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Phosphorus Speciation in Swedish Arable Soils with High Leaching Potential

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Abstract

Eutrophication is threatening biodiversity and ecosystem functions in inland water bodies and estuaries world-wide. Phosphorus (P) export from arable land by *e.g.* leaching is a major contributor to eutrophication, with high P leaching losses from long-term manured mineral soils and cultivated organic soils (Histosols). The forms of P present in these soils and their role in P mobilisation were examined in this thesis. Spectroscopic techniques (P *K*-edge XANES and ^{31}P-NMR) were combined with extensive analysis of chemical and physical soil properties to characterise P in two cultivated fen peats profiles and the profile of a long-term manured mineral soil . Risk of P leaching from these soils was determined in rainfall simulation studies using 20-cm topsoil columns.

Topsoil P content (P-pstot) was with around 40 mmol kg^{-1} similar in the three profiles and thereby clearly elevated as compared to the P-pstot content in the sub soil of the profiles (maximum 20 mmol kg^{-1}). When accounting for the higher bulk density the mineral sol profile was however substantially richer in total P than the organic profiles. Organic profiles were dominated by organic P (P-org) and the highest P-pstot proportion (80%) was observed in the topsoil, which was attributed to peat subsidence and transformation of mineral fertiliser P into organic P by soil microbiota and crops. According to P *K*-edge XANES, 20-40% of P in the organic soils was inorganic and primarily adsorbed to Al-(hydr)oxides.

Long-term manuring resulted in accumulation of inorganic P in the mineral topsoil. Up to 70% of total P was adsorbed to Fe-(hydr)oxides and Al-minerals. Most remaining topsoil P was present as secondary amorphous calcium phosphates. In the subsoil, the dominant P species was crystalline apatite, which declined in abundance towards the soil surface, reflecting soil weathering. Organic P content was very low throughout the mineral profile, consisting primarily of phosphate monoesters.

The rainfall simulation experiments indicated a risk of high P leaching from the manured mineral soil and cultivated Histosol, with cumulative P load mobilised from topsoil of 10 and 15 kg P ha^{-1}, respectively. Phosphorus leaching was found to be driven by processes involving mobilisation of inorganic phosphate adsorbed to Fe or Al mineral surfaces, which was high relative to the size of the leachable P pool. This may reflect competition between phosphate and organic anions for sorption sites.

There was no indication that P-org is currently contributing to P leaching from Histosols, but continued soil subsidence over time will eventually lead to microbial mineralisation of organic soil P, increasing the availability of leachable inorganic P forms.

Keywords: phosphorus, organic soil, manured mineral soil, P leaching, XANES, chemical P analyses, phosphate, iron and aluminium (hydr)oxides

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Dedication

To Jens and Werner Grunewald

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List of publications

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

I Schmieder*, F., Bergström, L., Riddle, M., Gustafsson, J.-P., Klysubun, W., Zehetner, F., Condron, L. & Kirchmann, H. (2018). Phosphorus speciation in a long-term manure-amended soil profile – Evidence from wet chemical extraction, 31P-NMR and P *K*-edge XANES spectroscopy. *Geoderma* 322, 19-27.

II Schmieder*, F., Bergström, L., Riddle, M., Gustafsson, J.-P., Klysubun, W., Zehetner, F. & Kirchmann, H. (2019). Phosphorus speciation in cultivated organic soils revealed by P K-edge XANES spectroscopy. (submitted to Journal of Plant Nutrition and Soil Science)

III Riddle*, M., Bergström, L., Schmieder, F., Kirchmann, H., Condron, L. & Aronsson, H. (2018). Phosphorus leaching from an organic and a mineral arable soil in a rainfall simulation study. Journal of Environmental Quality 47, 487-495

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My contribution to Papers I-III was as follows:

I Planned the study together with the co-authors. Performed sampling, sample preparation and data collection with help from the co-authors and laboratory staff. Performed data analysis and writing, with some assistance from the co-authors.

II Planned the study together with the co-authors. Performed sampling, sample preparation and data collection with help from the co-authors and laboratory staff. Performed data analysis and writing, with some assistance from the co-authors.

III Assisted in planning the study and sampling. Helped with sample preparation and data collection. Took part in the data analysis and contributed to writing the paper.

Abbreviations

Al-ox	Oxalate extractable aluminum
Al-P	Phosphorus associated with aluminum
Al-Pstot	Pseudo.total aluminum
Al-pyr	Pyrophosphate-extractable aluminum
Ca-P	Phosphorus associated with calcium
C-org	Organic carbon content
C-tot	Total carbon content
DOC	Dissolved organic carbon
DOM	Dissolved organic matter
Fe-ox	Oxalate extractable iron
Fe-P	Phosphorus associated with iron
Fe-pstot	Pseudo-total iron
Fe-pyr	Pyrophosphate-extractable iron
LCF	Linear Combination Fitting
NMR	Nuclear Magnetic Resonance spectroscopy
N-tot	Total nitrogen content
PCA	Principal Component Analysis
PO_4	orthophosphate
P-org	Organic phosphorus
P-ox	Oxalate extractable phosphorus
P-pstot	Pseudo-total Phosphorus content
P-pyr	Pyrophosphate-extractable phosphorus
PSI	Phosphorus saturation index
SOM	Soil organic matter
XANES	X-ray Adsorption Near-edge Structure
XAS	X-ray absorption spectroscopy

1 Background

Modern industrialised agriculture is around 100-fold more productive than pre-industrial agriculture. Among the many technological and sociological advances making this increase in productivity possible, the development of synthetic fertilisers may be one of the most important. John Bennet Laws and Justus Liebig were among the first to experiment with synthesising fertilisers in the 19th Century, for instance by treating bone meal with sulphuric acid (Mazoyer & Roudart, 2006; Leikam & Achorn, 2005).

An unwanted downside of the industrialisation of agriculture was an unprecedented deterioration in the natural environment, which at a global level is threatening biodiversity and human development. One of the most severe environmental problems associated with modern agriculture is the loss of nutrients from fields and their transport into natural freshwater, estuarine and marine ecosystems (Correll, 1998). The accumulation of nutrients in these ecosystems causes eutrophication, *i.e.* uncontrolled proliferation of micro- and macroalgae in aquatic ecosystems, which can interrupt food webs, lead to enrichment of toxic substances and cause oxygen depletion in the water column when algal biomass decomposes (Parma, 1980). It is widely acknowledged that phosphorus (P) plays a crucial role in eutrophication. It has been found to limit primary productivity in lake ecosystems, where algal blooms could be directly linked to excess input of P (Schindler, 1977).

Phosphorus is an essential macronutrient for all forms of life, accounting for 2-4% of the dry weight of living cells (Karl, 2000). As adenosine triphosphate, it acts as energy currency in cell metabolism. It is also a crucial component in DNA and cell membrane molecules (Butusov & Jernelöv, 2013).

The importance of agriculture as a contributor to surface water eutrophication has been known for decades and agriculture continues to be the major non-point source of anthropogenic P inputs to aquatic ecosystems (Jarvie *et al*., 2013; Bogestrand *et al*., 2005). It is estimated that, of approximately 14 M tons of fertiliser P applied world-wide every year, more than 50% is lost from fields and potentially contributes to eutrophication (Butusov & Jernelöv, 2013).

Development of measurement and management strategies to minimise P losses from arable land while at the same time ensuring a sufficient supply for crops is a challenge, due to the complex behaviour of P in soils (Pierzynski *et al.*, 2005). There are several transport paths for P export from arable land, including via surface runoff and via leaching with the soil solution through to groundwater reservoirs or drainage pipes (Fortune *et al.*, 2005).

Phosphorus may be present in soils in a great variety of forms, including metal phosphates, organic P forms and orthophosphate (PO_4) adsorbed to Fe and Al mineral surfaces. These different forms of P may differ in solubility depending on soil chemical and physical status and microbiological activity (Glæsner *et al.*, 2012; Gustafsson *et al.*, 2012; Pierzinsky *et al.*, 2005; Stewart & Tiessen, 1987).

In order to understand the processes of P mobilisation in soils, it is therefore crucial to obtain detailed knowledge about the P species present. Advances in understanding P behaviour in soils were slow in the past, because P speciation in soil was a methodological challenge (Condron & Newman, 2011; Kizewski *et al.*, 2011). However, the emergence of advanced spectroscopic analytical techniques for P speciation has helped to overcome some of the limitations related to conventional wet chemical extraction methods (Kizewski *et al.*, 2011). Progress began in the 1980s with the introduction of ^{31}P-nuclear magnetic resonance spectroscopy (^{31}P-NMR) into soil science (Newmann & Tate, 1980). More recently, studies applying synchrotron-based techniques such as X-ray absorption near-edge structure (XANES) have been providing valuable new insights into the nature of P in soils (*e.g.* Eriksson *et al.*, 2016; Prietzel *et al.* 2013; Sato *et al.*, 2005). In this thesis, advanced spectroscopic analytical techniques were combined with established wet chemical methods for P speciation in two types of soils with known potential for high P leaching losses.

2 Aims and Objectives

The overall aim of this thesis was to identify the P species present in arable soils rich in P and determine how P speciation relates to leaching.

Specific objectives were to:

- Carry out a thorough characterisation of physical and chemical properties of mineral and organic arable soil profiles and their vertical distribution (Papers I and II)

- Identify P species in soil profiles enriched in P due to soil type and cultivation history, using different analytical methods (Papers I and II)

- Comparatively quantify leaching of P from organic and mineral soils (Paper III)

- Investigate links between P speciation and observed P leaching from mineral and organic soils (Papers I ,II, and III)

3 Introduction

3.1 Phosphorus forms in soils

Phosphorus in soil can roughly be divided into organic P and inorganic P. The proportions of these P forms present in soil depend on soil type and degree of weathering, but also on fertilisation history (Annaheim *et al*., 2015; Condron *et al*., 2005).

3.1.1 Mineral phosphorus

Inorganic P in soil can roughly be divided into P that is adsorbed to mineral surfaces and P that is a component of primary or secondary mineral phosphates. The former is the primary source of P in most virgin soils. The most important primary phosphate mineral is apatite, with a sum formula of $Ca_{10}(X)(PO_4)_6$ where X refers to a number of different possible substitutes such as fluoride (F^-), chloride (Cl^-) or hydroxyl (OH^-) ions (Pierzynski *et al.,* 2005). Primary iron (Fe) and aluminium (Al) phosphates common in soils include strengite and variscite, respectively. With increasing soil age, primary phosphates are gradually dissolved as part of a more general soil weathering process (Prietzel *et al*., 2013). The weathering of primary minerals is facilitated by biological acidification of soil horizons, which occurs for instance due to microbial decomposition of soil organic matter (SOM) that accumulates after plants have started to colonise a newly formed soil (Prietzel *et al*., 2013). The time frame in which these processes occur ranges from decades to millennia.

Phosphorus released via dissolution of primary phosphate minerals may subsequently be adsorbed to charged clay mineral edges, carbonates and hydrous Fe and Al oxides, which themselves may be products of soil weathering (Pierzynski *et al*., 2005; Zhou & Li, 2001). Iron and Al oxides are thereby of particular importance for P retention in soil. These minerals are ubiquitous in soils, although often in low concentrations. Examples of Al-containing minerals naturally formed in soil are boehmite and gibbsite. Important Fe oxides is soil are ferrihydrite and goethite. These minerals are found in soil in the form of discrete crystals, as coatings on clay minerals or associated with humic substances (Sparks, 2003). The capacity of soil constituents to bind P depends on, among other things, the surface area, which in turn depends on the degree of crystallinity and type of mineral. The surface area of ferrihydrite is commonly considered to be particularly large, more than 200 m^2 g^{-1}. In comparison, the surface area of a less poorly ordered Fe-(hydr)oxide such as goethite is less than 100 m^2 g^{-1}.

Secondary phosphates may form when the soil solution P concentration exceeds the solubility product of a possible secondary P mineral. The high levels of soil solution P required to induce precipitation of secondary phosphates may be achieved in the near vicinity of P fertiliser granules (Pierzynski *et al.*, 2005). Secondary precipitates are usually less stable than primary phosphate minerals, due to low crystallinity and resulting higher surface area. Secondary phosphate precipitation reactions involve the same metal cations as primary metal phosphate precipitation reactions. In acid soils, Fe and Al phosphate precipitation dominates, while in neutral to alkaline soils secondary calcium (Ca) phosphates are common (Börling, 2003). In contaminated soils, other base metals such as lead (Pb) and zinc (Zn) may be involved in phosphate mineral formation (Cotter-Howells & Caporn, 1996).

3.1.2 Organic phosphorus

Organic P compounds are by definition compounds where P is in some way covalently bound to carbon. This association may be indirect via other atoms within a molecule, for instance as in the case of deoxyribonucleic acid (DNA), or direct in the form of a C-P bond, as in the case of phosphonates (Pierzynski *et al.*, 2005). The great majority of organic P originates from metabolic activity of living organisms such as plants and microorganisms. Synthetic pesticides, herbicides, insecticides or fungicides that contain P can also contribute to the organic P pool in soils (Gerke, 2010; Condron *et al.*, 2005). Organic P (P-org) forms naturally constitute the major fraction in organic soils, up to 95% (Condron *et al.*, 2005). In mineral soils, the P-org content is often dependent on the stage of soil development and vegetation cover and, in the case of cultivated soils, on P fertilisation (Turner *et al.*, 2007). In mineral soils, the relative P-org proportion tends to increase with soil age, because of P immobilisation by plants or microbes and microbial organic P transformation to more recalcitrant forms (Prietzel *et al.*, 2013).

Organic P compounds found in soils may belong to different groups such P esters, phosphonates and organic PO_4-anhydrides. Phosphate esters, in particular phosphate monoesters, are the most abundant organic P forms in soils (Pierzynski *et al.*, 2005). The prefix mono- indicates that there is a single carbon moiety per P atom in the ester. Phosphate diesters, which are also found in soils, are accordingly characterised by two carbon moieties per P atom.

Orthophosphate monoesters have the general structure $R\text{-}O\text{-}PO_3^{2-}$. Examples of monoesters are sugar phosphates, such as phosphoenol pyruvate or glucose 6-phosphate and mononucleotides. The single most abundant species of P monoester in soils is inositol hexakisphosphate or phytic acid (Gerke, 2015). The base of this compound is a six-fold alcohol of cyclohexane with the trivial name inositol. Phytic acid is a principal storage form of P and energy in plants and is especially abundant in plant seeds (Condron *et al.*, 2005; Turner *et al.*, 2002). Turner *et al.* (2002) reviewed the role of inositol phosphates in the environment and compiled data from studies where the proportion of this group in total soil organic P amounted to up to 100%. In some studies, however, a dominance of P monoesters has not been observed (Turner & Newman, 2005).

Organic molecules such as nucleic acids, phospholipids and teichoic acid belong to the group of P diesters with the general structure $R_1\text{-}O\text{-}PO_2^{2-}\text{-}O\text{-}R_2$. While P diesters make up a large proportion of the fresh organic P input into soils, they are generally found to be less abundant in soils than monoesters and their proportion of total organic soil P content generally does not exceed 10%. However, higher proportions of phosphate diesters have been found in acidic forest and wetland soils (Turner & Newman, 2005). Moreover, it has been debated whether phosphate-diesters are accurately quantified with the commonly used liquid-state ^{31}P-NMR spectroscopy, as the alkaline extraction of soil samples prior to NMR analysis may cause hydrolysis of ribonucleic acids and partly also of phospholipids. This could lead to overestimation of phosphate monoester content in the sample (Turner & Newman, 2005; Makarov *et al.*, 2002).

Phosphorus can be bound to humic substances both in organic form and as PO_4. Orthophosphate has been proposed to be associated with humic substance surfaces via cation bridges of Al and Fe (Bedrock *et al.*, 1994; Gerke, 1992). The binding of PO_4 to these Al/Fe-humic matter complexes is similar to the binding of PO_4 to Fe and Al hydroxides, with ligand exchange and the release of OH- or water (H_2O) (Gerke, 2010). Humic acid-metal complexes may contribute substantially to the P adsorption capacity of organic soils with low mineral content. Since Fe-humic substance complexes have up to 10-fold higher adsorption capacity than mineral forms of Fe, this might also be the case for some mineral soils (Gerke, 2010; Gerke & Herman, 1992).

3.2 Phosphorus leaching from organic and mineral soils

For decades, P losses via surface runoff and erosion were considered the only environmentally relevant transport paths for agricultural P export to surface waters. Accordingly, previous research focused on these processes (Fortune *et al.*, 2005). However, in the past two decades this paradigm has been changing. Leaching of P is now recognised as the dominant transport path for P losses from arable fields in areas with flat landscape topography (Fortune *et al.*, 2005), which are generally tile-drained. In Sweden, where agriculture is concentrated on flat, clay-rich plains soils, 47% of arable land is artificially drained (Jeglum *et al.*, 2011).

In a review by King *et al.* (2015), P concentrations in drainage water are reported to vary between 0.1 and 8 mg L^{-1}. A P concentration of only 0.02 mg L^{-1} is considered to lead to eutrophication of surface waters. In the same review, P loads to tile drains are reported to vary between 0.4 and 1.6 kg ha^{-1}.

In general, P dissolved in the soil solution represents only a small fraction of total soil P. Exchange between soil solution P and P fixed in the solid phase may occur via several chemical and biological processes (Schoumans, 2015; Djodjic, 2001). These include sorption and desorption processes as the dominant mechanism in most soils. In alkaline soils and P-enriched soils, precipitation and dissolution of calcium phosphate minerals may become important (Zhou & Li, 2001). Biological processes that affect soil solution P concentration are microbial immobilisation and mineralisation and plant uptake of P (Schoumans, 2015).

Phosphorus sorption in soil refers to both physisorption and chemisorption of P to the solid soil phase. The sorption process can be divided into a fast, almost instantaneous, sorption stage and a following slower reaction stage. These stages each represent different sorption mechanisms. Fast sorption of P is associated with ligand exchange on mineral surfaces occurring as a monolayer and with physisorption involving Van der Waals forces (Huang *et al.*, 2014; Persson & Jansson, 2012). Besides being fast, these processes are also considered highly reversible. In contrast, slow sorption reactions such as surface precipitation and P occlusion, *i.e.* the incorporation of P into the inner structure of soil minerals, are considered practically irreversible (Huang *et al.*, 2014; Djodjic, 2001).

The extent to which each of the different P sorption processes contributes to equilibrating P in the soil solution depends on a large number of physical, chemical and biological factors (McGechan & Lewis, 2002). Examples are soil pH, soil structure facilitating preferential flow, ionic strength of the soil solution, soil redox potential and SOM content (Yang *et al.*, 2019; Gustafsson *et al.*, 2012; Barrow & Shaw, 1979).

The availability of potential sorption sites throughout a soil obviously plays a crucial role, as does the degree of saturation of these reactive sites with P or possible competitor ions such organic acids (Qin & Shober, 2018; Jarvie *et al*., 2013; Guppy *et al*., 2005).

High P leaching losses are frequently reported for heavily manured soils (Qin & Shober, 2018; Hansen *et al*., 2004; Sharpley *et al*., 2004; Koopmans *et al*., 2003; Whalen & Chang, 2001). Continuing inputs of P in excess of crop demand will eventually exceed the capacity of topsoil horizons in such soils to retain P. Unless subsoil horizons provide additional sorption sites, this will increase the risk of P leaching (Andersson *et al*., 2013; Butler & Coale, 2005). However, even subsoil horizons can become saturated (Novak *et al*., 2000).

Moreover, the P concentration in the soil solution of soils with highly elevated P status is permanently increased, leading to higher losses during flow events. Thus, the P concentration in drainage water from these soils may remain problematically high even after additional P inputs have ceased (Qin & Shober, 2018). Such ‘legacy’ P build-up in soils can, in the worst case, render management practices to reduce P export from arable land ineffective for decades (Fiorellino *et al*., 2017).

A less widely recognised category of soils with potential for substantial P leaching losses is cultivated Histosols. Histosols, or peat soils, are soils whose parent material is comprised of incompletely decomposed plant tissue. According the United States Department of Agriculture (USDA), a general rule in classifying soils as organic soils is an SOM content above 50% in the upper 80 cm of the soil (USDA, 2014). Organic soils form at locations where net primary production is not balanced by decomposition of organic material. Most commonly, decomposition is limited by oxygen deficiency. However, extreme acidity or contamination with toxic substances can also impede organic matter decomposition. The most common initial process of peat soil formation in temperate regions is terrestrialisation, which refers to the filling of shallow water bodies with organic material and sediment (Zhang *et al*., 2012; Chesworth, 2008). Underlying mineral soils are commonly hydric, such as former marine sediments (gyttja soils) consisting of mineral sediments and precipitates, often with a significant proportion of organic material derived from dead zooplankton and phytoplankton. Peat formation on these sediments sets in when organic material deposited in the bottom layer of the water body accumulates to such an extent that aerobic decomposition of the material causes persistent oxygen depletion. The anaerobic metabolism of adapted microorganisms allows only for incomplete decomposition of the organic material, which leads to its continuous accumulation. The gradual filling up of the water body with organic material is accompanied by a characteristic shift in vegetation (the main source of organic material) from submerged macrophytes towards a dominance of reeds and sedges. In cold and strictly humid climates, the layer of accumulated organic material may start to protrude over the former surface water level, eventually separating the developing peat body from inputs of groundwater or lateral surface runoff. At this stage, precipitation becomes the only source of water, changing the nutrient regime and growing conditions dramatically. Under the resulting acidic and nutrient-deprived conditions, mosses of the *Sphagnum* genus become the dominant plant species. Known as raised bogs, these ombrotrophic sphagnum peat soils can grow over millennia to several metres in thickness. From an agricultural point of view, a more relevant type of peat soil is groundwater- or surface runoff-fed Histosols from earlier stages of peat formation, which often have a more moderate pH and may be rich in nutrients. These Histosols, known as topogenous peats or fen peats, make up the majority of cultivated peatland (99% in Sweden) (Berglund & Berglund, 2010; Bridgham *et al.*, 2001).

The proportion of cultivated Histosols or gyttja soils in the total area of arable land is generally comparatively small. In Sweden the proportion is 9%, of which only 24% is used for intensive cultivation of annual row crops (Berglund & Berglund, 2010).

More recently, cultivated Histosols have received attention from researchers as significant sources of carbon dioxide (CO_2) and nitrous oxide (N_2O), which are climatically active greenhouse gases (Berglund & Berglund, 2010; Oleszczuk *et al.*, 2008; Grönlund *et al.*, 2006). It has also been suggested that, despite the small proportion they comprise of total agricultural area, these soils may contribute considerably to P losses from arable land (Table 1). A problem specific to the cultivation of organic soils is soil subsidence (Grönlund *et al.*, 2006; Ilnicki & Zeitz, 2003; Kasimir-Klemedtsson *et al.*, 1997). Drainage has fundamental and irreversible effects on physical and chemical properties and major functions of these soils (Bridgham *et al.*, 2001). One example is the settling of newly drained Histosols due to the loss of buoyancy caused by removal of water from the peat. Continuing aeration of drained peat soils also has profound consequences. Accelerating aerobic decomposition of the peat material in upper soil horizons changes fundamental soil properties. For instance, bulk density increases, while the hydraulic conductivity in affected soil horizons decreases. The ultimate outcome of this process is complete loss of peat horizons, and associated release of volatile decomposition products such as carbon dioxide. Peat subsidence is accelerated by additional measures to improve soil fertility, such as liming and fertilisation (Ilnicki & Zeitz, 2003).

Drainage depth has to be regularly adjusted to compensate for peat loss. Subsidence of the peat in a cultivated Histosol progresses through the peat body towards the underlying mineral soil, leading to complete loss of the peat horizons (Ilnicki & Zeitz, 2003). As shown in Table 1, previous studies have documented tremendous leaching losses of P from cultivated Histosols. In two studies (Miller, 1979; Duxbury & Peverly, 1978), the P concentration in drainage water from cultivated Histosols corresponded to annual loads of more than 30 kg ha^{-1} (Table 1). Reddy (1983) reported a staggering annual P loss of 168 kg ha^{-1} from cultivated Everglades organic soils. In studies in Sweden, annual P losses from mineral soils rarely exceed 2 kg ha^{-1} (*e.g.* Ulén & Jakobsson, 2005).

Knowledge gaps regarding the behaviour of P in organic soils are even greater than for minerals soils and little is known about the processes that lead to leaching of P from organic soils. Leaching losses of P from organic soils are in some cases related to low contents of extractable Al and Fe, suggesting that similar processes as in mineral soils control leaching of P. The content and distribution of mineral soil constituents in organic soils depend on the particle input via groundwater flow or runoff. In addition, precipitation processes may occur in organic soils, for instance via upflow of Fe-rich groundwater (Smieja-Król & Fiałkiewicz-Kozieł, 2014; Hill & Siegel, 1991). However, the natural concentrations of surface reactive minerals are low in comparison with those in most mineral soils (Simmonds *et al.*, 2015).

Soil redox conditions may be particularly important in the mobilisation of P from cultivated Histosols. This may be the case particularly when drainage of these soils is abandoned to re-establish wetlands. Re-flooding of wetland soils is intended to increase biodiversity in the landscape, reduce greenhouse gas emissions and create a sink for nutrients mobilised from agricultural fields. However, high concentrations of mobilised P in the soil solution of restored wetland soil are frequently observed, and this P mobilisation has been linked in several studies to reductive dissolution of surface ferric Fe minerals initiated by decreasing soil redox potential after the re-establishment of permanently waterlogged conditions (Zak & Gelbrecht, 2007; Jensen *et al.*, 1998).

Table 1. *Phosphorus leaching losses reported for cultivated organic soils in different studies*

Reference	Phosphorus losses [kg ha^{-1} yr^{-1}]	Comments
Longabucco & Rafferty, 1989	2.4-4.8	Calculated load of dissolved reactive P measured in drain water from a catchment with a high proportion (27% of total area) of cultivated Histosols near Lake Ontario, Canada. 71% of the total P load originated from Histosols.
Cogger & Duxbury, 1984	1-30	Estimated values for leaching and incubation study sites in Western New York State. Best predictors for observed P losses were soil Al and Fe content.
Beek, 2009	5	Field study monitoring nutrient export from different soils used for intensive dairy farming. Leaching losses of P from a Histosol were higher than from sand and clay soils.
Reddy, 1983	4-16	Column leaching experiments with cultivated and virgin Histosols from Florida. Water saturation of the columns for 25 days increased P losses 4- to 8-fold.
Miller, 1979	37	P content of drainage water from cultivated organic soils in Ontario, plus laboratory leaching and absorption studies. Leaching of P was correlated with fertiliser application and P adsorption behaviour was correlated with Al and Fe content.
Duxbury & Peverly, 1978	30.6	Loads of P measured in drainage water from cultivated Histosol sites in the New York State (USA). Soil internal processes were found to be responsible for P loss variation, rather than extent of fertilisation. Higher P losses were observed when tile drains were situated in the organic layer.
Mejias-Bassaletti, 2005	4.8-7.8	Losses estimated from concentrations in drainage water from Histosols in North Carolina cropped with maize and pasture. Higher losses were observed for maize fields. Some of the P losses were explained by Fe^{3+} reduction processes related to seasonal flooding.
Tiemeyer *et al.*, 2009	0.54	Dynamics of P export monitored in a small lowland catchment in Germany. Generally low P losses were observed. Total P losses were significantly higher in drainage water from degraded Histosols than from mineral soils.

3.3 Methods of phosphorus speciation in soils

Soil P characterisation in the past has primarily relied upon sequential fractionation schemes, which are simple to apply and have been in use for more than 100 years. Since then, a number of specific fractionation schemes have been proposed. The principle of all these methods is to apply a specific set of extractants, each aiming to extract a specific operationally defined fraction of soil P (Pierzynski *et al.*, 2005). Different schemes and extractants thereby address different research objectives. A rather simple scheme, such as that devised by Hieltjes and Lijklema (1980), is suitable for a rough classification of inorganic P in soils by extraction with sodium hydroxide (NaOH) and hydrochloric acid (HCl), to account for Fe- and Al-associated P and P bound to calcium. More comprehensive schemes are required when plant availability or transformations between organic and inorganic forms of soil P are taken into account. A suitable approach for this is the widely used Hedley fractionation scheme and variants of this (Hedley *et al.*, 1982).

A major limitation of all fractionation schemes is that they are limited to operationally defined fractions. Hence, there remains uncertainty as to which specific P species are extracted with a specific extraction step. In fact, species extracted may even differ with soil type for a particular extractant (Kar *et al.*, 2011). Also, Kruse and Leinweber (2008) found indications that the Hedley fractionation cannot be considered compound-specific in organic soils. For a detailed understanding of the behaviour of P in soils, exact knowledge about the forms of P present in soils would clearly be highly beneficial, if not essential. While extraction schemes are undoubtedly still useful for evaluating nutrient availability in arable soils and for comparative studies, the limitations associated with these schemes have prompted the introduction of more advanced spectroscopic techniques into soil P research. Two of these, namely ^{31}P-NMR and phosphorus *K*-edge X-ray absorption near-edge structure (P *K*-edge XANES) were applied in this thesis (Hesterberg et al., 1999; Newman & Tate, 1980). These methods are described below.

3.3.1 Liquid-state ^{31}P-nuclear magnetic resonance spectroscopy (^{31}P-NMR)

The introduction by Newman & Tate (1980) of ^{31}P-NMR spectroscopy as a tool to study soil P represented a considerable leap forward in the identification and quantification of organic P forms. The method has since been widely applied, *e.g.* Cade-Menun and Liu (2014) list about 70 soil science-related ^{31}P-NMR studies published between 2005 and 2013.

The principle of NMR spectroscopy is based on the specific behaviour of certain nuclei when subjected to a magnetic field and electromagnetic radiation. Subatomic particles, such as neutrons, electrons and protons, can be described as having magnetic momentum or spin. If there is an odd number of neutrons and protons in a nucleus, the nucleus possesses an overall spin itself, designated

I. This is a prerequisite for isotopes to be suitable for NMR analysis. Examples for such isotopes, apart from ^{31}P, are ^{13}C and ^{1}H (Keeler, 2005).

According to quantum mechanics, there is a defined number of different spin orientations. For instance, the isotope ^{31}P possesses two possible spin directions. In the absence of a magnetic field, both orientation states are energetically equivalent. However, under the influence of a magnetic field, the two spin orientations constitute different energy contents depending on the spin, being aligned parallel or anti-parallel to the magnetic field. The parallel-oriented spin is energetically favourable. A switch from parallel to anti-parallel alignment can be triggered when nuclei in a magnetic field are exposed to electromagnetic radiation with a frequency corresponding to the energy difference between parallel and anti-parallel spin. This particular frequency is referred to as resonance frequency. In NMR spectroscopy, the net absorption of electromagnetic radiation occurring because of the switch from lower to higher energy state is measured. Information about the molecular structure around target nuclei can be obtained since the net absorption is dependent on *e.g.* the electron density around the nucleus (Keeler, 2015; Pierzynski *et al.*, 2005). A nucleus surrounded by a higher electron density will switch spin orientation and thereby absorb electromagnetic radiation at a lower frequency than a nucleus shielded by lower electron density (Keeler, 2005).

Modern Fourier transformation NMR spectrometers use a constant and very strong magnetic field and apply a pulse of electromagnetic radiation over a range of frequencies (Keeler, 2015; Pierzynski *et al.*, 2005). Figure 1 shows an example of a solution state ^{31}P-NMR spectrum from soil samples and reference materials. The chemical shift, plotted on the x-axis, denotes the difference between the resonance frequency of a compound in the sample and a standard compound. This difference is related to the operating frequency of the magnet for the applied external magnetic field, hence the units ppm. The diagram illustrates the potential of ^{31}P-NMR to distinguish between different P species commonly found in soils. A sharp signal around 6 ppm indicates the presence of PO_4 in the sample, while polyphosphate signals appear in a range of chemical shift between -5 and -20 ppm (Figure 1). Signals in the range 3 to 7 ppm indicate the presence of P monoesters. Signals at a chemical shift between 2.6 to -3 ppm are usually associated with different forms of P diesters (Figure 1). In the higher frequency region between 7 and 20 ppm, signals from phosphonates can be observed (Cade-Menun & Liu, 2014).

Liquid-state ^{31}P-NMR is currently the most widely used approach to study organic P forms in soils and requires extraction of P from the soil prior to analysis. A suitable extractant should extract a high proportion of organic and complex inorganic P, without chemically altering these compounds. It is also important to remove paramagnetic ions, which are often abundant in soils and sediments, from the sample solution to avoid line broadening. However, a certain concentration of paramagnetic ions in the solution may be desirable, as this decreases the delay time between two consecutive NMR scans. The delay time refers to the time required for the spin orientation of target nuclei in a sample to return to an equilibrium state (relaxation). This is especially important for quantitative measurements requiring a high number of scans (Cade-Menun & Liu, 2014; Keeler, 2005; Pierzynski *et al.*, 2005). For the removal of paramagnetic elements, chelating materials (*e.g.* Chelex 100) have been used as an additional treatment in some studies (Cade-Menun & Liu, 2014; Cade-Menun, 2005; Walsh *et al.*, 1991).

A great variety of different extraction procedures have been used in the past, but the majority of more recent studies have applied a mixture of 0.25 M NaOH and 0.05 M Na_2EDTA as the extractant and have extracted samples for 16 hours. Some variation still exists with regard to pre- or post- treatment of samples and extracts. The additional treatment of samples often aims at removal of PO_4 prior to NaOH extraction, or complexation of paramagnetic ions. Removal of PO_4 has been performed in some studies by extraction with H_2O or potassium chloride (KCl) prior to the alkaline NaOH extraction (Turner *et al.*, 2007; Robinson *et al.*, 1998). A decrease in PO_4 concentration in the sample solution is beneficial, since it improves the sensitivity for remaining P compounds in the subsequent NMR analysis (Cade-Menun & Liu, 2014; Turner *et al.*, 2007; Robinson *et al.*, 1998). The P concentration in extracts from soil and sediments is commonly too low to allow for adequate quantitative identification of P species in NMR analysis (Condron *et al.*, 2005). It has therefore become common practice to lyophilise extracts and then re-dissolve them, in order to maximise the sample P concentration prior to analysis. In most studies, deuterium (^2H) is added to the samples at this stage to function as a signal lock, allowing field fluctuations to be detected and corrected (Cade-Menun & Liu, 2014).

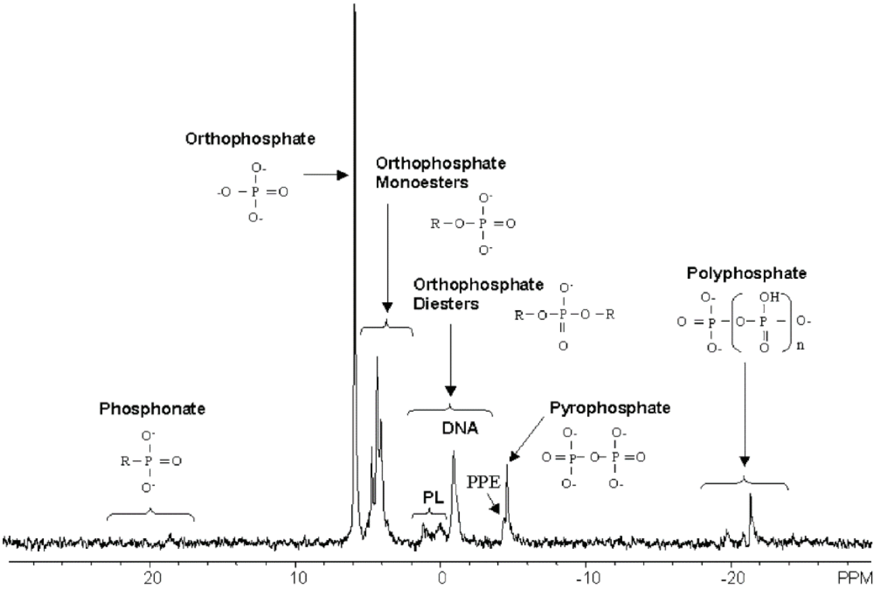

Figure 1. Example of a liquid-state ^{31}P-NMR spectrum of a forest floor sample. Arrows indicate forms of organic P assigned to particular peaks in the spectrum. Diagram modified from Cade-Menun (2005).

There is a huge body of literature available for comparison and for optimising the set-up and performance of ^{31}P-NMR analysis for a specific research objective (Cade-Menun *et al.*, 2014). The extraction step in liquid-state ^{31}P-NMR offers the possibility to increase the concentration of P in the extract and thereby improve the quality of the spectra obtained. It also offers the possibility to remove paramagnetic Fe or manganese (Mn) from the sample, to avoid line broadening and spectral artefacts. Therefore, liquid-state ^{31}P-NMR is often considerably more sensitive in identifying P species in soils than solid-state ^{31}P-NMR. Some techniques are available to enhance the informative value of spectra with poor resolution and broad overlapping peaks, such as deconvolution and least square fitting with standard spectra (Cade-Menun & Liu, 2014; Kizewski *et al.*, 2011; Lookman *et al.*, 1996).

A limitation of liquid-state ^{31}P-NMR is that the proportion of soil P that is recovered in the extract can vary depending on the P forms present in the sample and the type of extractant used. The extractant may also show selectiveness for specific forms of soil P, which could further limit the applicability of liquid-state ^{31}P-NMR for P speciation. Another important limitation of the method is the uncertainty related to the degree of chemical alteration of P compounds during extraction (Kizewski *et al.*, 2011; Condron *et al.*, 2005; Pierzynski *et al.*, 2005; Cade-Menun & Preston, 1996). In the study by Turner and Newman (2005), almost all phosphate monoesters identified with liquid-state ^{31}P-NMR in the wetland soils were likely to derive from alkaline hydrolysis of phosphate diesters occurring during the extraction.

3.3.2 Phosphorus *K*-edge X-ray absorption near-edge structure (P *K*-edge XANES) spectroscopy

X-ray absorption near-edge spectroscopy (XANES) is one of the spectroscopy techniques most recently introduced into soil science. Early publications on the potential of XANES in soil science-related P research emerged in the late 1990s (Hesterberg *et al.*, 1999). Since then, the number of P *K*-edge XANES studies has been steadily increasing. The method allows direct study of P forms in soil and sediment with minimal pre-treatment of the sample.

Phosphorus *K*-edge XANES requires radiation of high intensity and energy that also needs to be highly collimated and continuous over a wide range of the electromagnetic spectrum. Radiation with such properties is provided by synchrotron light source facilities (Kelly *et al.*, 2008). The working principle of XANES is based on excitation of core shell electrons in an atom subjected to radiation sufficiently high in energy to overcome the core shell binding energy. This binding energy, or absorption edge, is element-specific and increases with atomic number of the element and decreases with increasing distance of the shell to the nucleus. For the *K* shell in the P atom, it amounts to approximately 2145 eV. Radiation of such high energy lies in the X-ray region of the electromagnetic spectrum, hence the term X-ray absorption spectroscopy (XAS) (Kelly *et al.*, 2008; Jalilehvand, 2000).

Excited core shell photoelectrons sharing both particle and wave properties are referred to as photoelectrons. The wavelength of these photoelectrons is determined by the excess of energy of the incoming radiation in relation to the element and core shell-specific binding energy. Because of its wave properties, the photoelectron interacts with atoms closest to the absorber atom. These interactions involve *e.g.* backscattering and positive and negative interference. Depending on the wavelength of the photoelectron, as well as the distance and type of neighbour atoms, these processes contribute to the overall absorption of the incident radiation. In principle, a XANES experiment involves measuring the absorption of monochromatic radiation directed at the sample over an energy range around the binding energy for the core shell of the target element. With sufficiently small changes in the energy of the incoming radiation for each consecutive measurement, this results in a specific absorption spectrum that contains, among other things, information about the chemical forms in which the target element is present (Kruse *et al.*, 2015; Kelly *et al.*, 2008).

A P *K*-edge XANES experiment usually covers an energy range starting at 20 eV below, and ending about 100 eV above, the absorption edge. Plotting measured absorption against the energy of the incident radiation yields a P *K*-edge XANES spectrum, as shown in Figure 2a. Each dot in the graph represents the absorption measured for a specific incident radiation energy (Kizewski *et al.*, 2011; Kelly *et al.*, 2008; Jalilehvand, 2000).

In an experiment run in transmission mode, the radiation intensity of the beam after passing through the sample is usually measured with ionisation detectors, especially when absorber atom concentrations are high. For P *K*-edge XANES with soil samples, this approach is not suitable. The attenuation length of soft X-radiation at energies equivalent to the P *K*-edge is only a few microns (Henderson *et al.*, 2014). As an alternative, the absorption can be indirectly determined by measuring the fluorescence radiation emitted from the sample. The core hole left by an electron that is excited into the continuum represents an energetically highly unstable state, which causes an electron from a higher shell to fill the hole. The energy released, which equals the difference between the binding energies of the two shells, is emitted as fluorescence radiation. The intensity of this radiation is proportional to the radiation that is initially absorbed, which allows for indirect determination of the absorbance in the sample (Jalilehvand, 2000).

Spectra collected in fluorescence mode may be affected by self-absorption. This term refers to the re-absorption of fluorescence radiation by the absorber atoms in the sample, which attenuates the measured fluorescence signal (Kruse *et al.*, 2015; Kelly *et al.*, 2008). An important consideration for the interpretation of XANES data is *e.g.* that self-absorption manifests itself as reduced intensity of the absorption edge (Shober *et al.*, 2006). The significance of self-absorption effects on P and sulphur (S) *K*-edge X-ray absorption data has been shown in studies comparing data collected in transmission mode and fluorescence mode (Persson *et al.*, 2019; Almkvist *et al.*, 2010). In particular, *K*-edge XANES studies on materials with high P concentrations, such as manure or sewage sludge, report self-absorption effects (Massey *et al.*, 2018; Toor *et al.*, 2006).

Self-absorption increases with the concentration of the target atom in the sample (Kruse *et al.*, 2015). This is simply because the relative proportion of absorber atoms excited by the incoming X radiation is lower at higher concentrations. Thus, the potential for absorption of fluorescence radiation is increased (Kelly *et al.*, 2008). Therefore, it is common practice to dilute both references and highly concentrated samples with a chemically inert material with low absorption coefficient, such boron nitride (BN) (Kelly *et al.*, 2008). An alternative would be to collect spectra from high-concentration samples in total electron yield mode, based on measurement of the sample drain current (Kruse *et al.*, 2015). However, due to electrons interacting substantially more strongly with the solid sample phase than X-rays, the probing depth of this measuring mode is limited to 1-10 nm. This allows structural information to be obtained only from the very surface of sample particles (Henderson *et al.*, 2014)

Figure 2b shows XANES spectra for different standard preparations of P compounds. All these spectra show an intense peak, called white line, marking the absorption edge, but the shape of these peaks differs and each spectrum possesses further characteristic features. For instance, the white line of an apatite standard has a distinct shoulder on the high energy side of the white line peak, while the spectrum of Fe phosphate shows a characteristic pre-edge prior to the absorption edge (Ingall *et al.*, 2011; Hesterberg *et al.*, 1999). A typical feature of P compounds associated with Al is that, compared with other spectra, there is a flat ‘trough’ between the white line peak and a lower, broader peak associated with oxygen oscillation (Ingall *et al.*, 2011). Organic compounds, represented in Figure 2 by a lecithin standard, typically lack specific spectral features (Kruse & Leinweber, 2008; Lombi *et al.*, 2006; Hesterberg, 1999).

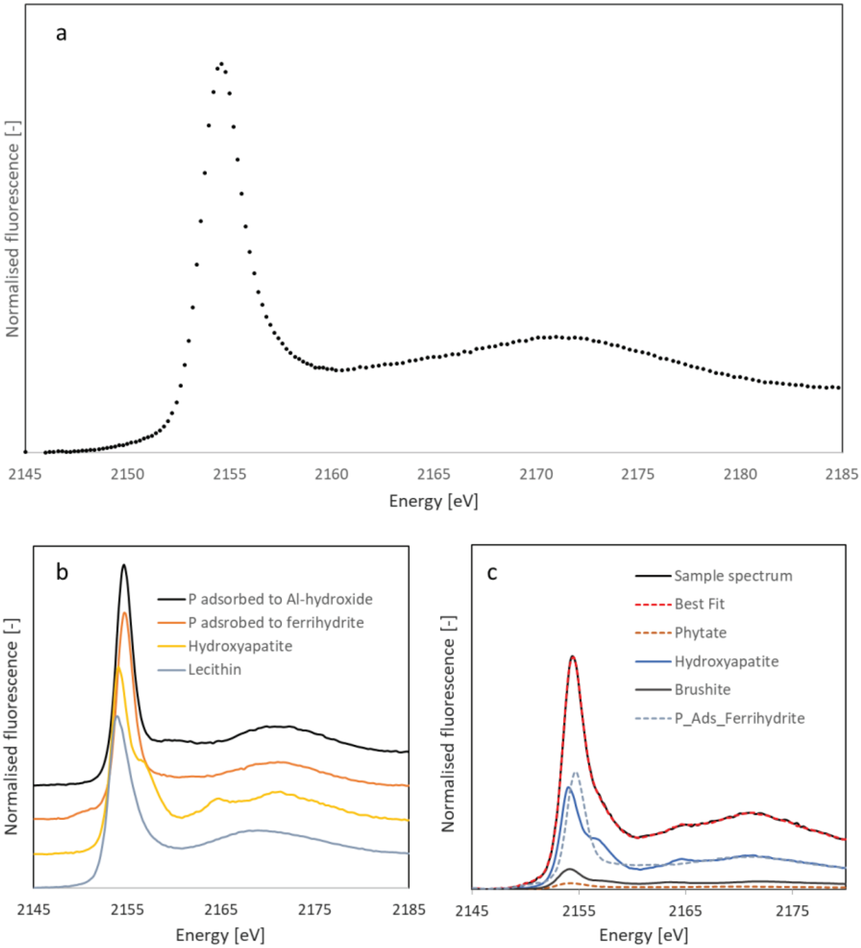

Figure 2. Normalised phosphorus *K*-edge X-ray absorption near-edge structure (P *K*-edge XANES) spectrum of: a) a soil sample, where each dot represents the fluorescence measured at a particular energy of the incident radiation; b) different phosphorus compounds; and c) a soil sample (black line) and a fitted curve obtained with quaternary linear combination fitting (LCF) (red dashed line). The standards included in the fit are also shown, weighted according their proportion in the total fit.

The P *K*-edge XANES spectrum of a sample containing several P species represents a weighted average of spectra of the P compounds present in the sample. For the identification and relative quantification of P species, linear combination fitting approaches (LCF) can be applied using P standard spectra to fit a sample spectrum (Kruse *et al.*, 2015; Kizewski *et al.*, 2011; Kelly *et al.*, 2008). An example of a normalised sample spectrum and fitted spectra that are a linear combination of three standard spectra is shown in Figure 2c. The fit was obtained using the LCF function in the X-ray absorption software Athena (Ravel & Newville, 2005).

The potential of LCF approaches to obtain quantitative information on P species from a XANES sample spectrum can be severely limited by the lack of unique distinguishable features in spectra for some P forms. This is particularly the case for organic P species and for P compounds in solution (Persson *et al.*, 2019; Kizewski *et al.*, 2011; Kruse & Leinweber, 2008). The uncertainty regarding the representativeness of standard spectra for the P compounds in the sample also has an influence on the validity of the LCF results (Ajiboye *et al.,* 2007)

However, P *K*-edge XANES provides a number of advantages that make the method a promising technique for P speciation in a complex matrix such as soil. It is element-specific, *i.e.* absorption measured in the P *K*-edge energy range is directly related to P in the sample and there should be no interference from other atoms. Therefore all the irradiated P atoms in a sample are probed without selectivity for any particular P species. Moreover, the non-destructiveness of the method prevents uncertainty regarding chemical alteration of P in the sample, which affects techniques such as liquid-state ^{31}P-NMR (Kizewski *et al.*, 2011; Kruse & Leinweber, 2008; Lombi *et al.*, 2006; Beauchemin *et al.*, 2003).

4 Materials and Methods

4.1 Soil sampling and characterisation

The long-term manured mineral soil profile examined in this thesis (in the following referred to as 'SMIN') was taken at a sampling site near the town of Kristianstad in Skania County, southern Sweden. Management of the field between 1973 and 2015 included addition of cattle manure amounting to an annual average of 45 kg ha^{-1}. Tile drains are present at the field site to prevent groundwater upflow (Gustafson *et al.*, 1984). The site is included in a national P loss monitoring programme and is frequently among those with highest annual P losses recorded (Stjernman-Forsberg *et al.*, 2016).

The two organic soil profiles (Histosols) examined in this thesis (in the following referred to as 'H1' and 'H2') were collected in the vicinity of Lake Hjälmaren, Örebro County, central Sweden. Both soils were fen peats that were reclaimed for agricultural use in the 1940s, when tile drains were installed. At present, the drains are located at around 100 cm depth. The H1 soil had been P-fertilised at a rate of approximately 20 kg P ha^{-1} in the nine years prior to the present analysis, while the H2 soil had received on average 18 kg P ha^{-1} year^{-1} over the past 10 years.

The SMIN profile was sampled at 10-cm intervals to a depth of 80 cm. For the H1 and H2 soils, the upper 20 cm were compiled to one sample and the rest of the profile was sampled at 10-cm intervals down through the underlying mineral soil, which was located at 100 and 90 cm depth in H1 and H2, respectively. Some general properties of the soils are summarised in Table 2.

Particle size distribution was determined according to an international standard method (European Committee for Standardisation, 2009). The pH of dried samples was determined in deionised water at a solid:liquid ratio (w/v) of 1:5. Total carbon (C-tot), organic Carbon (C-org) and total nitrogen (N-tot) and were determined using a Leco Tru-Mac analyser (LECO, St. Joseph, MI) following international standards (European Committee for Standardisation, 1998). The organic profiles contained no carbonate.

Texture throughout the SMIN profile varied between sand and sandy loam according to the FAO soil texture classification (FAO, 1990). The soil was slightly alkaline, but no significant content of carbonate was detected. In comparison, the organic soils were more acidic and naturally rich in organic material, resulting in low bulk density, but also contained significant proportions of minerals. A main difference between the two organic profiles was the distribution of mineral material throughout the profiles, with clay-enriched layers (30-60 cm depth) in the H1 profile and a more uniform clay distribution in the H2 profile.

4.2 Wet chemical analysis

Before elemental analysis, acid digestion of soil samples was carried out with hot concentrated nitric acid (HNO_3) at three temperature stages. The concentrations of Fe, Al, Ca and P in the digestion solution were given the suffix -pstot, referring to 'pseudo-total' (European Committee for Standardisation, 2015). The -pstot designation reflects the fact that complete digestion of the total element content in the sample cannot be expected with this method. Ammonium-oxalate extraction to estimate the content of surface-reactive, poorly crystalline Fe and Al and associated P (Fe-ox, Al-ox and P-ox, respectively) was carried out following Schwertmann (1964). Pyrophosphate was used to extract Fe (Fe-pyr) and Al (Al-pyr) associated with SOM, according to Mc Keague (1967). Crystalline and non-crystalline Fe and Al phases (Fe-dith, Al-dith) were extracted by the citrate-dithionite procedure described by Holmgren (1967). Element concentrations in the HNO_3 digests and in other extracts were determined using inductively coupled plasma atomic emission spectroscopy (ICP-OES) (Optima 7300 DV, PerkinElmer, Ma, USA) according to international standards (European Committee for Standardisation, 2015).

Phosphorus saturation index (PSI), an empirical index for P leaching risk assessment, was calculated as in Lookman *et al.* (1995)

$$PSI = \frac{P - ox}{\alpha(Fe - ox + Al - ox)} * 100\%$$

where P-ox, Fe-ox and Al-ox refer to ammonium oxalate-extractable P, Fe and Al, respectively, expressed in mmol kg^{-1} (Schwertmann, 1964). The empirical parameter α represents the fraction of Fe-ox and Al-ox that is actually available

Table 2. *Selected soil physical and chemical properties of the Histosol (H1, H2) and mineral soil (SMIN) profiles investigated in this thesis*

Profile	Soil layer	pH[a]	Bulk density[a]	Clay[a]	C-org[a b]	Tot-N[a b]	C:N[a b]	C:P[a c]
	[cm]	[-]	[kg dm^{-3}]	[%]			[-]	
H1	0-20	5.3	0.26	3.9	49.3	3.1	16	1077
	20-30	5.7	0.28	7.3	48.0	2.9	17	1061
	30-40	6.0	0.37	27.5	33.9	1.8	19	844
	40-50	5.9	0.38	31.4	27.6	1.4	20	1127
	50- 60	5.6	0.30	20.1	36.2	1.5	23	1873
	60-70	5.3	0.16	8.1	48.8	2.1	23	2259
	70-80	4.5	0.17	16.0	35.5	1.8	20	1960
	80-90	4.3	0.63	18.3	34.1	1.7	20	1834
	90-100	4.1	0.79	48.4	1.8	0.2	10	100
H2	0-20	5.1	0.28	3.5	45.8	3.3	14	875
	20-30	5.3	0.21	12.4	40.4	2.9	14	1034
	30-40	5.5	0.20	23.6	31.4	2.4	13	803
.	40-50	5.7	0.22	22.1	33.5	1.9	18	1366
	50-60	5.6	0.22	25.2	32.3	1.8	18	1423
	60-70	5.5	0.24	33.2	26.9	1.6	17	1382
	70-80	5.4	0.60	21.7	32.1	1.6	21	1701
	80-90	5.7	0.85	49.6	1.1	0.1	8	50
SMIN	0 - 10	7.46	1.2[I]	5.9	2.1	0.204	10	18
	10 - 20	7.15		6.0	1.9	0.195	10	16
	20-30	7.35	1.2[I]	6.4	1.8	0.181	10	14
	30-40	7.67		1.3	0.2	0.031	7	5
	40-50	7.68	1.2[I]	2.2	0.2	0.022	7	3
	50-60	7.76		2.7	0.2	0.025	9	5
	60-70	7.86	1.3[I]	2.1	0.1	0.008	11	2
	70-80	7.86		1.4	0.1	0.013	10	3

[a] Values presented are mean of duplicate samples.

[b] C-org = organic carbon content (European Committee for Standardisation, 1998); Tot-N = total nitrogen content (ISO 13878); C:N = ratio of total carbon to total nitrogen.

[c] C/P = ratio of total carbon content and pseudo-total P content (European Committee for Standardisation, 2007)

[I] Bulk density measurements for SMIN were carried at 20 cm depth intervals.

to bind P in the soil (Van der Zee *et al.,* 1990), As in Lookman *et al.* (1995) α was set to 0.5 being a mean of values of α as determined in previous studies.

4.3 Liquid-state ^{31}P-NMR

Extraction of soil samples for liquid-state ^{31}P-NMR analysis was done using using a solution containing 0.25 M NaOH and 0.05 M Na-EDTA at a soil-extract ratio of 1:20. An aliquot (5 mL) was removed for P-pstot analysis using ICP-OES. Lyophilised extracts were defrosted and re-dissolved in 1 M NaOH and 0.1 M EDTA solution. All NMR spectra were obtained using a 600 MHz Bruker Avance III spectrometer equipped with a smart-probe and a BACS sample changer. One-dimensional ^{31}P spectra were acquired with 512 scans and using 1H decoupling. All data processing, including peak identification and integration, was performed using the NMR processing software MestReNova. Concentrations of P species identified in the ^{31}P-NMR spectra were calculated using the corresponding peak area fractions and the relative recovery of P-pstot in NaOH-EDTA extracts.

4.4 P *K*-edge XANES

Sample and reference spectra were collected using the Beamline BL-8 at the Synchrotron Light Research Institute (SLRI) in Nakhon Ratchasima, Thailand. The facility features a 1.3 GeV beam storage ring with a beam current of 80-150 mA. The beam line was equipped with a InSb(111) crystal monochromator and 13 element Ge detector. The sample compartment was filled with helium (He) gas. Precautions to reduce thickness effects included grinding and sieving of samples (<0.05 mm). In order to minimise self-absorption, P reference standards and samples were diluted with boron nitride if the P concentration exceeded 800 mmol kg^{-1} (Hesterberg et al., 1999). The energy step size in the scans was kept at 2 eV between 2100 and 2132 eV, 1 eV between 2132 and 2144 eV, 0.2 eV between 2144 and 2153 eV, 0.3 eV between 2153 and 2182 eV, and 5 eV between 2182 and 2320 eV. The dwell time per energy step was 3 s. Elemental P was used for energy calibration at the edge of 2145.5 eV. During beam sessions, the edge position of a variscite standard was repeatedly determined as the maximum in the first derivative spectrum (2154.05 eV). Shifts in the edge position of variscite were used for correction of edge position shifts of sample spectra that were not related to molecular environment of P atoms (Eriksson *et al.*, 2016).

Data treatment after collection of spectra was carried out using the Athena software package (Ravel & Newville, 2005). This included baseline correction, normalisation routines and merging of multiple sample scans. The number of scans varied between three and 10, depending on P concentration and spectra quality. Normalisation and procedures for baseline correction were carried out as in Eriksson *et al.* (2016). A linear function was regressed to the P edge region (at -30 eV and -10 eV relative to the absorption edge energy position (E_0)). A quadratic function was used for the regression of the post-edge region, calculated across the post-edge region between 30 eV and 45 eV. Baseline trends and noise in a few spectra made it necessary to deviate slightly from these values in the range of a few eV.

For identification and relative quantification of P forms, an LCF approach was used (Tannazi & Bunker, 2005). Fitting was done with a collection of reference spectra of P species previously used by Eriksson *et al.* (2016) (Figure 3). The standard spectra were collected at the same beam line Phosphorus species represented in the library included several Fe, Al and Ca phosphates, phosphate adsorbed to different Fe- and Al- mineral phases including ferrihydrite and Al-hydroxide, and several organic P compounds such as phosphorus monoesters and diesters (Figure 3). Sample spectra were fitted over an energy region ranging from -10 eV to 30 eV relative to E_0 of sample spectra. A maximum of four standards was included in the fits. Ranking of fits was based on the goodness of fit factor R (Ravel, 2009), which indicates the mean of the misfit between sample and fit at each data point of the sample spectrum. It is calculated as:

$$R = \frac{\sum(data - fit)^2}{\sum(data)^2}$$

where data is the normalised fluorescence [-] of the sample spectrum and fit is the normalised fluorescence [-] of the fitted spectrum at a given energy.

4.5 Soil column P leaching experiment

Sampling of undisturbed soil columns was carried out using a hydraulic sampling device mounted on the rear of a tractor. Undisturbed soil columns (three replicates) with dimensions 18.8 cm diameter x 20 cm height were retrieved by pushing a polyvinyl chloride (PVC) sewer pipe into the soil with moderate and even velocity. Columns were collected for 20-cm depth intervals down to 80 cm. However, only results for the uppermost 20 cm (topsoil) are presented. The column sampling sites were identical to the sampling sites for P speciation studies. The columns were stored at approximately 5 °C until the start of the rainfall simulator experiment.

A detailed description of the rainfall simulator device is provided by Liu *et al.* (2012). The artificial rainwater used in the experiment had a pH of 5.8, an electrical conductivity (EC) of 0.008 mS m^{-1} and the following ionic composition: Ca: 278 µg L^{-1}; Fe: 6.85 mg L^{-1}; potassium (K): <400 µg L^{-1}; magnesium (Mg): <90 µg L^{-1}; sodium (Na): 352 µg L^{-1}; P: >1 µg L^{-1} (Löv *et al.*, 2017). The concentrations of these elements is based on analyses of natural rainwater in Sweden carried out by the Swedish Metrological and Hydrological Institute (SMHI). Precautions were taken when positioning the columns in the rainfall simulator to allow free drainage of water through the columns and to prevent any bypassing water from entering the sampling bottles. Moreover, columns were randomly rearranged after each individual simulation run.

The columns were brought to room temperature (22 °C) one week prior to the experiments. During this time, they were saturated with artificial rainwater for two days and then allowed to drain freely, in order to ensure that the water content in the columns approximately corresponded to field capacity.

Overall, 200 mm were applied in four consecutive rainfall events over a period of 12-14 days. During a single rainfall simulation event, rainwater was applied at an average rate of 5 mm h^{-1} for 10 hours. Between consecutive rainfall events, column leaching was allowed for 2-3 days.

Leachate from the columns was collected in sample bottles. Leachate volume was documented after each simulation and an aliquot was analysed for pH, total P, total dissolved P (P-tot) and dissolved reactive P (DRP). The latter was measured using the ammonium-molybdate method (European Committee for Standardisation, 2004). Absorbance was measured at 880 nm. Total P and P-tot were determined according a modification of Bran & Luebbe Method no. G-175-96. Total dissolved P was measured in samples filtered through a pore size of 0.2 µm. The difference between total P in filtered and unfiltered samples was defined as particulate P. The remaining P after subtracting DRP and particulate P from total P in leachate was designated residual P. Additional analyses were carried out for two of the three replicate columns. These complementary analyses included determination of elemental Fe and Al concentrations by inductively coupled plasma atomic emission spectroscopy (ICP-AES). Calcium concentration was determined in undigested samples by inductively coupled atom mass spectroscopy (ICP-MS). Electrical conductivity was determined with a CDM210 conductivity meter. Dissolved organic carbon (DOC) was measured in filtered (0.45 µm), acidified (HCl) samples using a Shimadzu TOC-VCPH analyser. Carbon dioxide was removed by flushing the samples with oxygen gas (O_2) prior to the analysis.

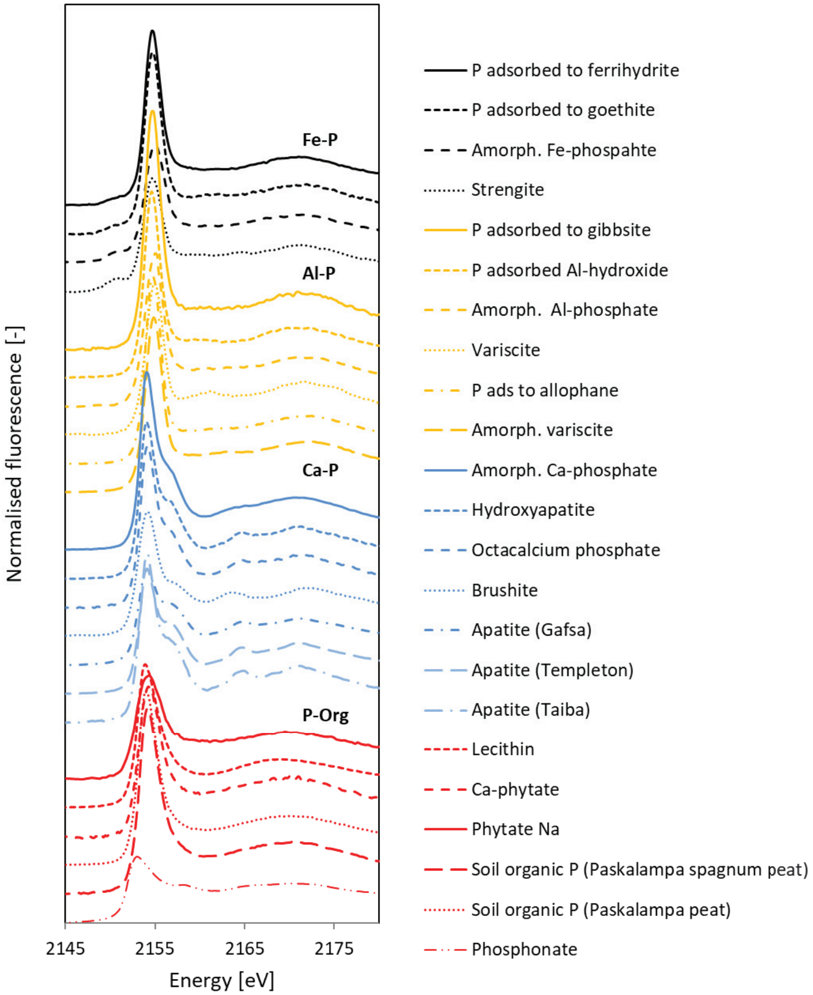

Figure 3. Normalised reference phosphorus *K*-edge X-ray absorption near-edge structure (P *K*-edge XANES) spectra used in linear combination fitting (LCF).

5 Results

5.1 General soil properties

As expected, the mineral soil SMIN differed from the organic soils (H1, H2) in terms of basic soil characteristics such as bulk density and organic carbon content, the latter being substantially higher in the organic profiles (Table 2) In all profiles the total carbon content was negligibly low. The organic carbon content in H1 and H2 varied between approximately 30 and 50 %, while it was a maximum of only 2% in SMIN. Carbon nutrient ratios were also typically lower in the SMIN profile. Moreover, soil pH in the SMIN profile was slightly alkaline, while both the organic soils were acidic.

The distribution of Fe and Al, and of other elements throughout the profiles, is shown in Table 3. The content of Fe-pstot in the two organic soils followed a similar vertical pattern, increasing from less than 200 mmol kg^{-1} in the topsoil layer to 380 mmol kg^{-1} in the subsoil. However, in both organic soil profiles, there was an exceptionally high Fe-pstot content of more than 600 mmol kg^{-1} in the peat layer directly above the mineral soil. This Fe-Pstot accumulation is most likely the result of Fe-rich groundwater upflow and complexation of dissolved Fe with organic material (Hill & Siegel, 1991). In both profiles, this Fe-rich layer coincided with the drainage depth, indicating groundwater level dynamics. The exceptionally high bulk density in these layers (Table 2) may be related to increased pressure from drained peat layers above due to the loss of buoyancy, which has been reported to increase bulk density in deeper peat layers (Wösten *et al.*, 1997)

Among the more pronounced differences between H1 and H2 were the content and distribution of Al-pstot and Al-ox throughout the profiles. In profile H1, both Al-pstot and Al-ox content peaked at between 30 and 60 cm depth. In this soil layer in profile H1, the Al-pstot content amounted to more than 1000 mmol kg^{-1}, whereas the content in the topsoil was substantially lower, around

130 mmol kg^{-1}. In the H2 profile, the Al-pstot content increased from less than 200 mmol kg^{-1} in the topsoil to around 650 mmol kg^{-1} in the subsoil.

Related to Al-pstot content, recovery of Al in ammonium-oxalate extract was overall less effective in H2. Hence, differences between the two profiles were even more pronounced regarding Al-ox content (Table 3). The Al-ox content amounted to, on average, 276 mmol kg^{-1} in the H1 profile and 92 mmol kg^{-1} in H2. The vertical distribution of Al-ox throughout the H1 profile generally followed that of Al-pstot. In summary, oxalate extraction of Fe and Al suggested higher capacity for P retention in H1 than in H2.

Pyrophosphate extraction revealed that in both organic soil profiles, a significant proportion of Al and Fe was associated with SOM, particularly in the topsoil (Table 3). In H1, the Fe-pyr and Al-pyr content corresponded to 60% and 50% of the Fe-pstot and Al-pstot content, respectively. In H2, recovery of both Fe and Al in pyrophosphate extract was generally lower, with a maximum of 35% relative to pseudo-total content of Fe and Al.

The content of Fe-pstot in the SMIN soil varied between 60 and 150 mmol kg^{-1}. On average, 25% of Fe-pstot in SMIN was ammonium oxalate-extractable. Overall, the content of Fe-ox was hence lower than in the two organic profiles. The vertical distribution of Al-pstot in SMIN was characterised by an elevated content in the uppermost 30 cm. The topsoil content reached a maximum of 10 mmol kg^{-1}, which was considerably lower than the maximum content observed in H1 and H2. Extractability of Al with ammonium oxalate was lower in SMIN than in the organic profiles, amounting to 40 mmol kg^{-1} or on average 22% of Al-pstot.

As could be expected due to the lower SOM content in SMIN, pyrophosphate extraction yielded only a small fraction of Fe and Al. Around 10 mmol kg^{-1} and 20 mmol kg^{-1} of Fe-pyr and Al-pyr, respectively, was measured in the upper 30 cm, which corresponded to around 10% of Fe-pstot and 10% of Al-pstot.

Table 3. *Selected results*^{a} *of wet chemical analysis carried out for Histosol profiles H1 and H2, and mineral soil profile SMIN*

Soil	Layer	Ca-pstot^{b}	Fe-pstot^{b}	Fe-ox^{c}	Fe-pyr^{d}	Fe-dith^{e}	Al-pstot^{b}	Al-ox^{c}	Al-pyr^{d}	Al-dith^{e}	P-pstot^{b}	P-ox^{c}	P-NaOH^{f}	PSI^{g}
	[cm]						[mmol kg^{-1}]							[%]
H1	0- 20	804.8	133.3	115.5	79.4	102.9	138.2	70.6	51.5	58.7	38.1	15.9	-	17
	20-30	1046.3	138	125.3	91.0	118.7	368	282.2	189.3	225.7	37.7	19.7	-	10
	30- 40	517.8	124.6	71.0	44.8	66.8	974.3	415.7	281.7	318.9	33.4	31.4	-	13
	40-50	399.5	159.8	60.4	37.6	57.2	1131.2	410	269	285.5	20.4	22.5	-	10
	50-60	429.1	194.5	114.8	75.4	115.9	809.2	333.9	227.1	251.7	16.1	5.5	-	2
	60-70	455.1	258.2	128.6	81.6	127.1	507.1	277.9	200.1	222.6	18	5.9	-	3
	70-80	267.9	274	128.3	71.8	126	516.1	181.9	119.6	124.4	15.1	4.4	-	3
	80-90	258.7	726	115.9	53.7	110.4	548.4	164.2	108.7	114.7	15.5	4.4	-	3
	90-100^{c}	183.1	168.6	90.7	24.5	77.7	1151.5	65.8	3.4	17.1	14.9	12.7	-	16
H2	0-20	587.2	102.9	67.1	36.8	57.5	152.1	69.8	54	54.6	43.6	18.2	-	27
	20-30	396.1	173.6	39.8	16	34.7	174.6	61	35.6	43	32.5	11.1	-	22
	30-40	370.6	320.8	57.2	22.9	51.5	344.4	84.2	42.7	58.3	32.6	14.3	-	20
	40-50	469.3	334.4	117.3	42.6	103.7	520.6	122.2	63.6	76.4	20.4	9.4	-	8
	50-60	406.1	366	113.7	46.1	101.5	552	118.1	55.7	66.2	18.9	8.2	-	7
	60-70	320.6	337	nd	nd	nd	656.6	nd	nd	nd	16.2	nd	-	nd
	70-80	366.5	695.5	102.4	33.9	88.8	514.8	98	45.1	48.8	15.7	7.5	-	7
	80-90c	157.1	124.9	53.3	9.8	29.1	1149.5	63.3	1.6	9.3	17.6	13.2	-	23
SMIN	0 -10	123.2	97.9	31.5	9.8	49.3	181.4	39.3	17.4	22.2	37.9	32.1	21.5	91
	10-20	125.5	115.7	32.6	9.8	45.7	186	40.6	18.1	20	39.2	34.2	17.5	93

Soil	Layer	Ca-pstot[b]	Fe-pstot[b]	Fe-ox[c]	Fe-pyr[d]	Fe-dith[e]	Al-pstot[b]	Al-ox[c]	Al-pyr[d]	Al-dith[e]	P-pstot[b]	P-ox[c]	P-NaOH[f]	PSI[g]
	[cm]						[mmol kg^{-1}]							[%]
SMIN	20-30	143.4	107.1	32.7	11.1	46.2	209.5	39.6	17.2	23.9	42.5	37.1	18.8	103
	30- 40	45.1	66.2	11.4	1.6	26.5	66.9	8	1.6	4.7	14.4	5	4.7	52
	40-50	58	146.6	34.7	2.4	84.6	98.6	9.7	1.4	8.1	18.1	6.3	3.2	28
	50-60	49.3	147.5	43	4.5	80.5	101.2	10.2	1.4	7	16.1	6.6	5.1	25
	60-70	53.8	97.2	15.5	2.2	46.4	89.8	6.5	0.6	4.4	17	3.7	4	34
	70-80	48.8	57.6	3.4	0.8	9.5	90.3	4	0.2	1.4	13.6	2.4	4.2	65

[a] Values presented are means of duplicate samples.
[b] pstot = pseudo-total, extractable with concentrated HNO_3.
[c] ox = ammonium oxalate extractable.
[d] pyr = pyrophosphate extractable.
[e] dith = dithionite extractable.
[f] NaOH extracted with EDTA-NaOH solution.
[g] PSI = phosphorus saturation index.

5.2 Extractable phosphorus

Regarding extractable soil P, a pattern common in all three profiles was for a clearly elevated P-pstot content in the upper 30 cm. In this topsoil layer, the content of P-pstot varied between 35 mmol kg^{-1} and 45 mmol kg^{-1} (Table 3). However, subsoil contents of P-pstot were also similar in the three profiles, at around 15 mmol kg^{-1}. In the SMIN topsoil, ammonium oxalate extraction was most effective, relative to Fe-pstot, and P-ox released more than 80% of P-pstot. For H1 and H2, similar percentage recoveries of P-ox were found in the deep mineral subsoil layers as in SMIN. In the 30-50 cm layer in the H1 profile, where clay and ash content were elevated, more P-ox was released. Otherwise, P-ox in organic layers of H1 and H2 corresponded to 40% or less of P-pstot.

The differences in bulk density between SMIN and the organic profiles (Table 2) resulted substantial differences in P content when it was related to unit volume instead of unit mass. In the topsoil of SMIN in particular, volume-related P-pstot content was four-fold larger than that in the topsoil of H1 and H2.

The content of surface-reactive Fe and Al relative to P-ox content was lower in SMIN than in the organic profiles. Phosphorus saturation index values indicated a higher P saturation in SMIN (Table 3). Values of PSI in SMIN were particularly high in the top 30 cm, indicating more than 90% P saturation. In contrast, the maximum PSI value in H1 and H2 was 17% (0-20 cm) and 27% (0-20 cm), respectively. Even in subsoil layers of SMIN, PSI values exceeded the threshold of 30% above which soils are at risk of high P leaching losses according to De Smet *et al.* (1995).

5.3 P *K*-edge XANES results

The signal to noise ratio of collected sample spectra was low (Figure 4). Spectral quality declined only slightly in deeper subsoil layers, reflecting a lower P content in these layers. The high quality of spectra allowed the identification of typical spectral features indicating the presence of P species already on visual inspection. For instance, the spectra of the deep mineral layers of H1 and H2 showed a shoulder at around 2156 eV, distinguishing these spectra from those of the upper peat layers. Moreover, the H1 and H2 mineral layer spectra both featured an additional post-edge peak at around 2165 eV. This combination of features typically indicates the presence of crystalline calcium phosphates (Zuo *et al.*, 2015). As can be seen in Figure 4, similar features were visible in spectra collected for subsoil layers of the SMIN profile and less pronounced in spectra of organic subsoil layers of H2 at 60-80 cm soil depth. In contrast, topsoil spectra of H1 and H2 were almost devoid of specific spectral features. They closely resembled the organic P reference spectra, such as lecithin used in the standard library. The absorption edge position of the sample spectra was shifted towards lower energy than that of spectra from mineral P species such as P adsorbed to Al-hydroxide. This shift is typical for spectra of organic P species and as such is an important feature for the identification of P-org species in mixed samples using XANES. As shown in Table 4, compiling edge energy positions for sample spectra and selected reference spectra revealed that the absorption edge of Ca-P spectra, represented by hydroxyapatite, was also positioned at low energy. However, due to the unique spectral features of Ca-P spectra, they are readily distinguishable from P-org spectra.

The absorption edge of spectra collected for the top 20 cm of H1 and H2 was positioned at the lowest energy of 2153.2 eV. The absorption edge collected from deeper organic layers in H1 and H2 was positioned at a slightly higher energy, around 2153.4 eV. The post-edge oscillation in these spectra indicated a higher proportion of inorganic P species in these layers. This was particularly

Table 4. *Absorption edge position [E_0] for phosphorus K-edge X-ray absorption near-edge structure (P K-edge XANES) sample spectra for the Histosol (H1, H2) and mineral soil (SMIN) profiles and selected reference spectra (defined as the maximum in first derivative of the spectra)*

Soil depth	E_0 [eV]			
[cm]	H1	H 2	SMIN	Reference spectra
0-10	2153.2	2153.2	2153.7	
10-20			2153.8	
20-30	2153.4	2153.4	2153.7	
30-40	2153.3	2153.5	2153.5	
40-50	2153.4	2153.4	2153.7	
50-60	2153.4	2153.5	2153.7	
60-70	2153.4	2153.4	2153.7	
70-80	2153.3	2153.5	2153.4	
80-90	2153.4	2153.4		
90-100	2153.4			
P adsorbed to ferrihydrite				2153.9
P adsorbed to gibbsite				2153.9
Hydroxyapatite				2153.4
Lecithin				2153

visible in H1 spectra collected at around 30-60 cm, where the post-edge oscillation showed similarities with some reference spectra for P adsorbed to Al- and Fe mineral surfaces (Figure 3). This included a slight peak in the 'trough' between absorption edges and a post-edge peak between approximately 2158 and 2163 eV.

There were also clearly visible differences between the spectra collected for the SMIN profile. Subsoil spectra showed visible indications of Ca-P presence. In the sample spectrum collected for 70-80 cm, these features were so pronounced that the spectrum clearly resembled the reference spectra for crystalline Ca-phosphates of apatite (Figure 3). This included a normalised edge intensity lower than for spectra collected for topsoil samples (Figure 4).

Compared with spectra of the organic soils H1 and H2, absorption edge positions of the SMIN spectra were generally at a slightly higher energy, around 2153.8 eV (Table 4), indicating a considerably lower contribution of organic P species. One exception was the spectrum for the deepest layer with an edge position at 2153.4 eV, which may be due to the high proportion of Ca-P in this layer.

A comparison of SMIN spectra with reference spectra for P adsorbed to Fe and Al minerals revealed that, with the exception of the deepest layer (70-80 cm), SMIN spectra featured a slight pre-edge/pre-shoulder at 2148 to 2152 eV, indicating the presence of Fe-associated P (Fe-P) (Prietzel & Klysubun, 2018; Hesterberg *et al.*, 1999).

5.3.1 Linear combination fitting (LCF) results

Organic soils

Results from LCF analysis generally reflected the P speciation in the profiles implied by visible features in sample spectra. The goodness of fit, expressed as R factor, was generally high, partly owing to the low signal to noise ratio in both the sample spectra and reference spectra. Values varied between 2.33E-04 and 4.30E-03, which was at the lower range of values reported in other studies (*e.g.* Eriksson *et al.*, 2016; Eveborn *et al.*, 2014). However, the R factor is only a measure of the similarity between fitted spectrum and sample spectrum, and does not cover all uncertainties related to LCF analysis, as discussed later in this thesis.

According to LCF, P speciation in the organic horizons of the H1 and H2 profiles was clearly dominated by organic P. Weights of P-org references in the best fits were highest in the top 20 cm (around 80%), while varying between 50 and 70 % in deeper organic layers of both profiles (Table 5). Most often, P-org was represented by a reference spectrum for lecithin and an organic P reference spectrum for mineral-poor peat material.

Linear combination fitting revealed that the proportion of P adsorbed to Al mineral phases (Al-P) was higher than that of P adsorbed to Fe phases (Fe-P) in both profiles. Aluminium-associated P was almost exclusively represented in the best fits by a reference spectrum of P adsorbed to gibbsite. Weight of fits ranged between 10 and 37 % for both profiles, with lower weights in the upper 20 cm and, in the case of H1, also in deeper subsoil layers. In both profiles, Fe-P was most often represented by a standard for phosphate adsorbed to goethite. However, throughout the profiles, Fe-P weights were lower than Al-P weights, particularly in H2, where the best fits for subsoil organic layers did not include Fe-P reference spectra at all. In H1, the contribution of Fe-P species to P speciation tended to increase slightly in the subsoil, to a maximum weight of 25% in the fit for the deepest organic layer.

For the H1 profiles, LCF weights of Al-P were significantly correlated with Al-ox (coefficient of determination $R^2 = 0.7$; $p<0.001$). In contrast, weights of Fe-P were not correlated with extractable Fe. In H1, correlations between LCF results and extractable element content were generally less strong, in part due to a lower number of samples for this profile (H1: $n = 8$; H2: $n = 6$). In both these profiles, pooled weights of Fe-P and AL-P, corresponding to the sum of adsorbed P according to LCF, were significantly correlated with Al-pstot (H1: $R^2 = 0.67$, $p<0.05$; H2: $R^2 = 0.73$; $p<0.05$). Likewise, a significant correlation with clay content was observed. While Al-P weights were only poorly correlated with Al-ox content in H2 ($R^2 = 0.1$), pooling weights of Fe-P and Al-P improved this correlation considerably, although significance at a level of 0.05 was not reached ($R^2 = 0.6$, $p = 0.07$).

For both Histosol profiles, the distribution of Fe-P and Al-P content calculated by relating LCF weights to P-pstot content corresponded well to the vertical distribution of P-ox in the profile, with R^2 of 0.8 for H1 ($p<0.05$) and 0.7 for H2 ($p\leq0.05$).

The mineral layers in the H1 and H2 profiles showed similar P speciation according to LCF, with a clear dominance of Ca-P, which was represented by a hydroxyapatite reference in the best fits. Weight of Ca-P amounted to 66% and 58% in H1 and H2, respectively. The contribution of P-org to soil P speciation in these layers was greatly reduced and did not exceed 13%.

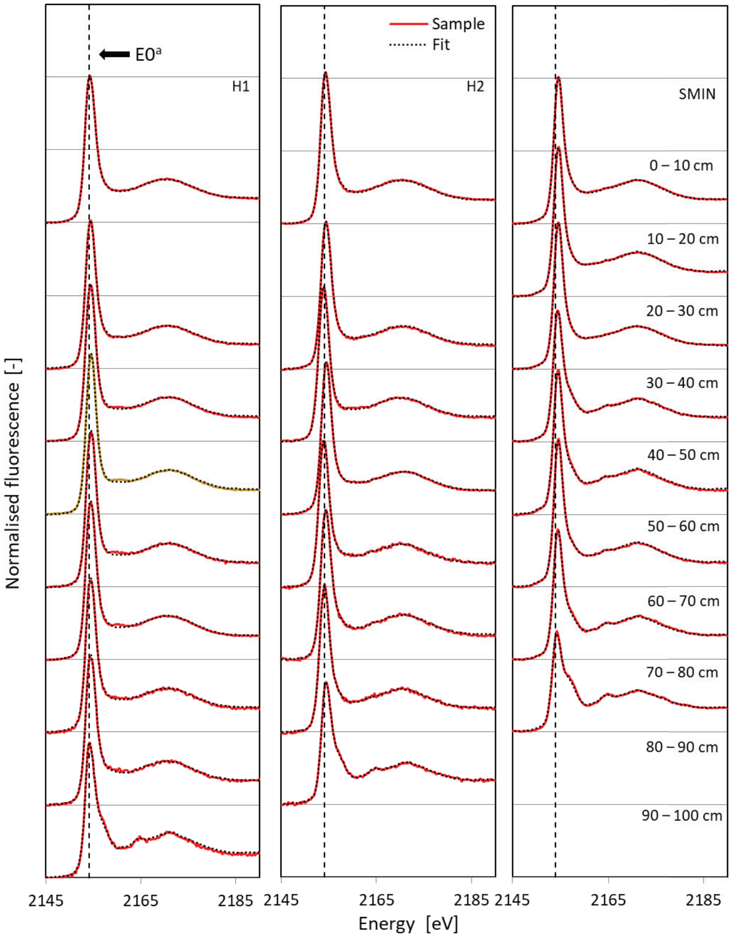

Figure 4. Phosphorus (P) *K*-edge X-ray absorption near-edge structure (XANES) sample spectra and best fit from linear combination fitting (LCF) for Histosol profiles H1 and H2 and mineral soil SMIN. Fits ranked according the goodness of fit factor R (Ravel & Newville, 2005). The dashed vertical line in the graphs represents absorption edge position E0 (2154.05 eV) of the variscite standard spectrum used for energy correction.

Table 5. *Results from linear combination fitting (LCF) for soil layers in Histosol profiles H1 and H2 and mineral soil SMIN. Phosphorus (P) reference spectra of the 10 best fits are summarised into P groups (P adsorbed to Fe; Fe-phosphates; P adsorbed to Al; Al-phosphates; Ca-phosphates; P-org). The relative contribution of each P group to the best fit (weight %) for a sample spectrum and the number of occurrences of reference spectra representing P groups within the 10 best fits (Count 10BF) are also shown. The best fit in this context refers to the fit with the lowest value of R (Ravel & Newville, 2005)*

Profile	Soil	P adsorbed to Fe		Fe-phosphates		P adsorbed to Al		Al-phosphates		Ca-phosphates		P-org		R
	depth	Weight	Count	Weight	Count	Weight	Count	Weight	Count	Weight	Count	Weight	Count	
	[cm]	[%]	10 BF[b]	[%]	10 BF	[%]	10 BF	[%]	10 BF	[%]	10 BF	[%]	10 BF	[-]
H1	0-20	10 ±1	2	0	0	10 ±0	10	0	0	0	3	79 ±8	10	3.0E-04
	20-30	0	0	0	0	29 ±3	10	0	0	0	0	71 ±5	10	3.7E-04
	30-40	5 ±5	3	0	0	28 ±6	10	0	0	0	0	67 ±11	10	1.3E-03
	40-50	8 ±0	6	0	0	35 ±5	10	0	0	0	0	57 ±11	10	9.9E-04
	50-60	17 ±4	10	0	0	20 ±2	10	2 ±3	2	0	0	61 ±1	10	1.2E-03
	60-70	8 ±2	2	0	0	30 ±0	10	0	0	0	0	62 ±8	10	1.0E-03
	70-80	22 ±3	3	0	0	8 ±2	5	0	0	0	0	70 ±13	10	1.2E-03
	80-90	25 ±4	10	0	0	0	0	6 ±3	2	0	0	69 ±13	0	1.4E-03
	90-100	14 ±6	8	0	0	9 ±5	3	0	0	66 ±4	10	12 ±3	10	4.3E-03
H2	0-20	8 ±0	2	0	0	14 ±1	10	0	0	0	0	78 ±5	10	2.6E-04
	20-30	10 ±0	2	0	0	19 ±1	10	0	0	0	0	72 ±3	10	7.3E-04
	30-40	4 ±6	2	0	0	27 ±6	10	0	0	0	0	69 ±12	10	1.3E-03
	40-50	26 ±4	3	0	0	14 ±3	10	0	0	0	0	60 ±13	10	4.3E-04
	50-60	0	0	0	0	33 ±1	10	0	0	11 ±2	7	56 ±12	10	9.4E-04
	60-70	0	0	0	0	32 ±1	9	0	0	11 ±1	7	57 ±5	10	7.7E-04

Profile	Soil depth [cm]	P adsorbed to Fe Weight [%]	P adsorbed to Fe Count 10 BF[b]	Fe-phosphates Weight [%]	Fe-phosphates Count 10 BF	P adsorbed to Al Weight [%]	P adsorbed to Al Count 10 BF	Al-phosphates Weight [%]	Al-phosphates Count 10 BF	Ca-phosphates Weight [%]	Ca-phosphates Count 10 BF	P-org Weight [%]	P-org Count 10 BF	R [-]
H2	70-80	0	0	0	0	37 ±1	10	0	0	17 ±2	10	46 ±6	10	1.1E-03
	80-90	0	3	9 ±1	3	20 ±1	7	0	0	58 ±2	10	13 ±1	0	1.0E-03
SMIN	0 -10	33 ± 3	8	14 ± 1	3	22 ±2	9	0 ±0	4	30 ±1	10	0	2	2.9E-04
	10-20	12 ± 3	3	27 ± 1	9	37 ± 2	10	0 ±0	3	24 ± 1	10	0	4	3.8E-04
	20 -30	45 ± 2	10	0	0	19 ± 1	9	0	0	22 ± 1	10	14 ± 1	8	2.3E-04
	30 40	39 ± 1	10	0	0	0	0	0	0	55 ± 3	10	5 ± 1	2	3.6E-04
	40-50	29 ± 5	9	21 ± 2	3	17 ± 3	3	0	8	33 ± 1	10	0	0	9.0E-04
	50-60	46 ± 4	10	12 ± 1	1	15 ± 2	4	0	9	27 ± 1	10	0	0	4.2E-04
	60-70	27 ± 4	10	10 ± 2	1	17 ± 2	5	0	9	46 ± 1	10	0	0	7.5E-04
	70-80	16 ± 2	8	7 ± 3	3	0 (5)	2	0	5	77 ± 11	10	0	0	2.2E-03

[a] Relative contributions of P forms in the best fit, *i.e.* with the lowest assigned R values.
[b] Number of occurrences of reference spectra representing a P group in the 10 best fits, *i.e.* assigned the 10 lowest R values.
[c] Goodness of fit factor R, calculated according Ravel and Newville (2005).

Despite the generally high fitting quality in LCF analysis, visual comparison revealed an obvious mismatch between sample and fitted spectra in the post-edge region for some sample spectra of the H1 and H2 profiles. This is shown for the example of the H1 sample spectrum at 30-40 cm soil depth in Figures 5a and 5b. Sample spectra that were affected by this were particularly those collected for subsoil layers with relatively elevated extractable Al and ash content. These spectra featured a visible indication of mineral P presence in the post-edge region. As illustrated in Figure 5b, the fitted spectrum did not adequately represent the 'trough' between absorption edge and the post-edge peak in an energy range between approximately 2158 eV and 2163 eV. Reflecting a P-org weight of 64%, the post-edge region of the fitted spectrum resembled more closely the sample spectrum for the top 20 cm. Eveborn *et al.* (2009) complemented LCF analysis by specifically fitting the sample spectra in the pre-edge region in order to increase the sensitivity for Fe-associated P. In a similar approach, LCF was carried out over the post-edge region from approximately +1 eV to +30 eV relative to E_0 for the H1 and H2 sample spectra. The composition of these fits differed from those carried out over the whole XANES energy region. The major difference was a reduced contribution of P-org references in favour of an increased weight of phosphate adsorbed to Fe/Al mineral phases. For instance, the P-org weight in the post-edge fit for the H1 sample at 30-40 cm depth decreased from 64% to 23%. As can be seen in Figure 5b, post-edge fits resembled the sample spectra in the post-edge region considerably more than the original fit over the complete XANES energy region. However, this came at the cost of a poorly fitted absorption edge in comparison with the sample spectrum (Figure 5c).

Nevertheless, post-edge fitting results regarding adsorbed mineral P for H1 were overall better correlated with extractable Fe, Al and P content. For instance, R^2 for the correlation between pooled weights of Fe-P and AL-P and Al-pstot content increased from 0.7 to 0.9 ($p<0.0005$). Moreover, an improved correlation ($R^2 = 0.8$; $p<0.005$) with Al-ox content was observed. A slight improvement in the correlation between the calculated content of adsorbed P and P-ox was achieved when using post-edge LCF results, with R^2 increasing from 0.8 to 0.9 ($p<0.0005$). For the H2 profile, a similar improvement in correlation between LCF results and results of wet chemical analyses was not observed. However, for this profile, differences between original and post-edge LCF results were less pronounced.

Mineral soil SMIN

According to the LCF results, P in the SMIN profile was almost exclusively present in inorganic forms (Table 5). The dominant P species in the topsoil were

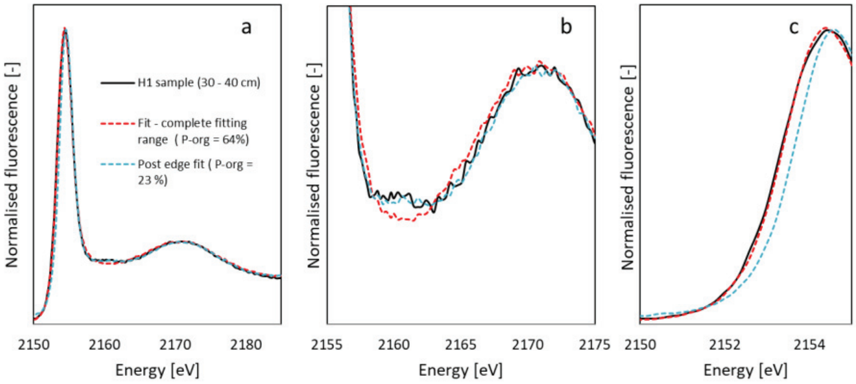

*Figure 5.*Sample spectrum for Histosol profile H1 at 30-40 cm depth and fitted spectra obtained with least square fitting over the whole XANES energy range (-10 eV to +30 eV relative to E0) and the post-edge region (+1 to +30 eV relative to E_0), shown a) for the default fitting range (-10 eV to +30 eV relative to E_0) and for better visibility b) zoomed into the post-edge region and c) the pre-edge region.

Fe-P and Al-P. With increasing soil depth, Ca-P gradually became the dominant P species. At 60-70 and 70-80 cm depth, the Ca-P weights in the best fits amounted to 47% and 77%, respectively. For the upper 30 cm, Ca-P weights amounted to a mean of 25%. Organic P references were only present in two of the best fits and a P-org weight above 10% was only observed in the fit of the sample at 20-30 cm soil depth.

With the exception of the deepest subsoil layer, the best-fit weights for Fe-P ranged between 40 and 60 %, which was in line with visible pre-edge features in the SMIN spectra (Figure 4). In contrast to the LCF results for the organic profiles, Fe-P references in the best fits also included those representing Fe-phosphates. In fact, in six out of eight best fits, an additional reference spectrum for amorphous Fe-phosphate was included, occupying weights ranging between 10 and 27 %. These fits included both a reference for an adsorbed form of Fe-P, most often P adsorbed to ferrihydrite, and the Fe-phosphate reference. With only one exception, the higher weight in the fits was thereby observed for the adsorbed Fe-P reference. The highest weight for Al-P, 37%, was observed at 10-20 cm depth. In other layers of the profile, the proportion of Al-P was approximately half as great. In all fits containing Al-P, it was represented by a reference for P adsorbed to gibbsite, *i.e*. the same form as in H1 and H2.

As found for H1 and H2, LCF results for SMIN were in part strongly correlated with wet-chemically determined content of Fe, Al and P throughout the profile. Weights of Al-P and, in contrast to H1 and H2, Fe-P were significantly ($p<0.05$) correlated with Al-ox and Fe-ox, with R^2 of 0.6 and 0.8, respectively. The strongest correlation was found between the pooled weight of Fe-P and Al-P and the pooled content of Al-ox and Fe-ox ($R^2 = 0.9$, $p<0.0005$). Correlating both P groups separately with results of wet chemical analyses revealed a significant correlation between calculated Al-P content and Al-ox content ($R^2 = 0.8$, $p<0.01$) and P-ox content ($R^2 = 0.8$, $p<0.05$). Calculated Fe-P content was not correlated to Fe-ox, but there was a strong correlation between observed Fe-P content and P-ox. The latter was equally strongly correlated to the sum of Fe-P and Al-P content. In both cases, R^2 exceeded 0.9 ($p<0.005$).

Calcium phosphates were represented in the best fits by hydroxyapatite, amounting to a weight of around 30%, and an amorphous form of Ca-P (ACP) in the 20-30 cm layer. Amorphous Ca-P included in the reference library differed from the crystalline form by a less pronounced peak at an energy of around 2164.7 eV.

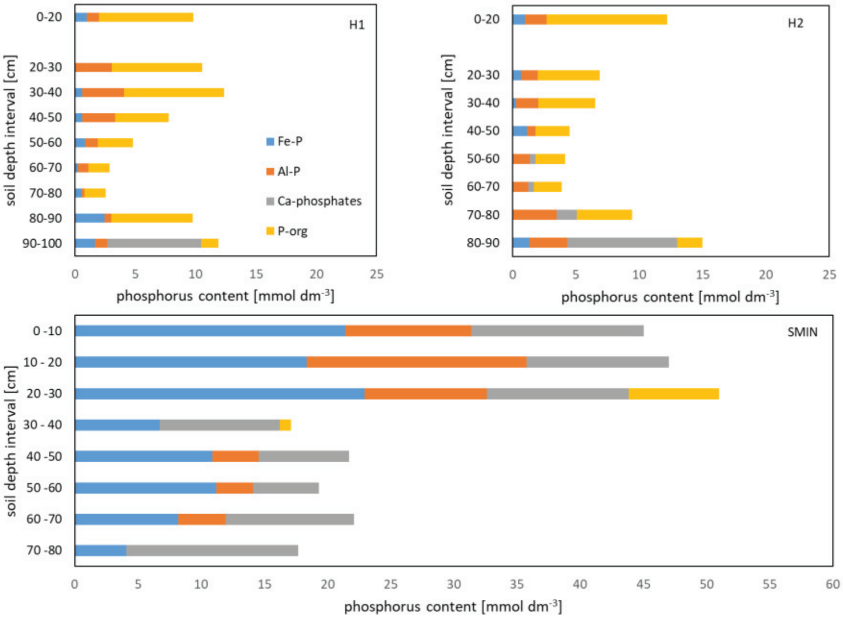

Figure 6. Volume-related phosphorus (P) content based on linear combination fitting (LCF) best fit weights and corresponding pseudo-total P (P-pstot) content in the soil layers of Histosol profiles H1 and H2 and mineral soil SMIN; Abbreviations: Fe-P = iron-associated P; Al-P = aluminium-associated P, Ca-P = calcium phosphate, P-org = organic phosphorus.

Impact of differences in bulk density between soil horizons in the organic profiles and between soil types

To illustrate the distribution of different P forms in the profiles when differences in bulk density were taken into account, Figure 6 presents the volume-related content of P forms in all three profiles. The content was calculated by relating LCF best fits weights to P-stot content in the corresponding soil sample. As mentioned, the SMIN profile contained overall substantially more P per unit volume than the H1 and H2 profiles. In both organic profiles, P-org content was higher in the topsoil than in subsoil layers, amounting at most to 8 and 10 mmol dm^{-3} in the uppermost 20 cm of H1 and H2, respectively. In the H1 profile, the P-org content remained high to a depth of 40 cm and decreased to 2 mmol below that. In H2, P-org decreased steadily with depth and deeper subsoil layers contained around 2 mmol dm^{-3}.

An exception to this pattern was the deepest compacted organic layer directly above the mineral soil in H1 and H2, where the P-org content was elevated to around 7 mmol kg^{-3} in both profiles. As levels of mineral P were also elevated in this layer relative to deeper subsoil layers, the higher P contents were the result of compaction rather than enrichment with P.

In H1, Al-P was elevated to 4 mmol dm^{-3} at 20-50 cm depth and decreased to 1 mmol dm^{-3} in deeper layers. With the exception of the compacted organic layer above the mineral soil, Fe-P content in H1 did not exceed 1 mmol dm^{-3}. In H2, the pool of adsorbed P, *i.e.* the sum of Fe-P and Al-P content, decreased with depth from 3 to 1 mmol dm^{-3}. The mineral layer of H1 and H2 mainly contained Ca-P, with a concentration of 8 mmol dm^{-3} in both profiles. The content of P-pstot (which corresponds to the sum of the content of each P group in Figure 6) was 12 and 15 mmol dm^{-3} in H1 and H2, respectively, and was hence similar to volume-related P-pstot content in surface layers of H1 and H2.

The calculated Fe-P content in the mineral soil was around 20 mmol dm^{-3} in the P-enriched upper 30 cm and, combined with the content of Al-P of 35 mmol dm^{-3}, adsorbed mineral P was the largest P pool in the top layer. In subsoil layers, less Fe-P and Al-P was adsorbed but the concentrations still exceeded that of adsorbed mineral P in deeper layers of H1 and H2. Although only a small fraction of soil P in SMIN was organic P, the content of 7 mmol dm^{-3} in the 20-30 cm layer was in the same range as in H1 and H2. The Ca-P content in the upper 30 cm was around 13 mmol dm^{-3}, which is similar to that in the mineral soil layer in H1 and H2. In subsoil SMIN layers, Ca-P decreased to 5-10 mmol dm^{-3}.

5.4 ^{31}P-NMR results

Liquid-state ^{31}P-NMR analysis of the organic profiles proved difficult. This was due to extremely high viscosity of freeze-dried concentrated extracts, which required strong dilution prior to the analysis. This in turn resulted in a decrease in the sample P concentration that led to the collection of low-quality spectra containing little information on organic P speciation in H1 and H2 samples. Therefore, only the ^{31}P-NMR spectra collected for the SMIN profile are presented here (Figure 7). The P concentrations in the NaOH-EDTA extracts for the upper 30 cm of SMIN corresponded to recovery of between 44 and 57 % relative to P-pstot content. In the subsoil, recovery was even lower, corresponding to around 30%.

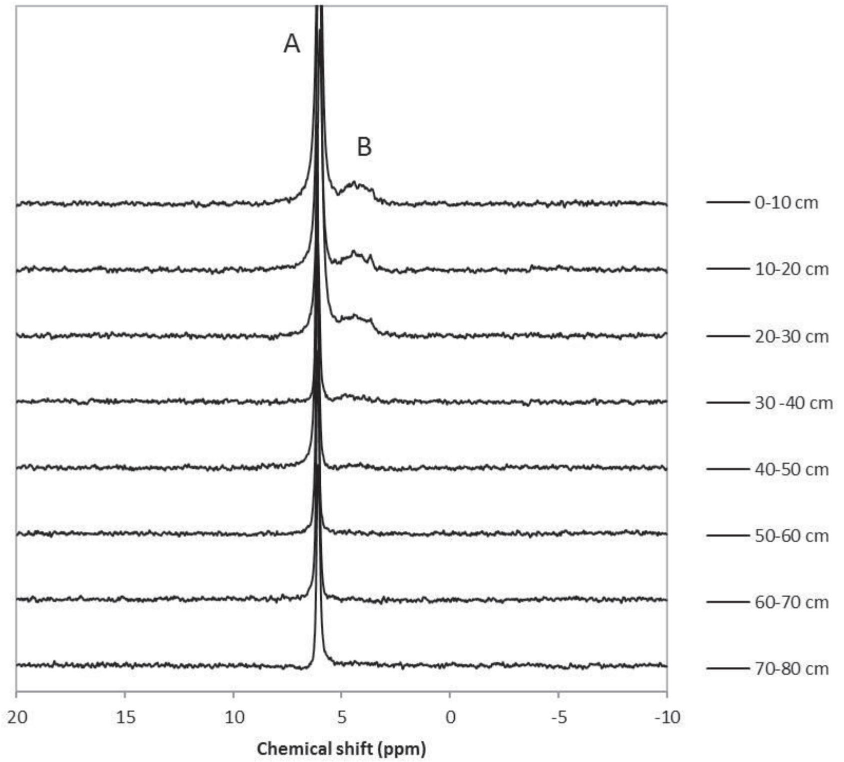

Figure 7. Solution ^{31}P-nuclear magnetic resonance spectroscopy (^{31}P-NMR) spectra of NaOH-EDTA extracts of soil samples of the mineral profile (SMIN). The resonance A is assigned to orthophosphate, while resonances B are situated in the chemical shift region assigned to phosphorus monoesters.

According to Figure 7, a central feature of all SMIN spectra was a peak at around 6.2 ppm, commonly assigned to PO_4 (Smernik & Dougherty, 2007). Clearly discernible additional signals were only present in spectra of the upper 30-40 cm of the profile. These signals were positioned in a chemical shift interval between 3 and 5 ppm and are commonly assigned to P monoesters. Integration of these peaks resulted in area proportions between 13% and 20%. This corresponded to a relative proportion of organic P in the top 40 cm of the SMIN profile ranging between 5 and 10 % of P-pstot. Thus, both XANES and ^{31}P-NMR analysis indicated a similarly low contribution of P-org to P speciation in SMIN.

5.5 Rainfall simulation study

Discharge volumes for each soil and each simulation event in the rainfall simulation study were not significantly different. On average, total discharge after four consecutive simulation events in which 50 mm rainwater was applied per occasion amounted to 191 mm and 195 mm in H2 and SMIN, respectively.

Figure 8 shows the geometric mean P concentration after each simulation event for the H2 and SMIN profiles. Phosphorus in leachate consisted almost exclusively of dissolved reactive P (DRP), *i.e.* inorganic PO_4. For the H2 profile, the highest P concentration in leachate (9.3 mg L^{-1}) was observed in the third simulation event, while in the case of SMIN the highest P concentration (7.6 mg L^{-1}) occurred in the fourth event. Visually, Figure 8 appears to suggest an increase in P concentration with each simulation step, particularly in the case of SMIN. Total P concentration in the first simulation event was only 2.7 and 4.9 mg L^{-1} in SMIN and H2, respectively. These concentrations corresponded to P loads for SMIN and H2 of 1.4 kg ha^{-1} and 1.8 kg ha^{-1} respectively in the first event in comparison with loads of 3.7 kg ha^{-1} and 4.6 kg ha^{-1} in the fourth simulation event. However, the differences were not statistically significant at $p<0.05$. The accumulated mean load of P that leached from both profiles after four consecutive simulation events amounted to 9.6 kg ha^{-1} and 14.8 kg ha^{-1} for SMIN and H2, respectively.

Results from complementary analysis of the leachate are presented in Table 6. The concentration of Fe, Al, and DOC in both soils was significantly correlated with the total P concentration in leachate. There was also a significant inverse correlation between Ca concentration and total P concentration in leachate ($R^2 = 0.5$-0.8; $p<0.05$; $n = 8$).

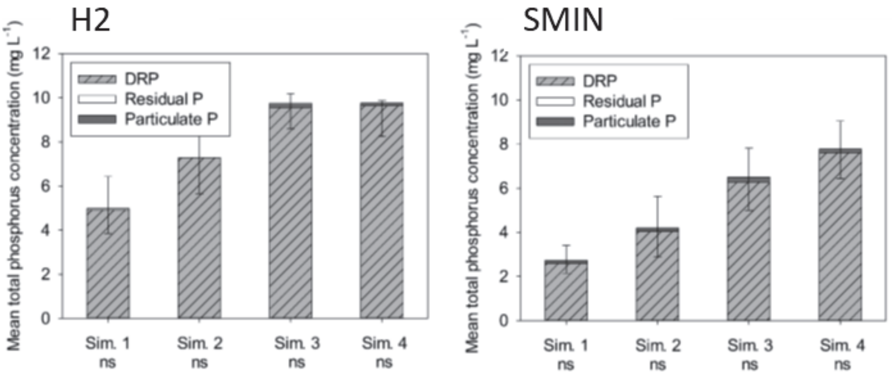

Figure 8. Geometric mean total phosphorus (P) concentration in leachate collected from top 20-cm soil columns of Histosol H2 and mineral soil SMIN after four rainfall simulation events (Sim.). Differences between simulation events were not significant (ns). Error bars represent geometric standard deviation (SD), which is multiplicative and therefore cannot be added or subtracted from the geometric mean. Upper and lower SD thresholds are calculated as geometric mean x geometric SD and geometric mean/geometric SD, respectively. DRP = dissolved reactive P.

Table 6. *Concentration of dissolved organic carbon (DOC), calcium (Ca), iron (Fe) and aluminium (Al) in leachate water from Histosol H2 and mineral soil SMIN columns. Values are mean of two replicates*

Soil	Simulation event	DOC	Ca	Fe	Al
				[mg L^{-1}]	
H2	1	117.5	185	0.225	0.71
	2	140.5	170	0.33	0.91
	3	206	89.5	0.67	1.4
	4	217.5	52.5	0.83	1.6
SMIN	1	29.5	195	0.065	0.01
	2	42.5	150	0.125	0.115
	3	57.5	52	0.21	0.15
	4	50.5	38	0.185	0.14

6 Discussion

6.1 Sources of P in enriched topsoil horizons (Papers I and II)

The three soil profiles investigated in this thesis were characterised by topsoil layers in which the P content was elevated relative to that in subsoil layers. Such enrichment is typically observed in arable soils that have received P in excess of crop demand over a long period and may be particularly severe for long-term manured soils, such as SMIN. Manure application rates are commonly determined by crop demand for nitrogen rather than for P, or simply by the amount of manure produced on farms (Annaheim *et al.*, 2015; Silveira *et al.*, 2006; Hooda *et al.*, 2001; Sharpley *et al.*, 1994). The speciation of P in the enriched topsoil and the processes leading to this enrichment appeared to be entirely different between the organic profiles H1 and H2 and the mineral SMIN profile.

6.1.1 Organic soils H1 and H2

Both organic profiles can be classified as mineral-rich fen peat soils, based on an ash content that was consistently above 5% (Steinmann & Shotyk, 1997; Tolonen, 1984). Elevated topsoil P content relative to that in the subsoil of drained peat soils has been reported in a number of previous studies (Kruse & Leinweber, 2008; Litaor *et al.*, 2003; Qualls & Richardson, 2000). It is commonly assumed that the proportion of P-org in drained peat layers decreases over time. This decrease is explained with increased microbial peat oxidation in drained peat soils (Litaor *et al.*, 2003). Increased peat mineralisation is assumed to result in a relative increase in ash content in drained layers, accompanied by formation of Fe and Al hydroxides. These mineral phases may act as binding sites for added fertiliser P. If not leached, mineralised organic P may add to the inorganic P pool in cultivated Histosols via adsorption or adsorption to mineral Fe- and Al-(hydr)oxides or co-precipitation with soil Al and Fe (Diaz *et al.*, 1993).

Studies that specifically reported an accumulation of P-org in topsoil of cultivated Histosols, as was the case in H1 and H2, are for instance those from Schlichting (2004) and Kaila & Missilä (1956). The latter attributed elevated P-org content in cultivated Histosols to incorporation of inorganic fertiliser P into soil microorganism biomass and crop biomass left in the soil as residues. An up to nine-fold increase in soil microorganism biomass in response to fertiliser P input has been observed for cultivated Everglades peat soils (Qualls & Richardson, 2000). However, it is also possible that a considerable part of the topsoil P-org originated from peat layers formerly present on top of the current soil surface, but broken down during soil subsidence.

The average subsidence rate for Nordic peat soil is reported to amount to around 20 mm per year (Stephens *et al.*, 1984). For study sites H1 and H2, this would correspond to loss of more than 1 m of the peat layer since their reclamation around 70 years ago. Assuming a P-org content similar to the current P-org content in the subsoil of H1 and H2, peat subsidence at the average rate could have contributed significantly to the elevated topsoil P-org content in H1 and H2.

This interpretation is clearly based on the assumption that a significant part of the P-org in lost peat layers was not mineralised. The C:P ratios observed throughout the organic profiles support this assumption. According to the LCF results, the molar ratio of C-org to P-org in the top 20 cm of H1 and H2 ranged between 1000 and 1500. It was even higher, up to 3500, in the subsoil layers.

Despite high taxonomic variety, soil microorganisms maintain a nutrient stoichiometry within narrow boundaries at an average C:P ratio of around 60 (Spohn, 2016). Hence, the relationship between stoichiometry of microorganisms and substrate such as peat is an important factor controlling the turnover of nutrients, including P, in soils (Spohn, 2016). According to this concept of critical substrate nutrient ratio, significant microbial net P mineralisation can only be expected if the substrate contains more P relative to C than decomposing microorganism biomass. With a C:P ratio substantially exceeding 60, the peat material in H1 and H2 represented a highly P-deficient substrate for microbial decomposers. Therefore, it is unlikely that there was significant net mineralisation of P-org from the decomposed former peat layers. Instead, incorporation of readily available fertiliser P into the decomposer biomass probably occurred, as proposed by Kaila and Missilä (1956). Bünemann *et al.* (2012) also found mineralised P in P-deficient grassland soil to be rapidly immobilised by the soil microbiota. A more detailed speciation of P-org in the organic soil to complement XANES LCF with its previously mentioned limitations was not carried out in this thesis. It was therefore not possible to corroborate that the P-org pool in the topsoil contained a relatively higher proportion of biomass P.

The fact that inorganic P was apparently not accumulated to a similar extent in the topsoil of the organic profiles H1 and H2 as in SMIN could be due to a better balance between P input and crop demand in the organic soils. However, it may also indicate that mineral P was more mobile in the organic soils. Column study results confirmed that the P mobilised from the topsoil of H2 was overwhelmingly inorganic. In addition, the observation that the maximum adsorbed P content (Fe-P and AL-P) in the H1 profile was not found in the topsoil, but at 30-60 cm soil depth, indicates higher mobility of P in the organic soils. The strong correlation observed between the pool of Fe-P and Al-P and oxalate-extractable Fe and Al content indicates vertical distribution of adsorbed P in H1 and H2 according to the presence of sorption sites. It also suggests high mobility of P in the organic profiles, where the content of Fe-ox and Al-ox was lowest in the topsoil. Adsorbed P in the subsoil peat layers may therefore constitute excess fertiliser P that could not be retained in the topsoil due to lack of available sorption sites.

6.1.2 Mineral soil SMIN

In contrast to the findings for the H1 and H2 profiles, the P in the enriched upper soil of SMIN was inorganic. This is in agreement with findings in the majority of previous studies on P speciation in excessively manured soils (Annaheim *et al.*, 2015; Silveira *et al.*, 2006; Hooda *et al.*, 2001; Sharpley *et al.*, 1995). Apparent confinement of P accumulation to the plough layer has also been observed previously (Szogi *et al.*, 2013). A common feature observed in previous studies on P speciation in manure-amended soil is that a substantial part of P to be adsorbed to Fe and Al surfaces (Ajiboye *et al.*, 2008; Beauchemin *et al.*, 2003).

A widespread assumption based on geochemical equilibrium models is that Fe and Al mineral phases are more important for retaining P in acid soils, while P solubility in neutral to acid soil is controlled by calcium phosphates (Lindsay, 1979). However, several previous studies have found Fe- and Al-(hydr)oxides also to be of importance for P retention in non-acidic soils (Ajiboye *et al.*, 2008; Bertrand *et al.*, 2003; Samadi & Gilkes, 1998; Hamad *et al.*, 1992). For instance, oxalate-extractable Fe and Al has been identified as the best predictor for P leaching in neutral to alkaline soils of Canada (Tran & Giroux, 1987).

In the SMIN profile, Ca-P was present in the topsoil and made up about 30% of P-pstot in that layer, in agreement with previous studies (Hansen *et al.*, 2004; Sharpley *et al.*, 2004; Koopmans *et al.*, 2003; Delgado & Torrent, 2000). Sample spectra indicated that topsoil Ca-P was in less crystalline form than in the subsoil, where it is most likely present as primary apatite. A high proportion of apatite is a common feature of Scandinavian soils such as SMIN, where current pedogenesis did not start before the retreat of the Weichselian glaciation (Eriksson *et al.*, 2016; Uusitalo & Tukanen, 2000). However, it has been shown that topsoil P speciation in pristine soils may be rapidly altered by biologically induced weathering, often within decades to centuries (Prietzel *et al.*, 2013). This includes apatite dissolution in response to accelerated soil acidification driven by organic acids excreted by soil microbiota. Such a decrease in the apatite content towards the soil surface has been reported for a Swedish arable soil by Eriksson *et al.* (2016). This trend was not apparent in the SMIN profile, but it seems likely that the nature and origin of Ca-P differed between topsoil and subsoil in that profile. As regards the origin of topsoil Ca-P, it may have been formed *in situ* from Ca and P added with manure under prevailing alkaline soil pH conditions. Neo-formation of Ca-P in long-term manured soil has been suggested by Sato *et al.* (2005). Alternatively, Ca-P compounds present in manure could have been added with manure. Several studies have confirmed a high proportion of Ca-P in different types of manures (Güngör *et al.*, 2007; Toor *et al.*, 2005).

6.2 General P speciation in the profiles (Papers I and II)

6.2.1 Calcium phosphate in the profiles

A high degree of crystallinity of Ca-P in the subsoil layer was evident, due to characteristic visible spectral features in the sample spectra. A higher degree of crystallinity of Ca-P in subsoil compared with topsoil was also supported by the oxalate extraction results and PSI values. The latter were extremely high (over 90%) in the topsoil. A reasonable explanation for this observation is that part of the oxalate-extractable P pool originates from Ca-P dissolved due to the acid pH in ammonium-oxalate extract. Previous studies reached similar conclusions when seeking to explain unreasonably high PSI values in alkaline soils (Koopmans *et al.*, 2007; Peltovuori *et al.*, 2002). This led Peltuvuori *et al.* (2002) to question the suitability of PSI as a tool for predicting P leaching risk for soils rich in primary apatite.

From the above, it follows that PSI values were most likely overestimated throughout the SMIN profile. In all but two layer, subsoil PSI values exceeded the 30% threshold indicating a high risk of leaching according to De Smed *et al.* (1998). The fact that PSI values were less extreme in the subsoil of SMIN may be explained by *e.g.* the presence of primary apatite, as opposed to secondary Ca-P in the topsoil. Crystalline apatite can be expected to be less readily dissolved by acid ammonium oxalate extraction.

6.2.2 Iron- and aluminium-associated P in the profiles

Frequent presence of the Fe-phosphate reference in SMIN best fits did not permit conclusions to be drawn on whether such P species were present in the suggested relative proportions in this profile. Reference spectra for P adsorbed to Fe mineral phases and Fe-phosphates are generally very similar and differ primarily in the intensity of the pre-edge shoulder, with the latter being more pronounced in spectra for Fe-phosphates (Hesterberg *et al.*, 1999). There is hence always a risk of spectra of both Fe-P forms being intermittently included in the best fits without predictive significance, as a form of non-unique fitting. Weights of Fe-phosphates reference varied widely between fits of the different soil layers and were totally absent in some. Overall, Fe-P was rather evenly distributed throughout most of the SMIN profile, with weights ranging between 40 and 50 %. Hence, a low weight of Fe-phosphate or the absence of such spectra in the fits was frequently compensated for by increased weights of adsorbed Fe-P forms. In general, Fe-phosphates are associated with acid soils (Lindsay, 1979). A significant proportion of Fe-phosphates such as strengite in the soil can influence the potential for P mobilisation, due to their low solubility (Bolan *et al.*, 1986).

Iron associated P being an important fraction of P in the SMIN soil was already indicated by slightly visible pre-edge features in the corresponding sample spectra. As regards the distribution between of P between Fe- and Al-mineral surfaces, it is worth noting that a distinction between Fe-P and Al-P based on LCF is difficult (Beauchemin *et al.* 2003). However, the significant correlation between LCF results and ammonium-oxalate extractable Fe, Al, and P do suggest that the distribution of both Fe-P and Al-P throughout the SMIN profile and the high portion of this P pool of total soil P is reasonable. Our results are hence in line with earlier findings from Beauchemin *et al.* (2003) and Ajiboye *et al.* (2008) who also observed high portions of P adsorbed to Fe and Al surfaces in long-term manure amended and/or non-acidic soils.

In contrast to the SMIN results, the majority of adsorbed inorganic P in H1 and H2 was associated with Al. In H1 this was reflected by a higher content of surface reactive Al in comparison with Fe. Predominance of inorganic P adsorbed to Al phases in H1 was furthermore supported by strong and significant correlations between Al-P according to LCF and extractable Al and P.

However, in H2, Al-P weights were higher in LCF despite the content of surface reactive Al and Fe being similar throughout this profile. With a similar shape of the post-edge oscillation, the major feature distinguishing Fe-P from Al-P spectra is the pre-edge shoulder typical for Fe-P reference spectra. Being subtle in general, this feature can be superimposed in spectra of samples containing high proportions of P-org or Ca-P, such as the H1 and H2 soils. Hence, a sufficiently high contribution from P-org or Ca-P species in a sample will cause the sample spectra to be shifted towards a slightly lower energy, which would hinder the identification and correct quantification of Fe-P and increase the risk for non-unique fitting. In fact, there was a peculiar total lack of Fe associated P in the sub soil of H2 in the LCF results. This, indeed, suggests that the distribution of Fe-P in the organic profiles was not correctly reflected in the LCF results. However, the fact that pooling LCF weights for Fe-P and Al-P in this profile improved the correlation with extractable Al and not with Fe may further indicate that Al-P was indeed dominant inorganic P form in the organic profiles.

Results from LCF in comparison with post-edge LCF for the organic soils can be interpreted as indicating the presence of a P species that was not adequately represented by any of the reference spectra in the standard library. A hypothetical reference spectrum combining a shape of the post-edge region similar to mineral P species with an absorption edge shifted towards lower energy, as in the case of P-org species, could theoretically improve LCF performance for some sample spectra, particularly in the H1 profile.

Candidates for P species that could reasonably be present in the two organic soils but were not represented in the standard library are organic P associations with Fe or Al mineral surfaces. Phytate, the presumably most abundant form of organic P in soils, binds strongly to mineral surfaces (Prietzel *et al.*, 2016; Gerke, 2015).

Prietzel *et al.* (2016) compared XANES spectra of phytate adsorbed to different Al and Fe mineral surfaces and Al- and Fe-saturated SOM with spectra collected for PO_4 adsorbed to the corresponding minerals. While the spectra shared many features, subtle differences were identified. In particular, the spectrum for phytate adsorbed to Al-saturated SOM featured an absorption edge which was slightly shifted towards lower energy in comparison with its PO_4 counterpart. At the same time, post-edge oscillations were positioned at nearly the same energy in the two spectra (Prietzel *et al.*, 2016). With these characteristics, the fitting quality for the subsoil spectra could potentially be improved. Subsoil organic layers in the organic profiles contained considerable amounts of mineral material and pyrophosphate extraction revealed major proportions of Al and Fe associated with SOM. Although there is no conclusive evidence, presence of associations between P-org and mineral phases seems probable in these mineral-enriched fen peat soils. This may also be of significance regarding the distribution of P between Al and Fe surfaces. According to Prietzel & Klysubun (2018), spectra of P-org adsorbed to goethite tend to feature a clearly less pronounced pre-edge shoulder than corresponding PO_4 spectra. This carries a risk of the relative contribution of Fe-associated P being underestimated if such spectra are not included in the reference library for LCF (Prietzel & Klysubun, 2018).

6.2.3 Organic P in the profiles

The ^{31}P-NMR and P *K*-edge XANES analyses independently revealed a low contribution of P-org in the SMIN profile. Other soils receiving regular and long-term inputs of organic material have also been reported to contain low proportions of P-org (Annaheim *et al.*, 2015; Koopmans *et al.*, 2003). This has been attributed to either mineralisation processes or leaching losses of P-org (Annaheim *et al.*, 2015).

The only organic P-related signals in the ^{31}P-NMR spectra were located in the P monoester region. Monoester P forms such as phytic acid are frequently reported to be the major organic form of P in soil and in manure (*e.g.* Hansen *et al.*, 2004; Koopmans *et al.*, 2003; Bedrock *et al.*, 1994; Condron *et al.*, 1990). A criticism is that the extraction step in liquid-state ^{31}P-NMR may cause hydrolytic destruction of P diesters. Some researchers argue that the monoester P dominance in soils might be an artefact related to the extraction step in liquid-state ^{31}P-NMR analysis (Cade-Menun & Liu, 2014; Kizewski *et al.*, 2011). A reference spectrum of the P diester P (lecithin) was included in fits for SMIN and the organic soils. However, as previously mentioned, more detailed identification of P-org species by means of LCF analysis was difficult, due to lack of unique spectral features in spectra of many P-org species. The presence of phosphate diester references in LCF fits is not sufficient to draw the conclusion that phosphate diester species constitute a major proportion of P-org in the profiles. Moreover, phosphate monoesters are known to be comparatively resistant to microbial degradation, through *e.g.* binding strongly to the mineral soil matrix (Gerke, 2015; Condron *et al.*, 2005; Turner *et al.*, 2002). Due to analytical difficulties, organic soils were not analysed by ^{31}P-NMR in this thesis. However, the argument of high recalcitrance supporting the presence of phosphate monoesters applies in principle to top soil layers of the organic profiles as well. Schlichting (2004) applied ^{31}P-NMR to cultivated Histosols and found both, P monoesters and diesters. The former dominated particularly in topsoils, reflecting accumulation of monoester P due to a higher degree of decomposition.

A tendency to strongly interact with the soil mineral matrix is one of the reasons for the proposed recalcitrance of phosphate monoesters such as phytate (Gerke, 2015; Doolette & Smernik, 2011). Almost no organic P was leached from H2 topsoil in the column experiment in this thesis, despite high simultaneous release of DOC being observed during the leaching experiment. This observation points towards P-org being strongly retained in the organic profiles.

6.3 Uncertainty related to P *K*-edge XANES data collection, treatment and P speciation based on least squares fitting approaches (Papers I and II)

Phosphorus *K*-edge XANES is a direct non-destructive analytical method requiring minimal sample pre-treatment, as such avoiding the potential for chemically altering P in the sample prior to or during analysis. However, the interpretation of XANES data based on LCF analysis introduces an element of uncertainty (Ajiboye *et al.*, 2007).

Ajiboye *et al.* (2007) studied the performance of LCF for binary mixtures of P compounds and observed the highest relative error on fitting a binary mixture of Fe-P (75%) and Ca-P (15%). In the fitted spectrum, the weight of the Fe-P reference amounted to 90% instead of the actual Fe-P proportion of 75% in the standard mixture. The error in soil samples containing an unknown number of unknown P species in a complex matrix can be expected to be considerably higher. This is especially the case for P-org rich samples, due to the lack of unique spectral features in XANES spectra of many organic P forms (Kruse & Leinweber, 2008). Quantitative P speciation based solely on linear fitting of sample XANES spectra is thus not reliable.

Uncertainty in P speciation based on a LCF approach for P *K*-edge XANES spectra may arise from several problems related to the quality of XANES data, data preparation and data treatment. For example, self-absorption is known to limit the potential of soft XAS data obtained in fluorescence mode for quantitative P speciation. Persson *et al.* (2018) showed that spectra obtained in transmission mode are superior to those obtained in fluorescence mode. Using an approach devised by Troeger *et al.* (1992), Hesterberg *et al.* (1999) calculated self-absorption effects in mineral P samples of 800 mmol kg^{-1} to be around 8%. Based on the results, those authors concluded that self-absorption does not critically diminish the potential to use fluorescence P *K*-edge XANES data for P speciation in soil samples. Standard P compounds in this thesis were prepared with the criterion of keeping the P concentration below 800 mmol kg^{-1}. If necessary, the samples were diluted using boron nitride, as widely done in previous studies (Kruse *et al.*, 2015; Kelly *et al.*, 2008). Blake *et al.* (2018) monitored the onset of visible effects of self-absorption on spectra for sodium pyrophosphate and hydroxyapatite by gradually increasing the sample thickness. The results confirmed that the effects were minimal when the sample was applied as a thin layer on kapton tape, as done in preparation of standard P samples in this thesis.

In soil samples the P concentration is often substantially lower, which may be a concern in itself regarding the collection of spectra with satisfactory signal to noise ratio. Eriksson *et al.* (2015) collected spectra from the P-enriched clay fraction of agricultural soils as a means of increasing the P concentration in samples to improve spectral quality. However, self-absorption may also affect spectra for low-P soil samples, due to the heterogeneous distribution of P in soils. Localised P accumulation in the sample may lead to significant self-absorption, despite the overall concentration in the sample being low (Hesterberg, 2010). In line with common practice, in this thesis the soil samples were finely ground and sieved to a particle size of less than 0.05 mm. The low P concentrations in soil commonly do not permit acquisition of XANES data in total electron yield mode (TEY), which would circumvent this problem. Therefore, studies on soil P speciation are overwhelmingly reliant on fluorescence P *K*-edge XANES data. Moreover, the low probing depth of TEY could have introduced additional uncertainty.

In summary, it must be acknowledged that sample and reference spectra collected in this thesis may been affected by self-absorption. However, due to the precautions undertaken to minimise these artefacts and the experience from previous studies, the effects can be expected to have been at an acceptably low level. Self-absorption effects admittedly contribute to the overall uncertainty related to LCF. Therefore, this thesis did not rely on LCF results alone to determine the P speciation in the three soil profiles studied. Normalisation of sample and reference spectra to reduce spectral differences that are not related to the molecular coordination environment is crucial for LCF analysis. Attempts should always be made to apply a similar normalisation procedure to all sample and reference spectra (Kruse *et al.*, 2015; Kelly *et al.*, 2008). However there is a lack of standardisation regarding the normalisation of XANES spectra between studies (Eriksson, 2016). Obviously, this may cause difficulties when different studies are compared.

In this thesis, the procedure outlined by Eriksson *et al.* (2015, 2016) was applied, where a quadratic function was regressed to the post-edge region between 30 eV and 45 eV relative to E_0. Data noise and baseline trends made it necessary to alter data points for some spectra.. This was in line with recommendations by Eriksson (2016) and was done to correct for visible misrepresentation of the post-edge region by the regression function due to data noise. Other protocols for data treatment and normalisation exist, for instance that developed by Werner and Prietzel (2015). It would certainly be interesting to test different approaches on the same data in the future. In summary, it needs to be stated that normalisation was an important source of uncertainty in the LCF analysis reported in this thesis. The establishment of a more generally accepted procedure would be an important first step in dealing with this problem.

Slight differences in energy position of less than 0.5 eV between sample spectra and reference spectra were interpreted in this thesis as an indication of the presence or absence of P-org species. However, possible shifts in the energy position of sample and reference spectra due to temperature differences and mechanical problems related to the monochromator introduce uncertainty regarding the interpretation of sample spectra energy positions. To minimize the impact of these shifts, not directly related to atomic structure of P atoms, the good practice of repeatedly collecting a variscite reference spectrum was followed during the beam sessions. The edge position from these spectra was subsequently used for energy correction of sample and reference spectra (Kelly *et al.*, 2008; Beauchemin *et al.*, 2003). The effectiveness of this practice is illustrated in Figure 9, which compares normalised spectra collected for a H1 sample in two different beam session. There was a clearly visible difference in edge energy between spectra when no energy correction was carried out, despite both spectra being collected from the same sample.

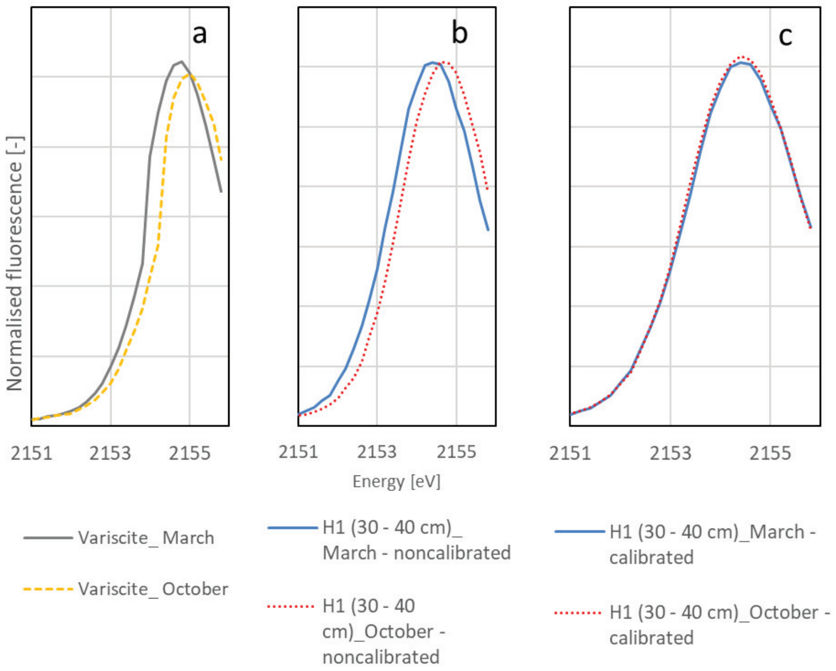

Figure 9. Energy correction of a sample spectrum collected during different beam sessions. a) Variscite standard spectra collected in beam sessions in March and October 2015; b) non-calibrated normalised spectra collected for the Histosol H1 sample (30-40 cm layer) during the same beam sessions; c) calibrated normalised spectra collected in March and October 2015, where calibration was done using the energy shift observed between the variscite spectra.

Linear combination fitting may be affected by non-unique fitting, *i.e*. different combinations of references may result in spectra with similar fitting quality. For example, Fe-phosphate and adsorbed Fe-P references were interchangeably included in the SMIN fits in this thesis. The risk of LCF results being affected by non-unique fitting decreases when the P speciation is dominated by unique characteristics, such as for Ca-P. However, it is rarely reduced to an extent that permits conclusive identification of a specific P species based on LCF results. Topsoil fits for the SMIN profile containing Ca-P references of different crystallinity serve as an example of this.

The goodness of fit factor (R) on which ranking of fits was based in this thesis and other studies is calculated over the entire fitted energy range (*e.g*. Eriksson *et al*., 2016; Eveborn *et al*., 2014). However, certain regions in the fitted spectrum may be of particular importance for the identification of P forms, such as the pre-edge region for Fe-P. It is therefore meaningful to complement the LCF analysis by fitting a sample spectrum over an energy range of particular interest, as done by Eveborn *et al.* (2009) for the pre-edge region. Moreover, as exemplified for H1 and H2 spectra in this thesis, this approach can provide useful additional information when addressing visible deviations between sample and fitted spectra. For these spectra, limiting the fitting rage to the post-edge region suggested that P in the samples was present in forms not represented by the standard spectra used for LCF. The risk of an insufficient standard library affecting the outcome of LCF analysis can be reduced by including a greater number of references in the standard library. However, this may increase the risk of non-unique fitting or overfitting. Some XANES studies have applied principal component analysis (PCA) to narrow the number of standards used for least square fitting to those that are statistically most likely to explain the sample spectra (Beauchemin *et al.*, 2002). This approach improves LCF analysis with regard to time consumption and ease of handling, but does not actually reduce the uncertainty.

As regards the identification of specific P species with LCF, Kelly *et al.* (2008) pointed out that P in a highly complex matrix such as soil is present in varying degrees of crystallinity and content of mineral impurities. This complexity cannot be expected to be adequately simulated with a set of pure standard spectra. Repeated inclusion of a particular reference spectrum in the best fits is not sufficient to assume that a particular P species is indeed present unless this can be confirmed by additional analysis.

In order to address the uncertainty of LCF, it is generally recommended to complement XANES experiments with additional analyses in order to obtain as much relevant additional information as possible about the system under study (Hashimoto & Watanabe, 2014; Negassa & Leinweber, 2009; Kruse & Leinweber, 2009; Kelly *et al.*, 2008). The selection of techniques will depend on the nature of the sample, the forms of P expected to be present and their concentrations. In the majority of XANES studies, complementary analyses include different wet chemical extraction methods (*e.g.* Kruse & Leinweber, 2008; Sato *et al.*, 2005; Beauchemin *et al.*, 2003). These analyses also proved to be a useful complement in this thesis. Results from LCF regarding the distribution of Fe- and Al-associated P throughout the three soils studied here were clearly corroborated by strong and significant correlations with the content of oxalate-extractable Fe, Al and P. Wet chemical extraction results were also beneficial in interpreting LCF results regarding the crystallinity of Ca-P included in fits for the SMIN profile. In addition, good agreement was observed between ^{31}P- NMR results and LCF-based P speciation in the SMIN soil.

In summary and in line with the previously mentioned studies it can be stated that the combination of P K-edge XANES with additional wet-chemical and spectroscopic techniques proofed to be suitable approach for P speciation in soil with reasonably high confidence. However while this approach helps to overcome limitations associated with each of the applied techniques, it does of course not eradicate all uncertainty related to P speciation in soil. Nevertheless, the overall high degree of consistence observed between results from the different techniques applied in this study indicate that the P speciation in the profiles as suggested in LCF results is realistic. Phosphorus leaching from soil columns and links between leaching and soil P speciation

6.4 Phosphorus leaching from soil columns and links between leaching and soil P speciation (Papers I, II, and III)

The results of the column study exemplified the potential for substantial P losses from long-term manured soils and from cultivated Histosols. Despite the volume-related P-pstot content in the mineral soil being four-fold higher than in the organic soil, P leaching losses from the H2 columns exceeded those from the SMIN columns. The main form of P in leachate was inorganic. Assuming that the P-org pools in H1 and H2 did not significantly contribute to P leaching, this leaves the considerably smaller pool of Fe-P and Al-P as the source of leached P. The cumulative mean amount of P leached per H2 column was 14.8 kg ha^{-1}. This corresponded to 9% of the total amount of Fe-P and Al-P contained in the column volume according to LCF. Even when related to P-pstot in columns, this percentage was as high as 2%. Even when acknowledging the artificial experimental conditions (e.g. only top soil columns, high rates of artificial rainfall) these figures are remarkable considering the short duration of the leaching experiment. Reddy (1983) reported P leaching from Histosol columns that corresponded to 2-20% of total soil P on an annual basis. High potential of cultivated Histosols to replenish removed P was demonstrated by Schlichting (2004). With only six consecutive extractions with double lactate (a German standard method for determining plant-available P) in that study, up to 14% of total P in the sample was mobilised. Cumulative P leaching from the SMIN columns in this thesis corresponded only to 0.3% and 0.4% of P-pstot of the pooled Fe-P and Al-P content, respectively. These results indicate potential of cultivated Histosols to contribute over-proportionally to P export from arable land.

The observed losses cannot be considered as representing leaching losses under field conditions but rather a potential of P mobilisation from topsoil layers. Interaction of mobilised P with deeper soil horizons could not occur. The potential of subsoil layers to affect P leaching is documented (Anderson *et al.*, 2013). For the SMIN sampling site, maximum annual losses to the drainage system of up to 2.5 P kg ha^{-1} have been recorded (Stjernman-Forsberg *et al.*, 2016). In contrast to this, P leaching from SMIN topsoil columns corresponded to 9.6 kg ha^{-1}.

Subsoil layers may function as a potential sink for P dissolved in soil solution by supplying additional sorption sites (Anderson *et al.*, 2013). Results from wet chemical Fe and Al extraction suggested this possibility for both H2 and SMIN. Moreover, it is unlikely that the ionic strength in the leachate from both soils would have been equally reduced after the rainfall simulation events if the leachate had been forced to pass through the whole profiles, rather than the 20 cm column. This is important, since the gradually decreasing ion strength in the leachate after each simulation event may be primarily responsible for the observed pattern of Ca and DOC in the leachate and also that of P.

The overall volume of 200 mm applied in four consecutive rainfall simulations over two weeks corresponded to approximately one-third of the annual average precipitation at the study sites (range 600-700 mm). Storm events similar to the simulated rainfall events have been documented in the sample area, but occur at a frequency of 1 in 100 years (Wern, 2012). Thus the column study was clearly a worst case scenario. The high rates of artificial rainfall appeared to cause depletion of exchangeable ions in the columns of both H2 and SMIN, which was reflected in the observed decrease in electrical conductivity and the increase in Ca concentration with each consecutive simulation event. Calcium is among the major readily exchangeable cations in soils (Lindsay & Moreno, 1960). The increase in DOC with each leaching event observed in both soils may be best explained as a response to a decrease in ion strength of the leachate water. It is well established that decreasing ion strength may promote the release of DOC (*e.g.* Hruška *et al.*, 2009; Kalbitz *et al.*, 2000).

Likewise, it has been reported that phosphate sorption in soils is affected by soil solution ionic strength (Wang et al., 2009; Ryden & Syers, 1975; Rájan & Fox, 1972). For instance, Bolan *et al.* (1986) observed a decrease in P adsorption with increasing ion strength of the soil solution. Therefore, the significant correlation observed between DOC and P-tot in leachate in this thesis may reflect that mobilisation of both was influenced by a reduction of the ion strength in soil solution with consecutive rainfall simulation events. The observed similarities regarding the variation in DOC, Ca and P concentration in leachate from H2 and SMIN columns suggests that this may have been also the case in the mineral in SMIN. This in turn, reduces the probability of *e.g.* a contribution of the P-org pool in H2 to P leaching via microbial P mineralisation. The organic P content in SMIN was low and consisted primarily of recalcitrant phytate monoesters according to ^{31}P-NMR analysis. It is unlikely that P mineralisation played an important role for P leaching from SMIN columns. In principle, microbial net P mineralisation in soils is difficult to measure due to methodological challenges in accounting for remobilisation and sorption of mineralised P onto soil mineral surfaces (Bünemann, 2015). Rates of net P mineralisation sufficiently high to replenish plant uptake in grassland soils have been reported, with mineralisation rates measured with isotopic dilution approaches ranging from 0.6 to 2.7 mg kg^{-1} day^{-1} (Bünemann, 2015). Only a mineralisation rate near the reported maximum could potentially make the organic P pool in H2 a significant source of leached P in the column study. A cumulative mean of more than 40 mg of P leached from the H2 columns over the course of the column experiment. Finally, and as previously mentioned, the results in this thesis suggest low net P mineralisation and a predominance of recalcitrant P-org forms in the H1 and H2 profiles.

The high SOM content in H2 may nevertheless help to explain why inorganic P leaching losses from this soil were exceeding those from the SMIN columns, despite a considerably lower P saturation according to PSI. This observation was in line with Kang *et al.* (2009) who found that non–crystalline and organically bound Fe and Al in high SOM soils is less effective for P sorption as compared to soil with lower SOM content. In addition, Hutchison & Hesterberg (2004) observed a strong correlation between DOC and soil P mobilisation from wetland soils under reducing conditions in incubation experiments. They argued that the increased formation of DOC under reducing conditions could have enhanced the release of P via competition for sorption sites and additonally via the formation of soluble ternary organo-metallic phosphate complexes. Similar processes may have also contributed to the high P leaching losses observed for the H2 columns, with the difference that DOC increase in the current study was caused by a decline in soil solution ion strength. This interpretation is supported by the fact that DOC concentration was substantially higher in leachate from H2 columns as compared to SMIN columns (Table 6).

Competition between organic anions and phosphate for adsorption sites has repeatedly been suggested to explain the observation of increased P mobility in soils with increasing SOM content (Lindegren & Persson, 2009).

Such competition will arguably have a higher impact on P sorption in organic soils than in mineral arable soils, where the SOM content is usually low (Pulleman *et al.*, 1999). The PSI index as a tool to predict the risk of leaching does not specifically consider competition for sorption sites between DOC and phosphate as it was primarily developed on minerals soils. Overestimation of P saturation in wetland soils using this index is known from previous publications (Schlichting, 2004). Use of PSI for comparison of organic soils with mineral soils would require further evaluation of how the actual P sorption capacity in these soils is represented by ammonium oxalate extraction of Fe and Al. Reddy *et al.* (1995) proposed that only 24% of Fe-ox and Al-ox may effectively be available to sorb P in Histosols.

Topsoil P speciation characteristics in the H1 profile, which was not included in the column study, were similar to that in topsoil of H2. Phosphorus leaching from this profile can be assumed to be driven by a similar mechanism. However, with regard to the considerably greater content of extractable Fe and Al in subsoil layers of H1, P leaching may be lower from this profile under natural conditions.

In both H1 and H2, the Al-pstot content was significantly correlated with ash and clay ash content ($p<0.005$). Temporarily changing redox conditions and input of Fe via groundwater upflow may explain why such a relationship was not observed in the case of Fe-pstot.

The different distribution of surface reactive metal (hydr)oxides in the two profiles reflects the different historical inputs of mineral material via lateral inflow or groundwater movement. The H1 sampling site was in close proximity to a river and hence the peak in ash content and extractable Al in the subsoil of this profile could be attributable to deposition of mineral material in previous flooding events.

This spatial heterogeneity in the content of surface reactive minerals should to be considered in risk assessments of P leaching from cultivated Histosols. Both organic profiles in this study demonstrated that the frequently observed accumulation of surface reactive metal phases in the topsoil (Schlichting, 2004) is not a universal feature of cultivated fen peats. While underestimating actual P saturation in H1 and H2 in comparison with the mineral soil, the PSI values determined throughout the profiles did reflect the different availability of P sorption sites.

The PSI values obtained for SMIN apparently overestimated the P saturation in this profile, due to dissolution of Ca-P in the acid ammonium-oxalate extract. The latter cannot be considered to be readily mobilised under natural conditions. On the contrary, the increase in soil pH often observed in long-term manured soils might actually lead to the formation of poorly soluble calcium phosphates (Lombi *et al.*, 2006) and thus reduce the risk of P leaching from these soils. Hence, the results in this thesis illustrate that the use of comparatively simple P saturation indices such as PSI to evaluate the risk of P leaching from soils may be problematic, particularly if used for comparative evaluation of different soil types.

6.5 Implications of P speciation for future risk of leaching (Papers I, II, III)

Leaching losses from H2 and SMIN in the column study in this thesis were most likely linked to exchangeable inorganic P associated with mineral Fe and Al surfaces. However, other forms of P identified in the profiles may have implications for the leaching risk if management of the study sites changes in the future. Calcium phosphate in the SMIN soil is currently rather stable due to the slightly alkaline soil pH. No clear indication was found that Ca-P dissolution contributed to P leaching in the column study, as the Ca and P concentrations in leachates showed a contrasting pattern for the two profiles tested. However, a decrease in soil pH over time would render the Ca-P in SMIN more vulnerable to leaching (Andersson *et al.*, 2016). It is clear that continued input of excess P in manure or fertiliser will likely exacerbate the risk and extent of P leaching from SMIN. However, it is also likely that the current soil pH in SMIN is maintained by regular manure addition. Manure application has been shown to increase soil pH (Walker *et al.*, 2004; Whalen *et al.*, 2000). Thus, discontinuation of manuring without compensatory liming will lead to the dissolution of amorphous topsoil Ca-P in particular (Sato *et al.*, 2005; Beauchemin *et al.*, 2003).

Reductive dissolution of Fe^{3+}-associated P has been proposed as the main process leading to environmentally critical P exports from re-flooded, previously cultivated wetland soils (Zak & Gelbrecht, 2007; Jensen *et al.*, 1999). The P speciation results for H1 and H2 showed that P was primarily associated with Al mineral surfaces. Moreover, the content of extractable Fe was low in H1 and H2 in comparison with that in other peat soils in which reductive Fe-P dissolution has been studied (Zak *et al.*, 2010). However, even a comparatively small Fe-P pool could lead to high P losses if the redox potential in H1 and H2 were allowed to decrease persistently by abandoning drainage. Moreover, the SMIN site with its considerable greater pool of Fe-P is tile-drained. Hydrological conditions at the SMIN site would otherwise lead to upflow of groundwater due to an underlying layer of low hydraulic conductivity clay (Gustafson *et al.*, 1984). Iron-associated P was a major P fraction in SMIN. Thus, an improperly functioning drainage system or the discontinuation of drainage could lead to a rise in groundwater level over a sufficiently long period to release P to groundwater, as described for re-flooded Histosols (Zak & Gelbrect, 2007; Jensen *et al.,* 1999).

Furthermore, P mobilisation in restored wetland soils may not only be driven by the reductive dissolution of ferric iron minerals. As previously mentioned, Hutchison & Hesterberg (2004) pointed out increased formation of DOC and subsequent competition with P for sorption sites and the formation of soluble organic-metal phosphate complexes as alternative processes potentially leading to P mobilisation in flooded organic soils. Such release of P through the interaction with DOC would not be restricted to ferric Fe bound P and could be particularly important for Histosols were P is not primarily associated with redox-sensitive Fe^{3+} minerals such H1 and H2 according to LCF results. The column study results do indeed suggest that there is a link between DOC release and P mobilisation.

A major proportion of the P in the organic profiles H1 and H2 is stored in rather stable organic forms. This P pool did not contribute to P leaching losses in the column study. However, continued cultivation of these soils will eventually lead to mineralisation of most of the P-org present, in conjunction with loss of organic peat material through soil subsidence. Assuming a subsidence rate of around 20 mm $year^{-1}$, this process may last for less than 50 years. Mineralised P could potentially contribute to increased P saturation in the underlying mineral soil layers and hence increase the risk of P leaching from these soils in the future. In addition, considering the size of the P-org pool in comparison to the pool of P that may potentially be mobilised under reducing conditions in the organic profiles H1 and H2, it would be recommended to abandon cultivation and restore water-saturated conditions.

7 Conclusions and future perspectives

The approach used in this thesis, which combined P speciation using advanced spectroscopic techniques with thorough characterisation of physical and chemical soil properties and a rain simulation column study, provided valuable information about the nature of P and its potential mobilisation in the three soils analysed. Most previous studies on P speciation in long-term manured soils and cultivated Histosols have relied on indirect wet chemical extraction methods, producing findings with the uncertainty inherent to these techniques. Other studies have focused on organic P characterisation using liquid state ^{31}P-NMR. The in-depth approach used in this thesis confirmed findings from previous studies and provided novel insights:

- One consequence of cultivation on P speciation in the three soils studied was an elevated P content in the topsoil relative to the subsoil. However, the source of P and possible accumulating processes differed between mineral and organic soils.
- Phosphorus in the organic profiles was predominantly organic including the P-enriched topsoil. Most likely, this reflects the accumulation of recalcitrant organic P in surface near soil layers due to soil subsidence and additional input of P-org with crop residues.
- Inorganic P in the organic profiles was adsorbed to surface reactive Al and Fe minerals. Our results suggest the P was predominantly associated with Al in the organic profiles.
- The capacity to retain excess P input via fertilisation in the topsoil of the organic profiles is very limited due to a low content of surface reactive Fe and Al minerals. Hence, P input in excess of crop uptake will likely leach to drainage pipes if not retained deeper in the profiles.
- Being minerogenic fen peat soils, historic input of mineral material during the formation of the Histosols was found to be more important for P retention than an accumulation of sesquioxides in topsoil layers resultant

from soil subsidence. Hence, for an evaluation of the P leaching risk from such Histosols, mineral material in subsoils should be considered.

- The distribution of Fe and Al associated P in the organic profiles indicates that mineral P is highly mobile in the organic profiles in comparison to the mineral profile, where obvious P enrichment was clearly restricted to the plough layer.
- The mineral soil profile featured substantially elevated P content in the topsoil as compared to the subsoil as a result of long-term external P input via manure amendment. Per unit volume, the top soil of the mineral profile was also substantially richer in P than topsoil of the organic profiles.
- External P input is primarily retained in the top soil in form of phosphate adsorbed to Fe and Al (hyrdr)oxides. Another important P pool is amorphous Ca-P that may have formed in-situ or had been added with manure. Organic P content was very low. Reflecting a geological young age of the mineral soil profile and ongoing soil weathering processes, primary apatite became the dominating P form in deeper sub soil layers.
- Topsoil column leaching experiments revealed potential for high P leaching from both organic and mineral soils. Phosphorus mobilisation relative to content of leachable P in the columns was however substantially higher from the organic soil. The results highlight the potential relevance of P leaching from cultivated Histosols, despite these soils comprising a comparatively small proportion of total arable land.
- Despite differences in soil properties and P speciation between mineral and organic soil columns, P mobilisation was most likely driven by a similar mechanism, involving the release of P adsorbed to Fe and Al (hydr)oxides upon a decrease in soil solution ion strength. The results furthermore suggest that interactions with DOC may considerably enhance P mobilisation form organic soils in comparison to mineral soils.
- A P saturation index (PSI) based on extractable content of Fe, Al and P, which used for P leaching risk assessments, did not adequately reflect the potential for P mobilisation observed in the column leaching study. In the organic soil studied, the index probably underestimated P saturation, since it does not consider competition between P and organic anions for sorption sites in these soils. In the mineral profile, dissolution of Ca-phosphates due to the low pH of the extractant solution may have led to overestimation of P saturation.

There is certainly a trade-off between P speciation relying on thorough soil characterisation and advanced spectroscopic analytical techniques and covering the enormous heterogeneity of different soil systems. The P speciation obtained for the profiles studied in this thesis can with high confidence be considered reasonable, supported by far-reaching coherence between results from the different independent analytical techniques applied. However, the generalisability of these findings to other organic or manured mineral soils remains unclear. This is an important issue, particularly since the development of effective strategies to reduce P leaching from arable fields relies on understanding P leaching processes over a wide range of soils and conditions. The use of advanced synchrotron radiation techniques such as P *K*-edge XANES with comparatively low sample throughput is certainly not suitable to cover this heterogeneity. Therefore, simpler wet chemical methods remain a valuable tool for studying P in soils, even though comparisons between different soils need to be made with great care. The species composition of P extracted with a particular technique may differ considerably between soils, as exemplified in this thesis for oxalate extractions of P. Nevertheless, within a particular soil types these techniques provided reasonable results that could be clearly linked to results from the advanced spectroscopic techniques used.

It was possible to deduce potential processes of P mobilisation from the P speciation results and the column leaching study. However, there is clearly a need for further work to confirm this and to corroborate whether the P leaching observed in the column study is representative for these soils on a greater scale and under conditions that are more realistic and include the influence of subsoil horizons. Moreover, it is important to test whether sources of leached P were correctly identified with the Al-P and Fe-P pool. Important is also further research on the influence of soil organic matter on P sorption dynamics in Histosols. The high proportion of P leached from the columns relative to the P status in the organic soil may justify collecting XANES spectra from samples of these columns for reasons of comparison.

In general, techniques such as P *K*-edge spectroscopy may best be applied strategically in the future for particular problems for which established methods have produced inconclusive results, or in combination with studies on specific processes of P mobilisation. With regard to cultivated organic soils, it is clearly important to study the fate of P upon restoring waterlogged conditions and the role of reductive dissolution of P associated with ferric Fe-(hydr)oxides.

8 Popular Science summary

Occasional algal blooms occur naturally in Swedish lakes and in the Baltic Sea, but they are now occurring more often and with increasing severity. One reason for this is artificially elevated nutrient concentrations in surface waters. Ruining your plans for a refreshing swim in the lake is only one of many negative consequences of this nutrient enrichment, also called eutrophication. Others include loss of habitat for many animal and plant species, negative impacts on tourism and fishery industries, and problems for drinking water supply.

One of the most problematic nutrients for eutrophication is phosphorus. It is actually essential for every living being and is involved *e.g.* in energy storage by living cells and in DNA. In natural waters, phosphorus concentrations are often so low that they limit the growth of algae even when growth conditions are otherwise suitable. When the phosphorus concentration in surface water increases strongly, algal growth can become rampant and turn a clear lake into a green slimy mess.

Today, most of the phosphorus that ends up in Sweden's lakes and rivers and in the Baltic Sea derives from fertilisers applied to agricultural fields. This link between agricultural phosphorus and eutrophication of lakes and enclosed seas has been known for decades, prompting years of scientific research into mobilisation of phosphorus from fields and transport pathways into surface water bodies. Reduction of phosphorus loads to surface waters remains difficult, partly because phosphorus in soil is present in a great number of different forms, *e.g.* phosphate minerals, PO_4 adsorbed to the surface of other soil minerals or organic P. All these P forms show complex behaviour in soils. In addition, there are a number of transport pathways by which agricultural phosphorus can leave a field. When attached to small soil particles, phosphorus can transported with water flow off the soil surface after heavy rainfall. In dissolved form, it can be transported with infiltrating water downwards to drainage pipes or to the groundwater, in processes generally referred to as leaching

One major obstacle in dealing with these processes is that it is difficult to identify the specific forms of phosphorus actually present in soil, because suitable analytical methods are lacking. In the past, scientists used an approach, which assumed that certain chemicals can extract certain forms of phosphorus from soil samples. However, it is difficult to verify that the different extracts are as selective as they are assumed to be.

Luckily, since soil scientists started studying phosphorus in soil, there has been great progress in the development of analytical techniques such as nuclear magnetic resonance spectroscopy (NMR) and X-ray absorption spectroscopy (XAS), which can be used today to examine phosphorus in soil. A combination of these new techniques and conventional extraction techniques was used in this thesis to analyse the phosphorus forms present in agricultural soils with potential for high phosphorus losses and to study whether these forms are linked to phosphorus leaching now and in the future.

Soils that have received excessive amounts of manure over a long period, often decades, can be classified as high-risk soils. Manure is generally rich in nutrients such phosphorus and nitrogen and is often applied in high doses to meet the crop demand for nutrients such as phosphorus. In the heavily manured soil analysed in this thesis, phosphorus had accumulated in the upper soil layers, mainly adsorbed to iron and aluminium (hyr)oxides. These compounds are very important for the phosphorus dynamics in most soils, as they bind or sorb phosphorus of P by reversible means. The equilibrium between adsorbed phosphorus and dissolved phosphorus in soil water is controlled by a complex of physical and chemical parameters. Adsorbed phosphorus can be released again if the phosphorus concentration in the soil solution decreases, for example when a large volume of water infiltrates into the soil after heavy rainfall, because crops take up phosphorus to grow. This release of adsorbed phosphorus can increase phosphorus transport to drainage pipes.

In manured soil, most aluminium and iron mineral sorption sites are already occupied by phosphorus, which means that the soil's capacity to retain phosphorus is almost exceeded. Following heavy rainfall, there is a high risk of phosphorus leaching from such soils. In an irrigation experiment in this thesis where heavy artificial rainfall was applied to excavated topsoil columns, there were indications that phosphorus leaching was linked to the pool of phosphorus adsorbed to aluminium and iron minerals. Another important phosphorus form identified in manured soil was calcium phosphates, which made up around one-third of the total phosphorus content in the upper soil. At the slightly alkaline pH in the manured soil, calcium phosphates are not readily dissolved and they did not contribute to phosphorus leaching in the irrigation experiment. Hence, excess phosphorus retained in the form of calcium phosphates in heavily manured soils can be considered rather stable. A future decrease in soil pH could reduce this stability, since the solubility of calcium phosphates is higher under acidic conditions. Ironically, regular manuring may help to stabilise the soil pH in the alkaline range, since manure is generally alkaline.

Another high-risk soil type is organic soils, which develop under waterlogged oxygen-free conditions in swampy areas through accumulation of incompletely decomposed organic material. They often contain only small amounts of iron or aluminium minerals that could function as phosphorus sorption sites. Drained and cultivated organic soils are unique in that they are slowly decomposed by microorganisms, since higher availability of oxygen during cultivation enables increased microbial activity. By far the greatest proportion of phosphorus in the organic soils analysed in this thesis was organic phosphorus. However, there was a much smaller pool of phosphorus adsorbed to iron and aluminium mineral surfaces than in the manured mineral soil. Organic P was not leached in the irrigation experiment. However, if these soils continue to be cultivated, much of the organic phosphorus is likely to be mineralised into leachable inorganic form during soil subsidence.

9 Populärvetenskaplig sammanfattning

Karakterisering av fosfor i åkerjord - Varför?

Tillfälliga algblomningar förekommer naturligt i våra i sjöar och i Östersjön, men de blir allt vanligare och ofta med ökande svårighetsgrad. En anledning till detta är artificiellt förhöjda näringskoncentrationer i våra ytvatten. Att förstöra dina planer för en uppfriskande simtur i sjön är bara en av många negativa konsekvenser som följer av denna näringsbelastning, även kallad eutrofiering. Några ytterligare konsekvenser är: förlusten av livsmiljöer för många djur- och växtarter, den negativa inverkan på turism och fiskerinäringen, samt problem med dricksvattenförsörjningen.

Ett av de mest problematiska näringsämnena när det gäller övergödning är fosfor. Fosforn är dock viktig för alla levande varelser. Fosfor är till exempel involverat i hur levande celler lagrar energi och en av DNA-byggstenarna. I naturliga vatten är fosforkoncentrationer ofta så låga att de verkligen begränsar tillväxten av alger även om tillväxtförhållandena annars är optimala. När fosforkoncentrationen i sådana vatten ökar alltför mycket kan algtillväxten gå över styr och göra en klar sjö till en grön slemmig soppa.

Idag kommer huvuddelen av fosforn som hamnar i Sveriges sjöar, floder och i Östersjön från jordbruksfält där det tillförts som gödningsmedel. Att det finns ett samband mellan jordbruksfosfor och eutrofiering av våra sjöar och Östersjön har varit känt sedan decennier. Under en lika lång tid har mobilisering av fosfor från fält och transportvägar till ytvattenförekomster varit föremål för vetenskapliga studier. Det finns en anledning till att denna forskning fortsätter även i framtiden. Fosfor i jorden kan förekomma i många olika former. Den kan existera i jordar som fosfatmineral. Som ortofosfat kan den adsorberas på ytan av andra jordmineraler eller det kan vara närvarande som organisk P. Beteendet hos alla dessa P-former i jord är komplicerat och utöver detta finns det flera transportvägar för jordbruks-P att lämna ett fält. Fäst vid små jordpartiklar kan den transporteras med vattenflöde på markytan efter kraftig nederbörd. Dessutom kan den i upplösta former transporteras med infiltrerande vatten nedåt till dräneringsrör eller till grundvatten. Denna process-kallas vanligen P-utlakning.

Ett stort hinder som har bromsat forskningsutvecklingen i förståelsen av dessa processer är att det fortfarande är en utmaning att faktiskt identifiera specifika former av fosfor i jord. Problemet är att forskare helt enkelt har saknat en adekvat analysmetod. Historiskt sett användes olika kemikalier för att utvinna fosfor från jorden och man antog att vissa kemikalier extraherar vissa former av fosfor. Det är emellertid svårt att verifiera att dessa olika extrakt är lika selektiva som de antas vara.

Sedan markforskare började samarbeta kring frågor relaterade till fosfor i jord har lyckligtvis utvecklingen av analytiska tekniker inte stått stilla. Avancerade analytiska tekniker som kärnmagnetresonansspektroskopi (NMR) och röntgenabsorptionsspektroskopi (XANES) kan användas idag för att titta närmare på fosfor i jorden. Vi har använt en kombination av dessa nya tekniker och traditionella extraktionsmetoder för att ta reda på vilka fosforformer som finns i åkerjordar som är kända för sin potential för höga fosforförluster. Dessutom var vi intresserade av frågan om hur olika fosforformer som finns i dessa jordar kan kopplas till fosforutlakning nu och i framtiden.

Jord som kan klassificeras som den med hög risk för utlakning är till exempel de som har fått stora mängder stallgödsel under en lång tidsperiod, ofta decennier. Bland annat är stallgödsel generellt rik på näringsämnen såsom fosfor och kväve. Ofta har större mängder stallgödsel applicerats på fält runt djurproduktionsanläggningar. Denna gödsel skulle ha behövts för att möta grödans behov av näringsämnen som fosfor. Ett resultat av denna stora tillförsel av fosfor i en mycket gödslad jord, vilket skett på en av de jordar som ingår i denna studie, är att stora mängder fosfor ansamlas i de övre jordhorisonterna. Därför har överskott av fosfor kvarhållits i jorden och inte förlorats. Det mesta av denna fosfor adsorberades till järn- och aluminiumoxider. Dessa mineraler är mycket viktiga för dynamiken av fosfor i de flesta jordar. Bindningen eller sorptionen av fosfor till dessa mineraler är reversibel och jämvikten mellan adsorberad fosfor och fosfor upplöst i jordvattnet styrs av en komplex mängd fysiska och kemiska parametrar. Adsorberad fosfor kan till exempel frigöras igen om fosforkoncentrationen i jordlösningen minskar eftersom grödor tar upp fosfor för att växa. Fosforkoncentrationen i markvattnet minskar också när en stor volym vatten infiltrerar i jorden efter kraftigt regn. Detta kan också utlösa frigörelse av adsorberad fosfor och dess transport till dräneringsrör.

I den gödslade marken var en stor del av dessa mineralsorptionsplatser för aluminium och järn ockuperade med fosfor. Därför överskreds jordens kapacitet att kvarhålla fosfor nästan helt. Vid kraftigt regnfall är risken hög att P lakas ur jorden. Vi testade detta i ett bevattningsexperiment där vi simulerade kraftigt regn på insamlade jordkolonner. Vi kunde verkligen hitta indikationer på att utlakning av fosfor var kopplad till denna pool av fosfor adsorberad till Al- och Fe-mineraler. En annan viktig fosforform som vi kunde identifiera i jorden var kalciumfosfater. Detta fosfatmineral utgör upp till cirka en tredjedel av det totala fosforinnehållet i övre jordskikt. Vid det något alkaliska pH-värdet som vi observerade i jorden löses dock inte kalciumfosfater lätt. Vi fann därför inte att dessa fosforformer bidrog till fosforlakning i bevattningsförsöket. Följaktligen kan överskott av fosfor som kvarhålles i form av kalciumfosfat i kraftigt gödslade jordar betraktas som ganska stabilt. En minskning av jordens pH i framtiden kan dock ändra detta eftersom lösligheten för kalciumfosfater är högre under sura förhållanden. Ironiskt nog kan stallgödsling med normala givor delvis bidra till att stabilisera jordens pH inom det alkaliska området eftersom stallgödsel i allmänhet har ett alkaliskt pH i sig.

En annan jordtyp som vi inkluderade i studien var organisk jord. Dessa jordar utvecklas under vattenmättade syrefria förhållanden i träsklika områden och deras modermaterial är ofullständigt nedbrutet organiskt material. Därför innehåller de ofta bara små mängder Fe- eller Al-mineraler som potentiellt kan fungera som sorptionsställen för fosfor. Odlad och dränerad organisk jord är unik genom att de sakta bryts ned av mikroorganismer. Med tiden kommer därför kultiverade organiska jordar att bokstavligen försvinna när kolet som lagrats i det organiska jordmaterialet släpps ut i atmosfären som CO2. Denna process beror mest på den högre tillgängligheten av syre i dränerade organiska jordar som möjliggör en ökad mikrobiell aktivitet. Vi fann att den överlägset största delen av fosfor i en sådan organisk jord var organisk fosfor. Men som i fallet med den stallgödslade mineraljorden var det en mycket mindre pool av fosfor adsorberad till Fe- och Al-mineralytor från vilka P var troligen utlakat i ett kolonnbevattningsförsök. Någon nämnvärd utlakning av den organiska fosforn förekom inte i detta experiment. Men om denna jord odlas kontinuerligt kommer mycket av den organiska fosforn att mineraliseras till en utlakningsbar oorganisk form, eftersom markprocesser fortsätter att bryta ned det organiska jordmaterialet.

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In this thesis, phosphorus (P) *K*-edge XANES in combination with complementary analytical methods was applied for P speciation in soils with a high potential for leaching. Organic P forms dominated in cultivated peat soils and they were relatively enriched in the top soil due to soil subsidence. The P enriched top soil of a long-term manure amended mineral soil P speciation was dominated by phosphate adsorbed to iron and aluminium (hydr)oxides. In a column rain simulation study, P leaching from the studied soils could be linked to these adsorbed forms of P.

Frank Schmieder received his graduate education at the Department of soil and Environment, SLU Uppsala. He holds a degree of Diplom-Ingenieur of Environmental Engineering (equivalent to a Master of Science) from IHI Zittau (Germany).

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