Citation for the published paper:
Ann Kristin Eriksson, Jon Petter Gustafsson, and Dean Hesterberg. (2015) Phosphorus speciation of clay fractions from long-term fertility experiments in Sweden. *Geoderma*. Volume: 241-242, Number: Nummeruppgift, pp 68-74.
http://dx.doi.org/10.1016/j.geoderma.2014.10.023.

NOTICE: this is the author's version of a work that was accepted for publication in Geoderma. A definitive version was subsequently published in *Geoderma* **241-242,** 68-74, 2015. http://dx.doi.org/10.1016/j.geoderma.2014.10.023

Phosphorus speciation of clay fractions from long-term fertility experiments in Sweden

Ann Kristin Eriksson[1], Jon Petter Gustafsson[1,2] and Dean Hesterberg[3]

[1]Department of Soil and Environment, Swedish University of Agricultural Sciences, P.O. Box 7014, 750 07 Uppsala, Sweden.

[2]Division of Land and Water Resources Engineering, KTH Royal Institute of Technology, Teknikringen 76, 100 44 Stockholm, Sweden.

[3]Department of Soil Science, North Carolina State University, Box 7619, Raleigh, NC 27695-7619, U.S.

E-mail: ann.kristin.eriksson@slu.se

Keywords: soils, X-ray absorption spectroscopy, Sweden, phosphorus, phosphate, clays

Abstract

Phosphorus (P) losses from agricultural soils constitute a main driver for eutrophication of the Baltic Sea. There is limited knowledge about sorption and release processes of P in these soils, especially concerning the effects of fertilization. In this study, P speciation of the clay fractions from six different soils in long-term fertility experiments in Sweden was investigated by P K-edge XANES spectroscopy. As expected, unfertilized soils had lower concentrations of acid-digestible P compared with fertilized soils. Based on best-fit standards that emerged from linear combination fitting (LCF) of XANES spectra, phosphate sorbed on iron (Fe) (hydr)oxides was a dominant P species in clay fractions from unfertilized soils containing more than 35 mmol kg^{-1} of oxalate-extractable Fe. In contrast, P sorbed on aluminum (Al) (hydr)oxides predominated in soils with lower concentrations of oxalate-extractable Fe. A greater proportion of organically bound P was fit for soil samples containing >2 % organic carbon. The soils included one calcareous soil for which a greater proportion of P was fit as apatite. After long-term fertilization, P had accumulated mainly as Al-bound forms (adsorbed species and precipitates) according to the XANES analysis. Our research shows that P speciation in fertilized agricultural soils depended on the level of P buildup and on the soil properties.

1. Introduction

Phosphorus (P) is a main driver of eutrophication in waters such as the Baltic Sea. The largest source of P from Sweden into the Baltic Sea is from agricultural fields (Boesch et al., 2006). Phosphorus in soils is found in mineral phases, as adsorbed species (surface complexes) on (hydr)oxide solids, and in organic forms. Adsorption / desorption processes are important in controlling P solubility in soils, but precipitation and dissolution of minerals may also affect the solubility, especially in soils enriched in P. Organically bound P species in soils are also important, in which case immobilization and mineralization affect the solubility of phosphate. Aluminum (Al), and iron (Fe) (hydr)oxides are important for phosphate adsorption (Hingston et al., 1967). Amorphous Al (hydr)oxides may be of greater importance for phosphate sorption on P-rich soil particles (e.g. Lookman et al., 1996; Pierzynski et al., 1990). Various sequential extraction methods are commonly used to estimate P speciation of soils. Examples are the procedures developed by Chang and Jackson (1957) and Hedley et al. (1982). However, a common criticism of these procedures is that they are not specific in dissolving particular chemical forms of P, and therefore they are not sufficient for determining P speciation (e.g. Barbanti et al., 1994).

A more direct method used for speciation of organic P is solution ^{31}P-NMR following alkaline extraction of a soil sample. However, certain forms of P can be hydrolyzed during the extraction, leading to artifacts. In addition, solid-state ^{31}P-NMR analysis of soil has been used without pretreatment for speciation (e.g. Cade-Menun, 2005; Lookman et al., 1996). There are, however, limitations with this method, e.g., high P and low Fe concentrations are needed to obtain an adequate spectrum with minimal paramagnetic effects (Cade-Menun, 2005).

Hesterberg et al. (1999), Beauchemin et al. (2003) and Toor et al. (2005) introduced the use of XANES spectroscopy to characterize P species in environmental samples. Dominant species of P are commonly estimated using linear combination fitting (LCF), where a weighted sum of XANES spectra from selected P standards are fit to the spectrum from a sample (Kelly et al., 2008). Different chemical species of P have unique spectral features, for example: (1) P associated with transition metals (e.g. Fe) gives a weak, but clear pre-edge shoulder (Franke and Hormes, 1995); (2) P in calcium (Ca) phosphates gives clear continuum resonances and post-edge shoulders (Franke and Hormes, 1995); (3) Al phosphates give a weaker pre-edge resonance that overlaps with the strong white line (Khare et al., 2007), but also weak post-edge features that commonly occur at higher energies than those of Ca phosphates (Franke and Hormes, 1995); and (4) organic P species commonly do not show any clear pre- or post-edge features, which makes it hard to differentiate between different organic P species (Doolette and Smernik, 2011; Hesterberg, 2010).

Accurate characterization of P speciation in fertilized soils is important to create better models for predicting P mobilization and movement to surface waters. Although the P speciation of fertilized soils has previously been estimated using XANES spectroscopy (e.g. Beauchemin et al., 2003; Lombi et al., 2006), these studies did not address long term changes of P speciation over time as a result of fertilization. In one of the few studies devoted to analyzing P speciation changes resulting from fertilization (Ajiboye et al., 2008), samples of a Vertisol and a Mollisol were incubated in the laboratory for short time periods, then characterized by P K-edge XANES spectroscopy. The results suggested an important role of adsorbed P species.

The Swedish soil fertility experiments represent a unique set of field plots for assessing the long-term effects of fertilization on soil-chemical properties (e.g. Börling et al., 2001; Carlgren and Mattsson, 2001; Gustafsson et al., 2012). At several sites, soil plots have been amended with different levels of nitrogen (N), P, and potassium (K) fertilizers for periods of 40 to 60 years. Recently, the P speciation of selected sites was studied by means of ^{31}P NMR spectroscopy (Ahlgren et al., 2013). According to this study, neither the absolute amounts nor the speciation of organic P changed as a result of fertilization, suggesting that added P was accumulating as inorganic P species. This result agrees with a similar study conducted in Finland (Soinne et al., 2011).

The aim of our investigation was to evaluate changes in P speciation due to long-term fertilization of some fine-textured agricultural soils, and we used P K-edge XANES spectroscopy. That is, our objective was to determine how added P was bound. Soil samples from the long-term Swedish soil fertility experiments were used, which have been extensively characterized in earlier studies (Börling et al., 2001; Djodjic et al., 2004; Svanbäck et al., 2013). Moreover, detailed speciation of organic P using ^{31}P-NMR has already been analyzed for these soils (Ahlgren et al., 2013), and our XANES analysis should be more sensitive to differences in inorganic P species.

2. Materials and methods

2.1. Soil sampling and preparation

Soil samples were collected from six different sites included in the Swedish soil fertility experiments (Carlgren and Mattsson, 2001): Fors, Kungsängen, Vreta Kloster, Bjertorp, Ekebo and Fjärdingslöv. A full description of the sites can be found in Kirchmann (1991), Kirchmann et al. (1999) and Kirchmann et al. (2005). The experimental plots were established between 1957 and 1969 and include two different crop rotations, with and without livestock (Carlgren and Mattsson, 2001). In this investigation we used samples from the plots with crop rotation without livestock. Nitrogen, phosphorus and potassium were applied as inorganic fertilizers. In total, there are 8 combinations of fertilizer treatment for each crop rotation (Carlgren and Mattsson, 2001). We used soil samples from plots receiving 125 kg N ha^{-1} yr^{-1} for the Fors, Kungsängen, Vreta Kloster and Bjertorp soils, and 150 kg N ha^{-1} yr^{-1} for the Ekebo and Fjärdingslöv soils. Samples from plots receiving three different phosphorus and potassium fertilization treatments were used; (1) control plots with no added P or K fertilizer, referred to as A3; (2) plots amended with P and K that replaced the P and K removed with harvest, plus 15 and 40 kg ha^{-1} yr^{-1}, respectively on Ekebo and Fjärdingslöv soils, or replacement of harvest + 20 P and 50 K kg ha^{-1} yr^{-1} on other soils, referred to as C3; (3) and plots receiving replacement + 30 P and 80 K kg ha^{-1} yr^{-1}, referred to as D3. Because of time limitations in collecting P K-edge XANES spectra, we used samples from only one replicate of each treatment.

Soil cores were collected from 0 to 20 cm around a 1-m diameter circle at a random location but at a minimum distance of 50 cm from the edge of each plot. All samples were collected during spring and autumn 2011, then immediately air-dried and sieved to <2 mm. One sample for each fertilization treatment (no replicates within or between plots) was taken at each site. The samples were analysed for bulk and clay mineralogy using X-ray diffraction (Hillier, 1999; Hillier, 2003; Omotoso *et al.*, 2006). No substantial mineralogical differences were found between samples taken across treatments at each site (data not shown).

Clay fractions of <2 μm (equivalent spherical diameter) were separated from the soils by sedimentation according to Stokes' law. A suspension of approximately 20 g soil and 200 cm^3 water was treated twice with ultrasonic dispersion for 5 minutes and stirred thoroughly in between. The suspension was left in a cylinder to settle under gravity for 16 h, and the top 20 cm suspension was siphoned off. The upper 20 cm was refilled with water and the sedimentation repeated once. The clay suspension was freeze-dried, and the clay fraction was stored dry until analysis.

2.2. Soil characterization

The particle size distribution was analyzed according to ISO 11277 (1998). The soil pH was measured in a suspension of 10 g air-dried soil to 30 cm^3 of deionized H_2O. The organic carbon content (OrgC) was measured by combustion using a LECO CNS-2000 analyzer (LECO, St. Joseph, MI). The calcite content was measured by full pattern fitting of XRD data (Omotoso et al., 2006) of a bulk soil sample after spray drying (Hillier, 1999). Soil test P was determined according to the Swedish standard ammonium lactate (AL) method of Egner et al. (1960), for which 5 g dry soil was equilibrated for 1.5 h with 100 cm^3 solution containing 0.1 M AL and 0.4 M acetic acid. Hydrochloric acid-digestible P was measured by boiling 2 g dry soil in 50 cm^3 of 2 M HCl for 2 h. Oxalate extractions were made according to van Reeuwijk (1995) using 1 g dry soil to 100 cm^3 solution and an equilibrium time of 4 h in darkness. The extract was then filtered through a 0.2 µm single-use filter and diluted 1:5 in H_2O. Phosphate in the oxalate extract (PO_4-ox) was analysed colorimetrically according to Wolf and Baker (1990) using a Tecator Aquatec 5400 spectrophotometer with flow injection analysis. Oxalate-extractable aluminum (Al-ox) and iron (Fe-ox) were determined by ICP-OES using a PerkinElmer 5300 DV instrument.

Pyrophosphate-extractable iron (Fe-pyro) and aluminum (Al-pyro) were determined in an extract of 1 g dry soil in 100 cm^3 of 0.1 M $Na_2P_2O_7 \cdot 10H_2O$ equilibrated for 16 h. The extract was filtered through a 0.2 µm single-use filter and diluted 1:5 in H_2O. Pseudo-total P (PsTotP) was measured by acid digestion in aqua regia (modified from ISO 11466, 1995), for which 3 g dry soil was equilibrated for 16 h with 30 cm^3 aqua regia solution, then the mixture was boiled for 2 h with a water condenser to minimize evaporation. The condenser was flushed with 20 cm^3 of 0.5 M HNO_3 and the rinsate was collected into the digestate, which was filtered and diluted to 100 cm^3 with 0.5 M $HNO_{3.}$ The final solution was analyzed for P using ICP-OES. Digestion in aqua regia is commonly used for measuring pseudo-total concentrations of elements, e.g. phosphorus, in soils (e.g. Stroia *et al.*, 2013). Previous research shows that between 55 and 102 % of the total P in soils is recovered by aqua regia digestion (Hornburg and Luer, 1999; Ivanov *et al.*, 2012). These investigations found strong correlations between PsTotP and total soil P determined by $HClO_4$ extraction.

2.3. Phosphorus K-edge XANES of clay fractions

The quality of synchrotron P K-edge XANES data from soil samples depends on the total soil P concentration, the intensity of incident synchrotron X-rays, the sensitivity of the fluorescence detector used, and concentrations of other elements such as Si that contribute to the total fluorescence signal to the detector. To improve the quality and reliability of our data, we collected XANES data on clay fractions separated from our fine-textured soil samples taken from the long-term fertility experiments. Williams and Saunders (1956) found that the majority of soil P in fine-textured soils is associated with the clay fraction. Our clay-fraction samples were packed into wells of acrylic holders (sample volume of 15 x 6 x 1.5 mm; w x h x d), and the surface was smoothed with a spatula and covered with 5 µm-thick polypropylene X-ray film

(Spex Industries, Columbia, IL). The P *K*-edge XANES data were collected at Beamline X-15B of the National Synchrotron Light Source at Brookhaven National Laboratory.

An Si(111) monochromator crystal was used, and the flux was approximately $1\cdot10^{12}$ photons s^{-1}. The beam was focused to approximately 1.1 mm diameter with focusing mirrors. Fluorescence signals were collected in a He atmosphere using a single-element solid-state Ge detector. The energy was calibrated to 2151±2 eV at the 1st-derivative maximum of a hydroxyapatite standard. Scans were recorded within the energy range of 2100 to 2470 eV. The step size was varied as follows: 2 eV between 2100 and 2130 eV, 0.2 eV between 2130 and 2156 eV, 0.5 eV between 2156 and 2153 eV, 1 eV between 2153 and 2180 eV, 2 eV between 2180 and 2250 eV, and 5 eV between 2250 and 2470 eV. Dwell times ranged from 2 to 6 seconds, with longer times used across the edge region. To decrease the fluorescence signal from Si in the samples, the detector window was covered with a ~40-µm thick polypropylene film. A minimum of 13 scans for the unfertilized samples and 9 scans for the fertilized samples were collected for each sample. A hydroxyapatite sample was run between each sample to ensure stability of the energy calibration.

2.4. Phosphorus K-edge XANES data analysis

All data analyses were performed using the Athena software in the Demeter suite of programs (Athena v0.8.056; Ravel and Newville, 2005 and Demeter v0.9.18). All sample and standard spectra were energy-calibrated to a common energy scale, where the derivative max of hydroxyapatite was set at 2151 eV and the shift applied to sample data collected after each calibration. The calibrated scans for each sample were aligned and merged. The spectra were baseline-corrected by subtracting a linear regression through the pre-edge region (approx. -20 to -5 eV relative to E_0 set at the 1st derivative maximum for a given sample or standard) and background-corrected using a quadratic function through the post-edge region (+30 to approx. +58 eV; except for the Fors sample, for which the background correction was extended to +100 eV). The pre-edge range for baseline subtraction was approximately parallel to the normalization range. The same data treatment procedure was used for all standards.

2.5. Linear combination fitting analysis

Linear combination fitting (LCF) was performed across an energy range from -10 eV to +30 eV relative to E_0 to investigate the P speciation. In total, 86 different standard spectra were used for the unfertilized samples. This group of standards contained (1) mineral samples from Ingall et al. (2011); (2) mineral standards and standards with adsorbed phosphate and organically bound P from Hesterberg et al. (1999); and (3) mineral standards and standards with adsorbed phosphate from Eveborn et al. (2009). Principal component analysis (PCA) was performed in the Demeter software to limit the number of independent standards needed to fit the spectra (Beauchemin et al., 2002). To determine which standards most likely accounted for the variation in the sample spectra and therefore to include in the fit, target transformation was performed using the same software. To quantitatively estimate P speciation, LCF analysis was performed. However, because of the relatively low signal-to-noise ratio in the data and the insensitivity of P K-edge XANES analysis to different species, a maximum of three standards were used in each fit (Beauchemin et al., 2003). To limit the number of standards in the LCF analysis, we excluded standards with the lowest probability to account for the variation based on target transformation.

Two approaches to fitting were used: (1) sample spectra from unfertilized plots were fit with all standards selected from the target transform; and (2) the best-fit model spectrum generated for the unfertilized samples was included as one standard when fitting the sample spectra from fertilized plots. The latter approach assumes that the speciation of the initial soil P did not change due to fertilization. Fits having a sum of the weight factors in the range of 80 to 120 % of total P were considered acceptable. The sums of fitted weighting factors were adjusted to a total sum of 100%. Additional standards needed to fit the fertilized sample, which were those used in the data set of Hesterberg et al. (1999), but re-collected on NSLS Beamline X15B, were assumed to represent the P species formed as a result of fertilization. Uncertainties in XANES fitting parameters were calculated by the Athena software (v0.8.056; Ravel and Newville, 2005). Other statistical analyses were done in MINITAB 16® 16.2.0.

3. Results

3.1.Extractable P in comparison to P speciation

The concentrations of ammonium lactate- and oxalate extractable P increased after fertilization for all soils (Table 1). This trend suggests an increase in inorganic P in adsorbed or mineral species, which are expected to be dissolved by acid extractants (e.g. Hartikainen et al., 2010).

The greatest relative increase of extractable P following fertilization was observed in the soil from Ekebo and Fjärdingslöv. The smallest change was observed in the soil from Fors, which also had the highest content of PsTotP (Table 1). By contrast, the soil from Fjärdingslöv had the lowest concentration of PsTotP, but also a low concentration of oxalate- and pyrophosphate extractable Al and Fe. The greatest change in PsTotP between the unfertilized sample and the one receiving the highest level of P fertilizer was observed for the samples from Bjertorp, whereas the smallest change was observed for the Fors soil.

3.2. Phosphorus speciation in unfertilized samples

Linear combination fitting analysis on clay fractions from the samples with no added P showed that P speciation differed between soil samples from different sites (Figure 1 and Table 2). Calcium phosphate (apatite) was observed in the best fit for all samples, except for the Ekebo and Fjärdingslöv samples. The Ekebo sample had the lowest pH of all samples (5.9-6.1). However, despite the low pH, Ca phosphates were fitted to the data in two of the five best fits; hence the presence of trace amounts of Ca phosphates could not be excluded. In the case of the Fjärdingslöv sample, Ca phosphates occurred in all but the first of the five best fits. It should be noted, however, that there might be signal overlap between Ca phosphates and organic P when only small amounts occur in the sample (Doolette and Smernik, 2011). There were statistically significant relationships between PsTotP in the soils from the unfertilized treatments and P bound as Ca phosphates (r=0.89*). A relationship between the ratio between oxalate extractable Fe and Al, and the amount of P adsorbed to Al surfaces was also found (r=0.92**). This suggests that for unfertilized soils containing more oxalate-extractable Al than Fe, P is bound predominantly to Al (hydr)oxides (see also Figure 2).

For the Fors soil, the best fits included 65 % of the P present as carbonate hydroxyapatite fluorian (a Ca phosphate standard from Ingall et al., 2011; Figure 1 and Table 2). Phosphate adsorbed to Al and/or Fe (hydr)oxides was also included in the best fits for all samples. In soils with >35 mmol kg^{-1} of oxalate extractable Fe (Table 1), XANES fitting indicated that a major part of P was bound to Fe (hydr)oxides. The Kungsängen and Ekebo soils, which had concentrations of oxalate-extractable Fe in the upper range (160 and 40 mmol kg^{-1}, respectively), also had the highest concentrations of organic C (2.2 and 2.3 %, respectively). For these soils organic P (as evidenced by P bound to phytate or lecithin) occurred in the best fit for the unfertilized samples. For the Ekebo sample, the best fit also included phosphate adsorbed to Al (hydr)oxides, consistent with its relatively high concentration of oxalate-extractable Al compared to Fe (Figure 2).

For the clay fractions from the unfertilized Bjertorp and Fjärdingslöv samples the majority of the P was bound to Fe (hydr)oxides. The molar ratio of oxalate-extractable P to Fe in these soils was rather low (<0.08) indicating additional capacity for adsorption of phosphate to Fe (hydr)oxides. The soils from Kungsängen and Ekebo had a P to Fe ratio higher than 0.08 in the oxalate extract; however in these soils less P was bound to Fe (hydr)oxides according to the XANES analysis (Figure 2).

For the soils from Fors and Vreta Kloster, the XANES results showed no significant contribution of Fe-bound P, which is consistent with the lower concentration of oxalate extractable Fe in these soils (<35 mmol kg^{-1}; Figure 2). Instead the XANES results of the clay fractions showed that the speciation of P was dominated by Ca phosphate (apatite) and by phosphate adsorbed to Al (hydr)oxides.

3.3. Phosphorus speciation in fertilized samples

For most samples the standard spectra giving the best fit for the phosphate added by fertilization was phosphate bound to Al (hydr)oxide (boehmite) or to Al-treated peat (Figure 1 and Table 3). The Vreta Kloster was an expection; here the P added by fertilization seems to have been bound as apatite. Although 20 % vivianite was fit to the XANES spectra for the Kungsängen sample (Figure 1 and Table 3), it seems more likely that other Fe-P mineral phases or sorbed P with similar spectral features may be present as this is a well-drained (well aerated) soil. In the best fit to the Kungsängen sample, the standard from phosphate adsorbed on Al-treated peat was also included. However, the pyrophosphate extraction indicated that 7 mmol Al kg^{-1} was bound to organic matter, which is comparably low in this soil set. Phosphate adsorbed to Al-treated peat was also observed for the sample from Ekebo, which had the highest concentration of organic C (2.3 %) and the highest concentration of pyrophosphate-extractable Al of all soils studied (70 mmol Al kg^{-1}). By contrast, the sample from Fjärdingslöv had a comparably low concentration of extractable Al (9 mmol kg^{-1}) and Fe (12 mmol kg^{-1}), and also a low concentration of organic carbon (1.37 %). In this sample, XANES fitting indicated that approximately 30 % of the added P had instead been precipitated as Ca phosphates.

4. Discussion

4.1.Phosphorus in clay fraction compared to soils

In this study, the clay fraction was used for the XANES analyses instead of the bulk soil sample. It has earlier been shown that a majority of the phosphorus is commonly found in the clay fraction (Williams and Saunders, 1956). The P speciation in the clay fraction may, however, not be identical to the one in bulk soils for the following reasons: (1) there is a risk of overestimation of organic phosphorus caused by an enrichment of organic P in the clay fraction (Williams and Saunders, 1956), and (2) there might be a risk of underestimation of crystalline calcium phosphates. Liu et al. (2014) showed that a majority of the P in the colloidal fraction (< 1 µm) from water extractions was associated with aluminum and iron. This indicated a smaller quantitative importance of calcium phosphates in these finer soil fractions. However, no organic P species was included in this investigation. Hence, because of this, the importance of iron and aluminum oxides may possibly be overestimated (Williams and Saunders, 1956). Clearly, further studies are required to investigate to what extent clay fractions, as used in this study, may be representative for the P in bulk soils.

The isolation of the clay fraction may also by itself affect the P speciation, but for P this effect seems to be smaller than that of, e.g. sulfur (Prietzel et al., 2007). In addition, no chemical pre-treatment was used in our method as described by Hillier (2003).

4.2.Speciation of P in unfertilized soils

For this diverse group of Swedish agricultural soils, the XANES fitting results show that P was mainly bound as Ca phosphates (predominantly apatite) and adsorbed to Al and Fe (hydr)oxides in the clay fraction. This result is consistent with other XANES studies that commonly reported Ca phosphates in soil (e.g. Ajiboye et al., 2008; Beauchemin et al., 2003; Lombi et al., 2006).

Further, our study confirms that a large part of the soil P is adsorbed to Al and Fe (hydr)oxides. The results also agree with those of Khare et al. (2004), who showed that phosphate is commonly bound to both Al and Fe (hydr)oxides when they occur in a mixture.

The identity of the Fe and Al sorbent phases is not clear, however. Concerning oxalate extractable Fe, it is likely that ferrihydrite is a main contributor, although other mineral forms such as biotite or magnetite may also be dissolved in this extraction (Parfitt and Childs, 1988). Concerning the Al phases the question remains even more open: allophane, amorphous Al (hydr)oxide or hydroxy-interlayered Al phases all seem to be possible candidates.

4.3. *Speciation of P in fertilized soils*

The XANES fitting results suggest that P added to the soils through fertilization was adsorbed mainly to the Al phases. This is consistent with earlier studies showing a strong correlation between extractable Al and P in Swedish agricultural soils (Börling et al., 2004; Ulén, 2006). In addition, our results confirm earlier NMR spectroscopic results showing that P added with fertilization is bound as inorganic forms in these soils (Ahlgren et al., 2013). Khatiwada et al. (2012) showed that directly after fertilization of a silt loam, P was mainly found as Ca phosphates (which was the fertilizer) but after six months it was recovered primarily as an adsorbed phase. Other studies have shown that added P was precipitated as Ca phosphates in soils with high pH (>7.6) and calcium carbonate (>3.4 %) content, but with low concentrations of oxalate extractable Al and Fe (< 27 mmol and < 56 mmol kg^{-1}, respectively; Ajiboye et al., 2008; Lombi et al., 2006; Kar et al., 2012). However, in the sample from Fors, which should be comparable to these samples, the added P was primarily adsorbed to Al (hydr)oxide surfaces. The Fors soil had a somewhat higher concentration of oxalate extractable Al, indicating the existence of Al (hydr)oxide phases in this soil.

However, for the Kungsängen soil, the XANES fitting analysis suggested the formation of Fe phosphate precipitates. Precipitation of phosphates into Al and Fe phosphates has also earlier been observed after P amendment to soils (Ajiboye et al., 2008). The differences between Fe phosphate and P bound to iron (hydr)oxides are, however, rather subtle when these phases occur in a mixture.

It is clear both from this study and from earlier modeling studies (Cui and Weng, 2013; Gustafsson et al., 2012) that the oxalate extractable Al in agricultural soils may represent a highly reactive P-sorbing phase, probably because of a high surface area and a high affinity for P. Thus to derive better mechanistically based geochemical models that can predict P sorption/desorption and leaching patterns, more emphasis should be placed on understanding the interactions between Al and P in agricultural soils.

4.4.Comparison to earlier studies in the Swedish fertility experiments

Svanbäck et al. (2013) investigated P losses from columns of topsoil using samples from four of the sites of our investigation, Vreta Kloster, Bjertorp, Ekebo and Fjärdingslöv. They showed that phosphate losses from the unfertilized sites were of similar magnitude, except for the soil from Fjärdingslöv, where the phosphate loss was higher. This is consistent with the results of the present study, which showed that the latter soil was the one with the lowest concentration of extractable Al and Fe, indicating low P adsorption capacity (Ulén, 2006). For the fertilized samples, the losses observed by Svanbäck et al. (2013) were of similar magnitude as could be expected for the soil from Ekebo, where the P loss was lower. The present investigation showed that the added P was adsorbed mainly to Al (hydr)oxides in this soil. Moreover Ekebo was the soil with the highest concentration of oxalate-extractable Al, and therefore it probably had the greatest potential to adsorb the added phosphate. Svanbäck et al. (2013) also added manure and measured the P losses one week after application. No increase in P losses was observed from the soil from Ekebo, which may be explained by high concentrations of non-crystalline Al-hydroxide as indicated by oxalate extraction. Phosphorus losses by leaching were minor for the unfertilized soil from Vreta Kloster, and somewhat greater for the soils from Bjertorp and Fjärdinglöv.

5. Conclusions

Phosphorus K-edge XANES analysis indicated that in clay fractions of unfertilized soils from long-term Swedish soil fertility experiments, the speciation of P was dominated by P adsorbed onto Al and Fe (hydr)oxide phases, and by Ca phosphate (apatite). In soils with > 2 % organic C, organic P was also indicated. In soils containing > 35 mmol kg^{-1} oxalate extractable Fe, P was mainly adsorbed to Fe (hydr)oxides, whereas P was adsorbed mostly to Al (hydr)oxides in soils after fertilization. After long-term fertilization, acid-digestible P increased. Results from XANES spectroscopy showed that P adsorbed to Al (hydr)oxide phases usually increased more than Fe (hydr)oxide-adsorbed P, Ca-phosphate, or organic P fractions.

6. Acknowledgement

The Swedish Research Council for Environment, Agricultural Sciences and Spatial Planning (Formas) is acknowledged for financial support (contract no. 2010-1677). This research was partly carried out at the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory, which is supported by the U.S. Department of Energy. We credit Paul Northrup, beamline scientist at X15B, NSLS for help and support during data collection. Christina Öhman is acknowledged for performing textural analyses, Roger Lindberg for ICP analysis of extracts and Inger Juremalm for extractions of P in ammonium lactate, HCl and measurements of organic carbon. Thanks also to Anders Lindsjö for providing soil samples and data.

7. References

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

Ajiboye, B., Akinremi, O.O., Hu, Y., Jurgensen, A., 2008. XANES speciation of phosphorus in organically amended and fertilized Vertisol and Mollisol. Soil Sci. Soc. Am. J. 72(5), 1256-1262.

Barbanti, A., Bergamini, M.C., Frascari, F., Miserocchi, S., Rosso, G., 1994. Critical aspects of sedimentary phosphorus chemical fractionation. J. Environ. Qual. 23(5), 1093-1102.

Beauchemin, S., Hesterberg, D., Beauchemin, M., 2002. Principal component analysis approach for modeling sulfur K-XANES spectra of humic acids. Soil Sci. Soc. Am. J. 66(1), 83-91.

Beauchemin, S., Hesterberg, D., Chou, J., Beauchemin, M., Simard, R.R., Sayers, D.E., 2003. Speciation of phosphorus in phosphorus-enriched agricultural soils using X-ray absorption near-edge structure spectroscopy and chemical fractionation. J. Environ. Qual. 32(5), 1809-1819.

Boesch, D., Hechy, R., O´Melia, C., Schindler, D., Seitzinger, S., 2006. Eutropication of Swedish seas. Report 5509, Swedish Environmental Protection Agency, Stockholm.

Börling, K., Otabbong, E., Barberis, E., 2001. Phosphorus sorption in relation to soil properties in some cultivated Swedish soils. Nutr. Cycl. Agroecosys. 59(1), 39-46.

Börling, K., Otabbong, E., Barberis, E., 2004. Soil variables for predicting potential phosphorus release in Swedish noncalcareous soils. J. Environ. Qual. 33(1), 99-106.

Cade-Menun, B.J., 2005. Characterizing phosphorus in environmental and agricultural samples by P-31 nuclear magnetic resonance spectroscopy. Talanta 66(2), 359-371.

Carlgren, K., Mattsson, L., 2001. Swedish soil fertility experiments. Acta Agric. Scand. Sect. B-Soil Plant Sci. 51(2), 49-78.

Chang, S.C., Jackson, M.L., 1957. Fractionation of soil phosphorus. Soil Sci. 84(2), 133-144.

Cui, Y.S., Weng, L.P., 2013. Arsenate and phosphate adsorption in relation to oxides composition in soils: LCD Modeling. Environ. Sci. Technol. 47(13), 7269-7276.

Djodjic, F., Börling, K., Bergström, L., 2004. Phosphorus leaching in relation to soil type and soil phosphorus content. J. Environ. Qual. 33(2), 678-684.

Doolette, A.L., Smernik, R., 2011. Soil organic phosphorus speciation using spectroscopic techniques p. 3-36. In: E.K. Bünemann, A. Oberson, E. Frossard (Eds.), Phosphorus in action, biological processes in soil phosphorus cycling. Springer.

Egner, H., Riehm, H., Domingo, W.R., 1960. Investigations on chemical soil analysis as the basis for estimating the nutrient status of soils. II. Chemical methods of extraction for phosphorus and potassium determinations. Kungliga Lantbrukshogskolans Annaler 26, 199-215.

Eveborn, D., Gustafsson, J.P., Hesterberg, D., Hillier, S., 2009. XANES speciation of P in environmental samples: an assessment of filter media for on-site wastewater treatment. Environ. Sci. Technol. 43(17), 6515-6521.

Franke, R., Hormes, J., 1995. The P K near-edge absorption spectra of phosphates. Physica B 216(1-2), 85-95.

Gustafsson, J.P., Mwamila, L.B., Kergoat, K., 2012. The pH dependence of phosphate sorption and desorption in Swedish agricultural soils. Geoderma 189/190, 304-311.

Hartikainen, H., Rasa, K., Withers, P.J.A., 2010. Phosphorus exchange properties of European soils and sediments derived from them. Eur. J. Soil Sci. 61(6), 1033-1042.

Hedley, M.J., Stewart, J.W.B., Chauhan, B.S., 1982. Changes in inorganic and organic soil-phosphorus fractions induced by cultivation practices and by laboratory incubation. Soil Sci. Soc. Am. J. 46(5), 970-976.

Hesterberg, D., 2010. Chapter 11 - Macroscale chemical properties and X-ray absorption spectroscopy of soil phosphorus. In: S. Balwant, G. Markus (Eds.), Developments in soil science. Elsevier, pp. 313-356.

Hesterberg, D., Zhou, W.Q., Hutchison, K.J., Beauchemin, S., Sayers, D.E., 1999. XAFS study of adsorbed and mineral forms of phosphate. J. Synchrotron Rad. 6, 636-638.

Hillier, S., 1999. Use of an air brush to spray dry samples for X-ray powder diffraction. Clay Miner. 34, 127-135.

Hillier, S., 2003. Quantitative analysis of clay and other minerals in sandstones by X-ray powder diffraction (XRPD). Int. Assoc. Sedimentol. Spec. Publ. 34, 213-251.

Hingston, F.J., Atkinson, R.J., Posner, A.M., Quirk, J.P. 1967. Specific adsorption of anions. Nature 215, 1459-1461.

Hornburg, V., Luer, B., 1999. Comparison between total- and aqua regia extractable contents of elements in natural soils and sediments. J. Plant Nutr. Soil Sci. 162, 131-137.

Ingall, E.D., Brandes, J.A., Diaz, J.M., de Jonge, M.D., Paterson, D., McNulty, I., Elliott, W.C., Northrup, P., 2011. Phosphorus K-edge XANES spectroscopy of mineral standards. J. Synchrotron Rad. 18, 189-197.

ISO 11277, 1998. Soil quality – Determination of particle size distribution in mineral soil material.

ISO 11466, 1995. Soil quality - Extraction of trace elements soluble in aqua regia.

Ivanov, K., Zparjanova, P., Petkova, M., Stefanova, V., Kmetov, V., Georgieva, D., Angelova, V., 2012. Comparison of inductively coupled plasma mass spectrometry and colorimetric determination of total and extractable phosphorus in soils. Spectrochim. Acta B71-72, 117-122.

Kar, G., Peak, D., Schoenau, J.J., 2012. Spatial distribution and chemical speciation of soil phosphorus in a band application. Soil Sci. Soc. Am. J. 76(6), 2297-2306.

Kelly, S., Hesterberg, D., Ravel. B., 2008. Analysis of soils and minerals using X-ray absorption spectroscopy. p. 387-463 In A. L. Ulery and R. Drees (Eds.) Methods of Soil Analysis. Part 5. Mineralogical Methods. Soil Sci. Soc. Am., Madison, WI.

Khare, N., Hesterberg, D., Beauchemin, S., Wang, S.L., 2004. XANES determination of adsorbed phosphate distribution between ferrihydrite and boehmite in mixtures. Soil Sci. Soc. Am. J. 68(2), 460-469.

Khare, N., Martin, J. D., Hesterberg, D., 2007. Phosphate bonding configuration on ferrihydrite based on molecular orbital calculations and XANES fingerprinting. Geochim. Cosmochim. Acta 71, 4405-4415.

Khatiwada, R., Hettiarachchi, G.M., Mengel, D.B., Fei, M.W., 2012. Speciation of phosphorus in a fertilized, reduced-till soil system: in-field treatment incubation study. Soil Sci. Soc. Am. J. 76(6), 2006-2018.

Kirchmann, H., 1991. Properties and classification of soils of the Swedish long-term fertility experiments. 1. Sites at Fors and Kungsängen. Acta Agric. Scand. B41(3), 227-242.

Kirchmann, H., Eriksson, J., Snäll, S., 1999. Properties and classification of soils of the Swedish long-term fertility experiments - IV. Sites at Ekebo and Fjärdingslöv. Acta Agric. Scand. B49(1), 25-38.

Kirchmann, H., Snäll, S., Eriksson, J., Mattsson, L., 2005. Properties and classification of soils of the Swedish long-term fertility experiments: V. Sites at Vreta Kloster and Högåsa. Acta Agric. Scand. B 55(2), 98-110.

Liu, J., Yang, J.J., Liang, X.Q., Zhao, Y., Cade-Menun, B.J., Hu, Y.F., 2014. Molecular speciation of phosphorus present in readily dispersible colloids from agricultural soils. Soil Sci. Soc. Am. J. 78, 47-53.

Lombi, E., Scheckel, K.G., Armstrong, R.D., Forrester, S., Cutler, J.N., Paterson, D., 2006. Speciation and distribution of phosphorus in a fertilized soil: A synchrotron-based investigation. Soil Sci. Soc. Am. J. 70(6), 2038-2048.

Lookman, R., Geerts, H., Grobet, P., Merckx, R., Vlassak, K., 1996. Phosphate speciation in excessively fertilized soil: a 31P and 27Al MAS NMR spectroscopy study. Eur. J. Soil Sci. 47(1), 125-130.

Omotoso, O., McCarty, D.K., Hillier, S., Kleeberg, R., 2006. Some successful approaches to quantitative mineral analysis as revealed by the 3rd Reynolds Cup contest. Clays Clay Miner. 54, 748-760.

Parfitt, R.L., Childs, C.W., 1988. Estimation of forms of Fe and Al: A review, and analysis of contrasting soils by dissolution and Moessbauer methods. Austr. J. Soil Res. 26(1), 121-144.

Pierzynski, G.M., Logan, T.J., Traina, S.J., Bigham, J.M., 1990. Phosphorus chemistry and mineralogy in excessively fertilized soils - quantitive analysis of phosphorus rich particles. Soil Sci. Soc. Am. J. 54(6), 1576-1583.

Prietzel, J., Thieme, J., Salome, M., Knicker, H., 2007. Sulfur K-edge XANES spectroscopy reveals differences in sulfur speciation of bulk soils, humic acid, fulvic acid, and particle size separates. Soil Biol. Biochem. 39, 877-890.

Ravel, B., 2009. ATHENA User's Guide.

Ravel, B., Newville, M., 2005. ATHENA, ARTEMIS, HEPHAESTUS: data analysis for X-ray absorption spectroscopy using IFEFFIT. J. Synchr. Rad. 12, 537-541.

Soinne, H., Uusitalo, R., Sarvi, M., Turtola, E., Hartikainen, H., 2011. Characterization of soil phosphorus in differently managed clay soil by chemical extraction methods and P-31 NMR spectroscopy. Commun. Soil Sci. Plant Anal. 42(16), 1995-2011.

Stroia, C., Berbecea, A., Baghina, N., Gaica, I., Stroia, M., Radulov, I., 2013. Phosphorus dynamics on acidic grassland soil. Res. J. Agric. Sci. 45, 78-83.

Svanbäck, A., Ulen, B., Etana, A., Bergström, L., Kleinman, P.J.A., Mattsson, L., 2013. Influence of soil phosphorus and manure on phosphorus leaching in Swedish topsoils. Nutr. Cycl. Agroecosys. 96(2-3), 133-147.

Toor, G.S., Peak, J.D., Sims, J.T., 2005. Phosphorus speciation in broiler litter and turkey manure produced from modified diets. J. Environ. Qual. 34(2), 687-697.

Ulén, B., 2006. A simplified risk assessment for losses of dissolved reactive phosphorus through drainage pipes from agricultural soils. Acta Agric. Scand. B56(4), 307-314.

Van Reeuwijk, L.P., 1995. Procedures for Soil Analyses. International Soil Reference and Information Centre, Wageningen, Netherlands.

Williams, E.G., Saunders, W.M.H., 1956. Distribution of phosphorus in profiles and particle-size fractions of some Scottish soils. J. Soil Sci. 7, 90-108.

Wolf, A.M., Baker, D.E., 1990. Colorimetric method for phosphorus measurements in ammonium oxalate soil extracts. Commun. Soil Sci. Plant Anal. 21(19-20), 2257-2263.

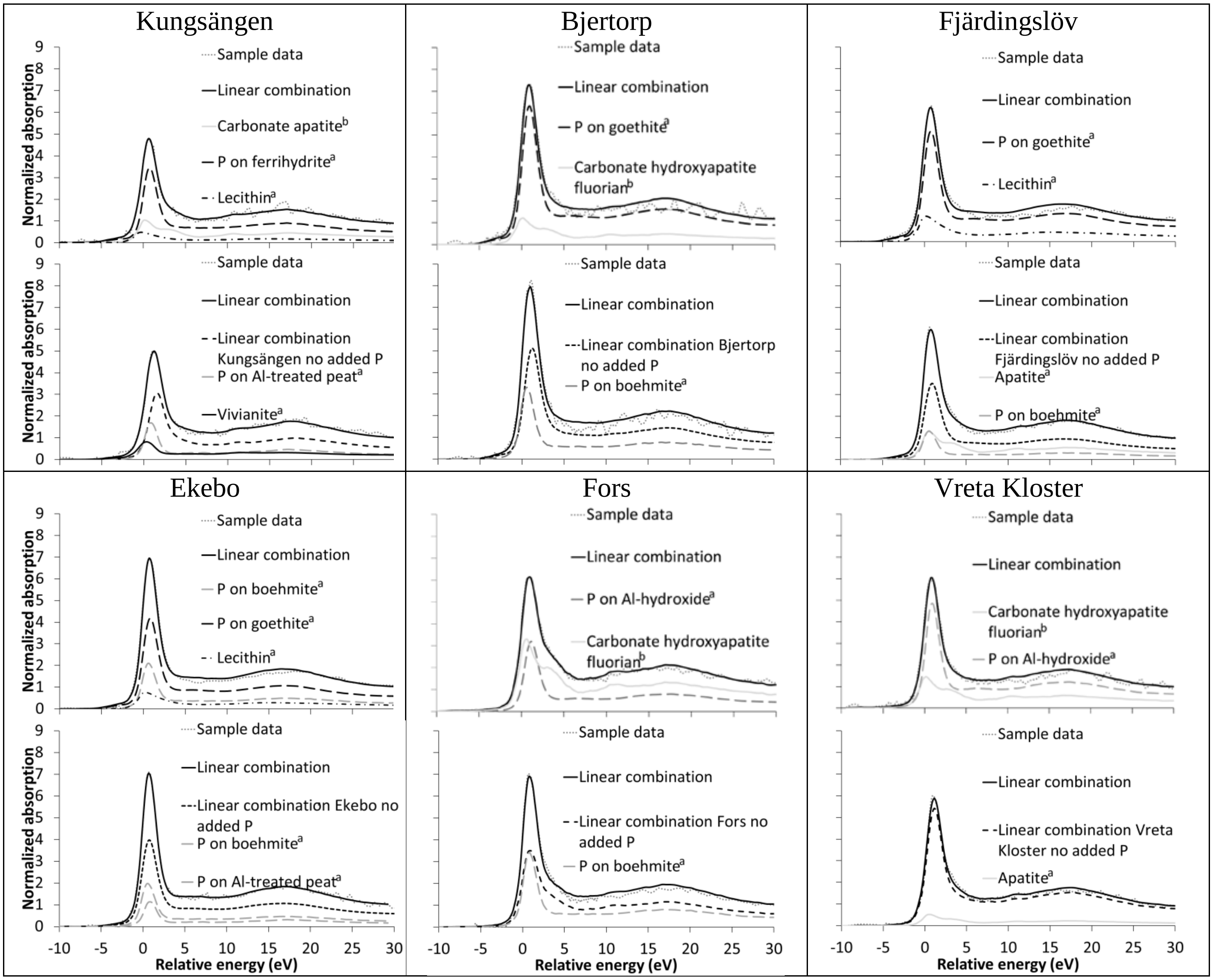

Fig. 1. Linear combination fitting of XANES spectra. For each soil, the upper spectrum is the best fit of the unfertilized sample, and the lower is for the fertilized sample. Fits from the unfertilized soils were used as a component in the fit of the fertilized treatment for each site. The grey dashed line shows the measured data and the black line is the linear combination fit. The other lines represent standards included in the fit. [a]Standards from Hesterberg et al., 2009; [b]standards from Ingall et al., 2011.

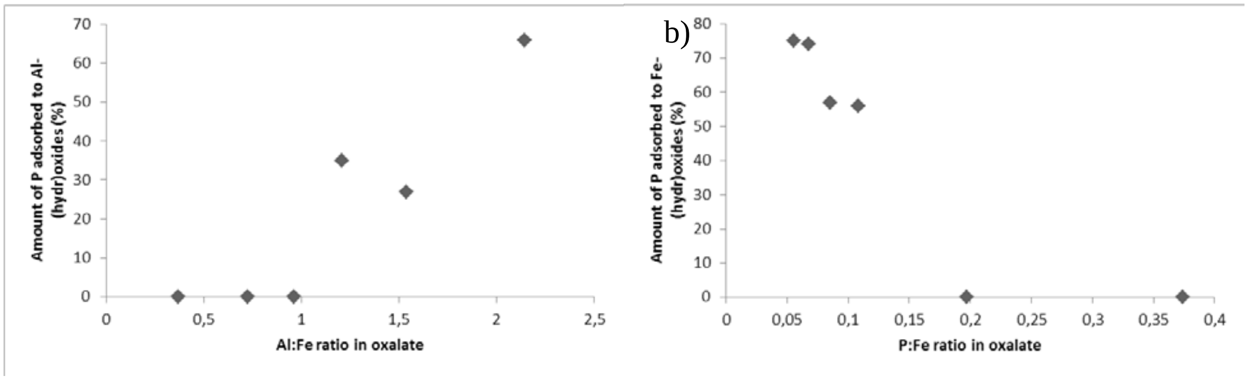

Fig. 2. Left: the relationship between the ratio of oxalate-extractable Al and Fe to the calculated amount of phosphate adsorbed to Al (hydr)oxides for unfertilized samples. Right: the relationship between the ratio of oxalate-extractable P and Fe to the calculated amount of phosphate adsorbed to Fe (hydr)oxides for unfertilized samples.

Table 1

Selected properties of the soil samples studied.

Site		Texture	Clay	pH	OrgC	Calcite	Al-ox	Al-py	Fe-ox	Fe-py	P-AL	P-ox	P-HCl	PsTotP
			(%)		(%)		(mmol kg^{-1})							
Fors	A3	silt loam	17	7.71	1.50	5.59	37.4	5.9	31.0	2.3	3.6	11.6	23.6	34.5
	C3	silt loam	15	7.72	1.47	7.39	33.0	5.6	31.0	3.0	4.8	13.2	22.9	36.5
	D3	silt loam	16	7.65	1.47	6.53	32.6	5.6	31.0	3.6	5.5	14.5	27.1	37.8
Kungsängen	A3	Clay	56	6.47	2.18	0.12	58.9	4.8	159.7	21.3	1.0	13.6	17.1	26.8
	C3	Clay	56	6.49	2.04	0.06	72.6	6.7	189.6	25.4	2.3	16.5	21.3	32.3
	D3	Clay	56	6.47	2.12	0.10	70.0	7.0	204.1	27.2	2.9	17.4	23.2	34.2
Vreta Kloster	A3	silty clay loam	39	6.52	2.03	0.12	63.0	13.3	29.4	6.4	1.0	5.8	14.2	20.7
	C3	silty clay	44	6.56	2.03	0.08	67.5	13.0	34.0	6.3	4.5	13.2	20.3	27.8
	D3	silty clay	45	6.56	2.04	0.13	61.2	13.3	32.2	6.4	5.2	14.5	22.9	30.7
Bjertorp	A3	silty clay loam$^{1)}$	30	6.29	2.05	0.09	54.9	11.5	75.7	5.6	0.6	4.2	15.8	18.7
	C3	silty clay loam$^{1)}$	31	6.39	1.98	0.11	51.9	12.6	66.3	6.1	2.6	11.6	23.6	25.8
	D3	silty clay loam$^{1)}$	32	6.45	2.02	0.07	56.3	13.0	75.0	6.3	4.2	14.9	27.8	30.7
Ekebo	A3	Loam$^{1)}$	16	5.91	2.32	0.05	63.7	36.0	41.5	25.6	1.0	4.5	19.0	19.4
	C3	Loam$^{1)}$	14	6.07	2.31	0.05	81.9	52.6	44.2	26.5	3.2	11.3	22.9	23.9
	D3	Loam$^{1)}$	12	6.03	2.55	0.14	94.1	70.0	39.9	24.5	6.5	16.1	30.7	30.7
Fjärdingslöv	A3	sandy loam$^{1)}$	18	6.49	1.23	0.17	32.6	7.4	34.0	7.3	0.6	2.3	11.0	11.9
	C3	sandy loam$^{1)}$	16	6.58	1.36	0.13	33.4	8.9	28.3	9.0	3.2	5.8	15.8	16.5
	D3	sandy loam$^{1)}$	16	6.59	1.37	0.19	34.1	9.3	31.9	12.4	6.1	11.6	20.3	22.6

Clay = clay content from pipette method, Al-ox = oxalate extractable Al, Al-py = pyrophosphate extractable Al, Fe-ox = oxalate extractable Fe, Fe-py = pyrophosphate extractable Fe, P-AL= ammonium lactate extractable P, P-HC l= P after hot extraction with 2 M HCl, P-ox = Oxalate extractable PO_4, PsTotP = aqua regia-digestible P .

Table 2

Phosphorus speciation in clay fractions from unfertilized soils as evidenced from linear combination fitting of XANES spectra. The five best fits are numbered from 1 to 5 in italics.

		CaP	FeP	AlP	P on Fe (hydr)oxides	P on Al (hydr)oxides	OrgP	R-factor[a]
Fors	weight (%)	65±1%				35±1%		0.003
	presence[b]	*1,2,3,4,5*				*1,2,3,4,5*		
Kungsängen	weight (%)	31±7%			57±4%		12±1%	0.004
	presence[b]	*1,2,3,4,5*			*1,2,3,4,5*		*1,2,3,4,5*	
Vreta K	weight (%)	34±2%				66±2%		0.005
	presence[b]	*1,2,3,4,5*				*1,2,3,4,5*	*4,5*	
Bjertorp	weight (%)	25±1%			75±1%			0.008
	presence[b]	*1,2,3,5*			*1,2,3,4,5*		*4*	
Ekebo	weight (%)				56±11%	27±9%	17±1%	0.003
	presence[b]	*3,5*			*1,2,3,4,5*	*1,2,3*	*1,2,4*	
Fjärdingslöv	weight (%)				74±1%		26±1%	0.005
	presence[b]	*2,3,4,5*	*5*		*1,2,3,4,5*	*3*	*1*	

CaP = calcium phosphates, FeP = crystalline iron phosphates, AlP = crystalline aluminum phosphates, P on Fe-oxides = Phosphate adsorbed on iron (hydr)oxides, P on Al-ox = phosphate adsorbed on aluminum (hydr)oxides, orgP = organic phosphorus. [a] R-factor calculated according to Ravel (2009).

Table 3

Phosphorus speciation in clay fractions from fertilized soils as evidenced from linear combination fitting of XANES spectra. The five best fits are numbered from 1 to 5 in italics.

		A3	CaP	FeP	AlP	P on Fe (hydr)oxides	P on Al (hydr)oxides	Org P	R-factor
Fors	weight (%)	57±1%					43±1%		0.004
	presence	*1,2,3,4,5*				*4*	*1,2,3,4,5*		
Kungsängen	weight (%)	59±6%		20±1%			21±5%		0.003
	presence	*1,2,3,4,5*		*1,3,4*	*4,5*		*1,2*	*2,3*	
Vreta K	weight (%)	88±1%	12±1%						0.003
	presence	*1,2,3,4,5*				*3*	*1,2,4,5*		
Bjertorp	weight (%)	62±1%					38±1%		0.006
	presence	*1,2,3,4,5*				*2,4*	*1,2,3,5*		
Ekebo	weight (%)	56±5%					44±6%		0.001
	presence	*1,2,3,4,5*			*3,5*	*4*	*1,2,3,4,5*		
Fjärdingslöv	weight (%)	54±1%	29±2%				17±2%		0.002
	presence	*1,2,3,4,5*	*1,2,3,4,5*			*3,4*	*1,2,5*		

A3 = fit for the unfertilized treatment from the same site, CaP = calcium phosphates, FeP = crystalline iron phosphates, AlP = crystalline aluminum phosphates, P on Fe-oxides = phosphate adsorbed on iron (hydr)oxides, P on Al-ox = Phosphate adsorbed on aluminum (hydr)oxides, orgP = organic P. ^{a} R-factor calculated according to (Ravel, 2009).