxalate and citrate (Colombo *et al.*, 2014; Schwertmann, 1991), which may release Fe(III) that form Fe(III) (hydr)oxides.

According to the XANES results, the best fit for organic P was with lecithin, which is a phosphate diester compound. However, ^{31}P-NMR analysis by other workers showed that monoesters dominate in the organic P fraction of Swedish agricultural soils (Ahlgren *et al.*, 2013). The reason for this discrepancy is not clear. One explanation may be degradation or lyophilisation of diesters forming monoesters during the extraction in sodium hydroxide which is performed prior to NMR analysis (Ahlgren *et al.*, 2013). Another possible reason is that K-edge XANES spectroscopy is not sensitive enough to distinguish between different organic P compounds, due to their relatively featureless XANES spectra on the K edge. To obtain more conclusive evidence on the true nature of organic P, the use of P $L_{2,3}$-edge XANES spectroscopy may be preferable (Kruse *et al.*, 2009).

## 6.3 Phosphorus speciation, which P is available? (Papers II, III and IV)

A major proportion of P in all soils was present as calcium phosphates, $PO_4$ bound to Al hydroxides and organic P forms. Furthermore, accumulation of $PO_4$ adsorbed to Al hydroxides after fertilization was suggested for both bulk soil and clay fraction.

The issue of which extraction agent best reflects available P in soil is an ever-going (and possibly never-ending) discussion due to the inherent lack of specificity and operational nature of destructive chemical fractionations. In this study, it was concluded that the P extracted by ammonium lactate (P-AL) is fairly well related to the initial adsorbed P in the sample, as shown by sorption isotherm experiments with 7 d equilibration (Figure 16). However, this is not true for soils that contain reactive apatite. For the samples from the Swedish long-term fertility experiment, Bergström *et al.* (2015) observed that during the last 50 years the P-AL pool in the unfertilized treatments slowly decreased with time. This finding indicates that adsorbed $PO_4$ is potentially available to plants, and therefore the (hydr)oxide-adsorbed P content will decrease during P depletion.

Concerning the pH-dependent solubility of $PO_4$, it was observed that the solubility increased at lower pH, which can be explained by various processes: (1) Dissolution of the Al hydroxide sorbents responsible for P sorption; and (2) dissolution of calcium phosphates or apatite. There is reason to believe that both of these processes are involved. An example is the Lanna soil, where both the 0-10 cm and 70-100 cm horizons displayed increased P dissolution at lower pH, despite the former containing little apatite, while the P speciation of the latter sample was dominated by apatite. Gustafsson *et al.* (2012) argued that the pH dependence may also be affected by the texture in the soil. In general, the soils included in this thesis all showed the same trend (Figure 13). However for the unfertilised Ekebo and Bjertorp samples, $PO_4$-P did not increase until pH decreased below 5, which represents a slightly different behaviour than that of the other clay soils, and of the clay soils examined by Gustafsson *et al.* (2012). This may be explained at least in part by the lower content of apatite in the Ekebo and Bjertorp soils (Figure 9). Thus, the relatively high solubility of $PO_4$ at low pH often found in Swedish clay soils may be explained by relatively high accumulation of apatite and hydroxy-Al compounds that are unstable under low pH conditions. Moreover, because the chemical conditions in the soil generally do not allow neoformation of Ca phosphates (except possibly after heavy fertilisation in some soils), (hydr)oxide surfaces are likely to be the most important for P sorption.

At pH >7, an increase in the P solubility can be observed. This is most probably caused by the pH-dependent adsorption/desorption behaviour of $PO_4$ on Fe and Al (hydr)oxide sorbents, caused in turn by *e.g.* an increased negative charge of the sorbent at higher pH.

## 6.4 Is it possible to develop a standard procedure for XANES data treatment?

There is no unequivocal answer that can be given to the question of what set of parameters should be used for background subtraction and normalisation of P K-edge XANES spectra. At the same time, small changes in these parameters can make a large difference to *e.g.* the height of the white line, and this will affect any interpretation concerning *e.g.* quantitative estimates of different phases using LCF, or any similar method.

One example of the above, which is important in the context of this thesis, is the relative proportions of $PO_4$ adsorbed to Al and Fe (hydr)oxides determined in XANES fitting analyses. The XANES spectra of these phases showed great similarities: the main difference was that Fe-bound $PO_4$ had a small pre-edge feature, while there were also small differences in the post-edge

region. However, in the LCF analysis of soil samples that only contained low concentrations of P, these two phases may be difficult to differentiate. When analysing such small differences, good data quality (*i.e.* high signal-to-noise ratio) is very important. It is possible that the noise may explain the difference observed between the P speciation of the bulk soil and of the clay fractions from Kungsängen (Figure 10). The bulk soil samples, the spectra of which were collected at SLRI, had much better data quality, and therefore these results (showing predominance of P sorbed to Al over P sorbed to Fe) can be deemed more reliable. Consequently, in the conclusions of this thesis, more weight is placed on the XANES results from SLRI (Papers III and IV) than on the NSLS results (Paper II), although for the most part the trends in both cases were in qualitative agreement.

A certain pre-edge and post-edge normalisation range is commonly used to get a consistent method for XANES data interpretation. Eveborn *et al.* (2009) used a wide normalisation range with a quadratic equation, whereas others have suggested the use of smaller ranges for environmental samples, *e.g.* Werner & Prietzel (2015). The former alternative could be preferred in cases in which the absorbance is strong enough for clear EXAFS oscillations to occur. Normalisation has been shown to be the most important factor affecting the outcome and performance of LCF and principal component analysis (PCA) (Werner & Prietzel, 2015; Beauchemin *et al.*, 2003).

Based on the experience gained during the work presented in this thesis, I suggest a given set of normalisation parameters to start with for background subtraction and normalisation (for P K-edge XANES spectra from SLRI: -30 to -10 eV for the pre-edge range and +30 to +45 eV for the normalisation range). However, theoretically the background subtraction and normalisation equations would ideally result in parallel lines across the XANES spectrum, and this is not always observed with the starting parameters. Therefore I suggest small changes in the normalisation range to get the lines parallel or, if this is not possible, nearly parallel. Another way to get more reliable results when differences or similarities are assessed is to use one of the samples as a standard to fit to the other as was done for the speciation of the additional P derived from fertilizer application. It is sometimes also important to limit the number of standards before performing LCF to get an acceptable fit. In this study, PCA was used for this purpose (suggested by Beauchemin *et al.*, 2003). Furthermore, as mentioned by Werner & Prietzel (2015), it is important to verify the result with other methods. After all, LCF analysis is a statistical method with its own limitations.

## 6.5   Evaluation of hypotheses

1.    *Soils with a large proportion of hydroxy-Al-interlayered clay minerals have higher P sorption capacity than those with a small proportion.*

Yes, but it remains uncertain if this is a result of sorption to hydroxy-interlayers. The strong relationship between the amount of hydroxy-interlayering and P sorption may also be explained by a common source of formation of hydroxy-Al-interlayers and P-sorbing Al hydroxides, as there is a strong relationship between the latter.

2.    *a) In clay soils with low P status, P is mainly sorbed to Al hydroxide phases.*

Yes, as observed in the XANES analyses of the unfertilised soil samples from the long-term fertility experiments

*b) In clay soils with high P status, P is bound to both Al and Fe (hydr)oxide phases.*

In three of the six soils from the fertilised treatment in the long-term fertility experiments, sorption to Fe (hydr)oxides was observed by XANES analysis. These soils commonly have a high content of oxalate-extractable Fe. Therefore this hypothesis can be confirmed for soils with a high Fe content.

*c) Ca-bound P as apatite is only reactive in calcareous soils.*

No, reactive apatite was observed after fertilisation by XANES analysis in two non-calcareous soils. This observation was supported by pH-dependent solubility experiments.

3.    *Apatite increases with depth in the soil profile as a result of its dissolution in the upper horizons during pedogenic weathering.*

Yes, as observed by XANES analysis in the Lanna soil profile.

4.    *Solubility of phosphate ($PO_4$) in Swedish agricultural clay soils is lowest at near neutral pH and increases with both increasing and decreasing pH.*

This was true for most unfertilized soils (exception: Ekebo, for which the minimum solubility of $PO_4$ occurred at pH 4.5). After fertilization, the pH dependence became smaller except in cases where reactive apatite was present.

# 7   Conclusions

- A new hydroxy-Al-interlayering index was developed, in which the shift in the centre of gravity of the XRD pattern between 250 and 450 $^{o}$C was determined. The amount of hydroxy-interlayering was found to be different in different soils from the Swedish long-term soil fertility experiments.

- There is a strong relationship between the amount of hydroxy-interlayers and the concentration of Al hydroxides, as evidenced by oxalate extractions. This makes it difficult to evaluate whether the Al-hydroxide sorbent that retains P is present as a mineral phase or in an hydroxy-interlayer.

- For a soil profile from a Swedish agricultural soil, a more or less gradual shift of P speciation was observed with increasing soil depth. In the topsoil, P speciation was dominated by $PO_4$ sorbed to Al/Fe (hydr)oxides and organic P, whereas in the subsoil most P was present as apatite.

- Apatite, organic P and $PO_4$-P sorbed to Al hydroxides are common P constituents in topsoils. Fertilisation brings about an increase in the pool of P adsorbed to oxide surfaces, mainly Al hydroxides. In unfertilized soils, the lowest solubility of P was generally found at neutral pH (6.5-7.5). The P solubility increased after long-term excess P fertilisation.

# 8 Implications and future perspectives

This thesis showed that $PO_4$ in clay soils usually has it lowest solubility at neutral pH and that its solubility increases at decreasing pH. The ammonium lactate extraction used in Sweden as soil test P (P-AL; e.g. Eriksson *et al.*, 2013) seems to be a good indicator of the adsorbed P, except for soils dominated by calcium phosphates, where 'available P' seems to be overestimated by the extraction. Soil mapping in Sweden is recommended every 10 years, which for P with its slow processes seems a relevant time period. However, more research is needed on ways to identify areas with apatite-rich soils, and also on ways to implement the value of P extracted in ammonium lactate in these soils.

In this thesis, it is suggested that oxalate-extractable Al and Fe could be used as an indication of the sorption properties of soil samples. However, for the fertilised soils studied an even stronger relationship was found between oxalate-extractable Al minus the ratio of organic C to the sum of oxalate-extractable Al and Fe. The latter could be seen as competition by organic acids for the sorbing surfaces, but Al surfaces seem to be the most important surface available. More research is needed to elucidate the P sorption processes and how they are affected by competition from other anions and organic acids. In Sweden, it has been suggested that measurements of Al and Fe extractable in ammonium lactate should be used to evaluate the properties of sorbing surfaces (Ulén, 2006). However, Eriksson *et al.* (2013) found a correlation between oxalate-extractable and ammonium lactate-extractable Al, but not as clear a correlation as for Fe. More research is needed to define a simple way to characterise the sorption processes in soils.

Svanbäck *et al.* (2013) found that soils with higher amount of oxalate-extractable Al and Fe also commonly had lower P losses from the topsoil, even after fertilisation. This thesis confirmed for these soils that most of the $PO_4$ was adsorbed to Al- and Fe (hydr)oxides. However, a combination of chemical and

physical parameters, *e.g.* infiltration capacity and structure, is needed to further understand the processes affecting the P losses (Djodjic *et al.*, 2004).

More research is also needed to really understand ongoing sorption/desorption processes in soil, and how they may be affected by soil pH. Such results may help understand the processes determining $PO_4$ availability in soils, and thereby decrease the need for fertilisation of apatite minerals and mitigation methods in order to decrease the P losses. However, the values obtained are just for the whole soil system, and may not represent what is available for the crops. More research is needed on how plants use this pH-dependent desorption behaviour and the effects on field scale.

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# Acknowledgements

Thanks to all the people that have helped me during these years. I would like to express special thanks to:

My main supervisor *Jon Petter Gustafsson*, for giving me the opportunity to work within this subject. I am very grateful that he has shared his deep knowledge of soil chemistry. Special thanks for all help, support and travel companionship during these years.

My co-supervisor *Stephen Hillier*, for welcoming me to the mineralogy lab at the James Hutton Institute and for sharing his deep knowledge of mineralogy.

My co-supervisor *Dean Hesterberg*, for introducing me to XANES analysis, for his encouragement and for sharing his deep knowledge within soil science.

My co-supervisor *Magnus Simonsson*, for critical discussion and for sharing his extensive knowledge about… everything.

My co-supervisor *Barbro Ulén*, for already in my Master's days introducing me to the subject of phosphorus and for sharing her wide knowledge about practical aspects of phosphorus management.

Former and present laboratory staff at the Department of Soil and Environment; especially *Roger Lindberg* for ICP analyses; *Lena Ek* for ICP analyses; *Inger Juremalm* for ICP and LECO analyses and different P

extractions; and *Christina Öhman* for soil texture analyses. Thanks also to *Mirsada Kulenovic* and *Gunilla Bergvall* for always being available for discussions.

Laboratory staff at the James Hutton Institute for helping with the mineralogy analyses. Special thanks to *Helen Pendlowski* and *Ian Phillips* for help in the lab during my visits to Aberdeen.

*Paul Northrup*, beamline scientist at X15B, NSLS; *Wantana Klushubun* beamline scientist at BL8, SLRI; thanks for help and support during data collection. Special thanks to *Panidtha Sombunchoo, Weeraya Wongtepa, Supanan Lapboonrueng* and *Chanakarn Cholsuk* for taking care of us during the beam times, and of course all other staff at BL8, SLRI.

*Bertil Nilsson* at KTH, for help with $PO_4$-P analyses.

*Helena Andersson* and *Anders Lindsjö*, for sharing soil samples.

*Aidin Geranmayeh*, for help with some of the pH-dependent P dissolution experiments.

*David Eveborn* at JTI, for cooperation with the XANES analyses.

*Magnus Simonsson* and *Dan Berggren Kleja,* for commenting on the thesis, and *Mary McAfee,* for language editing.

*Ragnar Persson* and *Håkan Karlsson,* for help with computers.

*Pia Edfeldt*, *Anne Olsson* and *Anna Wennberg,* for administrative help.

Former and present PhD students at the Department of Soil and Environment. Special thanks to the "soil chemistry students" *Maja, Charlotta, Sabina, Åsa* and *Marguerite*. Thanks also to the phosphorus PhDs *Jian, Masud, Helena, Annika, Pia, Julia, Ana, Frank* and *Matthew*. Great thanks to some really good friends at work, including those mentioned earlier and *Linnea, Martin, Johan, Joris, Veera, Kristin, Carina, Carin, Sabine, Abdul* and *Maria*. Thanks *Athefeh* for taking care of me in the Cunningham Building during my first trip to Aberdeen.

Former and present colleagues at the Department of Soil and Environment.

All students I have met in different courses, for giving inspiration and asking questions about the project, forcing me to think in a different way. Thanks for asking general questions about soil and environmental science, forcing me to gain deeper knowledge about these topics. Great thanks to *Bernt Andersson* at the teaching lab, for giving not only suggestions for the teaching, but also valuable comments on the project.

All friends for help and support during these years. *Axel*, "I Hope You Know That You're Invaluable".

My mother *Gun-Britt* and father *Jan-Erik*, for always taking care of me as your little daughter.

And last, but not least… Thanks to *Alice*, *Valentina*, *William*, *Sofie*, *Amanda* and all the other children in this world, who I hope can use this work to create a more sustainable world.