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Phosphorus dynamics in Swedish agricultural soils as influenced by fertilization and mineralogical properties: insights gained from batch experiments and XANES spectroscopy

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Highlights

- The dominant role of Al and Fe(hydr)oxides for accumulating added P was confirmed
- Neoformation of Ca phosphate occurred in 2 of 6 soils after long-term fertilization
- The P K-edge fluorescence intensity was strongly correlated with HCl-digestible P
- In unfertilized, non-calcareous soils, phosphate had a minimum solubility at pH 6–7
- Soil test P (P-AL) was related to the initial adsorbed P calculated from isotherms

Abstract

The soil chemistry of phosphorus (P) is important for understanding the processes governing plant availability as well as the risk of environmental losses of P. The objective of this research was to investigate both the speciation and the pH-dependent solubility patterns of P in clayey agricultural soils in relation to soil mineralogy and fertilization history. The study focused on soil samples from six fields that were subjected to different P fertilization regimes for periods of 45 to 57 years. Soil P speciation was analyzed by P K-edge XANES spectroscopy and chemical fractionation, sorption isotherms were constructed, and dissolved P was measured as a function of pH. The XANES fitting results showed that organic P and P adsorbed to Fe and Al (hydr)oxides were common P constituents in all soils. Calcium phosphates were identified in five of six soil samples. The XANES results also indicated an increase in P adsorbed to Al and to a lesser extent Fe (hydr)oxides as a result of fertilization. Moreover, the fluorescence intensity from the P K-edge XANES analysis was most strongly correlated with HCl-digestible P ($r = 0.81^{***}$). Consistent with the XANES analysis, laboratory sorption isotherm models showed that the Freundlich sorption coefficient (K_F) was most closely related to oxalate-extractable Al. Greater proportions of Ca phosphate in two of the heavily fertilized soils in combination with enhanced PO_4 solubilization upon sample acidification indicated neof ormation of Ca-phosphate precipitates. The results for the unfertilized soil samples generally showed a minimum in dissolved PO_4 between pH 6.5 and 7.5, with increases particularly at lower pH. This behavior can be explained either by the dissolution of Al-hydroxide-type sorbents or Ca phosphates at lower pH. In fertilized soils, there was no consistent trend in pH-dependent solubilization of P, with a complex relationship to solid-phase speciation. To conclude, inorganic P species changed most dynamically in agricultural clay soils over a period of several decades, and the role of pH in the solubilization of P depended mainly on P fertilization history and the content of reactive Ca phosphates.

Keywords: XANES spectroscopy, phosphorus, phosphate, apatite, secondary iron and aluminium (hydr)oxides, clay mineralogy

1. Introduction

Phosphorus sorption and dissolution in soils affect plant availability and transport of P to surface and subsurface waters. Chemical speciation of soil P has historically been determined by sequential extractions (e.g. Chang and Jackson, 1957; Williams et al., 1967; Hedley et al., 1982), but X-ray adsorption near edge structure (XANES) spectroscopy has gained use in the past two decades (e.g. Hesterberg et al., 1999; Beauchemin et al., 2003; Eveborn et al., 2014). XANES spectroscopy measures soil P speciation without any chemical pretreatment and results have been compared with those from sequential extractions (Beauchemin et al., 2003; Kar et al., 2011). For example, by linear combination fitting (LCF) of XANES spectra with pure standards of P compounds, a number of soils from Canada showed the presence of Ca phosphates, regardless of the soil pH, and a correlation between the sum of Ca phosphates and HCl-extractable P was observed (Beauchemin et al., 2003). XANES spectroscopy has also been used to investigate the effect of different fertilization techniques on P speciation (e.g. Sato et al., 2005; Lombi et al., 2006; Khatiwada et al., 2012; Khatiwada et al., 2014). These results show that the most likely P species accumulating after fertilization are P sorbed to Al- and Fe (hydr)oxides, and Ca-, Fe- and Al-phosphate compounds. In contrast, nuclear magnetic resonance (NMR) spectroscopy showed that the size of the organic P pool did not change in response to long-term fertilization (Ahlgren et al., 2013). However, to improve our understanding of P reactions in fertilized soils, P speciation must be complemented with soil chemical properties such as P sorption and pH-dependent solubility.

Several recent studies showed that dissolved PO_4 in clayey soils is lowest at neutral pH (6.5 to 7.5) and increased as pH decreased to < 6.5 (e.g. Devau et al., 2011; Weng et al., 2011; Gustafsson et al., 2012;). Three explanations for this behavior were discussed by Weng et al. (2011) and Gustafsson et al. (2012): (1) sorption of Ca^{2+} to Al and Fe (hydr)oxides leading to increased P sorption particularly between pH 4 and 7, as a result of electrostatic interactions at the (hydr)oxide surface; (2) dissolution of P-adsorbing Al (hydr)oxides or hydroxy-Al-interlayers at low pH, which removes sorption sites; and (3) dissolution of Ca phosphates that are progressively more unstable with decreasing pH. Further, Devau et al. (2011) suggested a dominant role of sorption to clay minerals with similar pH-dependent PO_4 sorption patterns.

Soil fertilization history may also affect the pH-dependent sorption behavior. Gustafsson et al. (2012) showed that the sorption behavior may be different depending on whether or not PO_4 was freshly added to the soil suspension. Moreover, there was a consistent difference in pH-dependent sorption depending on the soil texture. In soils with <10 % clay, PO_4 sorption increased monotonically with decreasing pH.

In our previous study, the speciation of P was determined for the clay fractions of soils from the same fertility experiments used in the present study (Eriksson et al. 2015). It was concluded that P accumulated as a result of long-term fertilization was bound mostly to Al hydroxides. However, due to the higher-quality spectra and lower spectral noise, clay fractions rather than bulk soils were used, and there was a slight uncertainty as to whether the conclusions are valid for the whole soils. In the current study, we used a beam line (SLRI, BL-8) with a much better signal-to-noise ratio at the P K edge. This allowed us to collect high-quality XANES spectra for bulk soil samples from these sites, which gave more reliable results to draw stronger inferences on fertilization effects on P speciation. In addition, the solubility of phosphate (PO_4) was investigated, and the mineralogical properties of the soils were considered, which enabled us to elucidate the mechanisms by which fertilization affected the P status of these soils.

The objective with this paper was to determine species of P that accumulate in clayey agricultural soils during long-term fertilization, and to relate P speciation to the soil PO_4 solubility and mineralogical properties. A combination of approaches were employed: (i) comparing P speciation in six clayey soils that have been subjected to different fertilization regimes for periods of 45-57 years, (ii) measuring pH-dependent solubilization of PO_4 in these soils, and (iii) evaluating the PO_4 sorption affinity as implied by a three-parameter Freundlich equation fit to sorption isotherms.

2. Materials and methods

2.1. Site description and soil sampling

Samples were collected from six different long-term fertility experiments in Swedish agricultural soils (Table 1; Eriksson et al. 2015). These sites were established between 1957 and 1969 to study the influence of different fertilization regimes on crop production and on soil nutrient status. The experimental plots are divided into two different crop rotations with

and without livestock. The soil samples were collected from plots without livestock where mineral fertilizer (inorganic NPK fertilizer) was used. The soils were subject to N fertilization with 150 kg N ha⁻¹ yr⁻¹ for the Ekebo and Fjärdingslöv sites and with 125 kg N ha⁻¹ yr⁻¹ for the remaining sites (Carlgren and Mattsson, 2001). Samples from three different fertilization levels were used: (1) plots with no P added (A3); (2) plots with replacement of P removed with the previous year's harvest plus an additional 20 kg P and 50 kg K ha⁻¹ yr⁻¹ except for the soils from Ekebo and Fjärdingslöv where 15 kg P and 40 kg K ha⁻¹yr⁻¹ was added (C3); (3) plots with replacement of last year's harvest plus an additional 30 kg P and 80 kg K ha⁻¹ yr⁻¹(D3). Soil samples were collected using soil cores (Ø = 2 cm) in a circle (Ø = 1 m) to 20 cm depth. In each plot, several soil samples were combined into 1-2 kg bulk samples. The samples were dried at 30°C and sieved to <2 mm.

Table 1

Coordinates, soil order and texture for the soils of the long-term fertility experiments.

Site	Coordinates	Soil order	Texture
Fors	60°20'N, 17°29'E	Calcaric Phaeozem ¹	Silt loam
Kungsängen	59°50'N, 17°40'E	Gleyic Cambisol ¹	Clay
Vreta Kloster	58°30'N, 15°30'E	Haplic Phaeozem ²	Silty clay (loam)
Bjertorp	58°14'N, 13°08'E	<i>n.d.</i> ³	Silty clay loam
Ekebo	55°59'N, 12°52'E	Haplic Phaeozem ⁴	Loam
Fjärdingslöv	55°24'N, 13°14'E	Haplic Phaeozem ⁴	Sandy loam

¹Kirchmann (1991)

²Kirchmann *et al.* (2005)

³n.d. = not determined

⁴Kirchmann *et al.* (1999)

2.2. General soil characterization and P extractions

Particle-size distribution was determined by use of the pipette method (ISO 11277; ISO, 2009). Soil pH was measured using a Radiometer PHM93 reference pH meter with a GK2401C combined pH electrode after equilibrating 6 g of dry soil with 18 mL of deionized water for 18 h. Organic carbon content was determined using a LECO CNS-2000 analyzer. Oxalate extraction (van Reeuwijk, 1995) was carried out to estimate the amounts of poorly crystalline aluminum (Al) and iron (Fe) as well as phosphate (PO₄) associated with these phases. In brief, 1 g of soil was equilibrated with an oxalate buffer (pH 3.0) for 4

h in darkness. Afterwards, the supernatant was filtered through a 0.2 μm single use filter and diluted 1:5 in water. The concentrations of Al and Fe in the extract were determined with ICP-OES using an ICP Optima 7300 DV instrument, whereas PO_4 was determined colorimetrically (Wolf and Baker, 1990). Pyrophosphate-extractable Al and Fe were determined by equilibrating 1 g of soil with 100 mL solution containing 0.1 M $\text{Na}_2\text{P}_2\text{O}_7 \cdot 10\text{H}_2\text{O}$ for 16 h. Again the supernatant was filtered (0.2 μm single use filter) and diluted 1:5 in water before measurement by ICP-OES using a Perkin Elmer 5300 DV instrument. Ammonium lactate-extractable P (P_{AL}) was determined using the method of Egnér et al. (1960) after equilibrating 3 g soil with 60 mL solution for 1.5 h. The suspension was then filtered prior to analysis with ICP-OES. Phosphorus was also measured after acid digestion of 2 g of soil in 50 mL of 2 M HCl for 2 h (KLS, 1965). Pseudo-total P was determined with aqua regia digestion according to ISO 11466 (ISO, 1995), letting 3 g of soil boil with 30 mL aqua regia solution for 2 h. To minimize evaporation, a condenser was connected to the digester. The samples were diluted in 0.5 M HCl and P was determined with ICP-OES using a Perkin Elmer 5300 DV instrument.

2.3. P K-edge XANES spectroscopy and data analysis

Speciation of P in the clay fractions of the six studied soils was previously analyzed by K-edge XANES spectroscopy (Eriksson et al. 2015). Here we collected P XANES data on bulk soil samples at a different facility, beam line BL8 at the Synchrotron Light Research Institute (SLRI) in Nakhon Ratchasima, Thailand (Klysubun et al., 2012). The beam line was equipped with an InSb(111) monochromator giving a beam flux of 1.3×10^9 to 6×10^{10} photons s^{-1} (100 mA) $^{-1}$ in a $12.5 \times 0.9 \text{ mm}^2$ beam. Soil samples were ground and sieved (<0.05 mm) to diminish thickness effects. Samples were packed into a $0.5 \times 1 \text{ cm}^2$ sample windows in 2 mm thick stainless steel holders and covered with P-free polypropylene film. Fluorescence data were collected using a solid state, 13-element Ge-fluorescence detector. The sample chamber was filled with He gas to minimize absorption of X-rays in the flight path. The energy step size was 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. All measurements were recorded using a dwell time of 3 s per energy step. The energy was calibrated at the elemental P edge at 2145.5 eV, and verified periodically on variscite for which the maximum in the first-derivative spectrum was 2154.05 eV.

The XANES data were processed using the Athena software, version 0.9.20 (Ravel and Newville, 2005). Multiple spectra were merged and normalized using the following procedure: a linear baseline function was subtracted from the spectral region below the edge (between -30 to -10 eV relative to E_0), and a quadratic function was used to normalize spectra across the post-white-line region between 30 and 45 eV relative to E_0 taken as the maximum in the first-derivative spectrum for each sample.

2.4. Linear combination fitting (LCF) analysis

Linear combination fitting (LCF) (Tannazi and Bunker, 2005) was performed using weighted combinations of spectra from 31 known standards (Eriksson et al., 2016) to fit the sample spectra. No energy shifts were permitted in the fitting procedure. The fitting range was constrained to between -10 to 30 eV relative to E_0 . For the unfertilized treatments (A3), at most four standards were included in each fit. To constrain the fits, lecithin was included as a mandatory diester-P standard to represent organic P, and apatite or another Ca-phosphate standard was included as a mandatory standard to account for a post-white-line shoulder that is indicative of Ca-phosphates (Hesterberg et al., 1999). For one soil (Ekebo), however, no calcium phosphate was included in the best fit. For the samples from the fertilized treatments (D3) the spectrum for the unfertilised treatment (A3) was used as a mandatory standard. A maximum of two additional standards was allowed in the fit. Only fits for which weighting fractions summed to 100 ± 10 % were accepted, and fractions were re-normalized to a sum of 100 %.

2.5. pH-dependent batch experiments

The pH dependence of dissolved PO_4 was analysed as described previously (Gustafsson et al., 2012). Two grams of dry soil were equilibrated with 30 cm^3 solution of varying composition (c.f. below) for 7 d in darkness at room temperature. The suspensions were shaken in polypropylene centrifuge tubes with screw caps. All suspensions contained 0.01 M NaNO_3 as a background electrolyte. Varying concentrations of acid (as HNO_3) or base (as NaOH) were added to produce a range of pH values. The acid treatments contained 5, 4, 3, 2 and 1 mM of HNO_3 , and the base treatment contained 1 and 2 mM of NaOH . All treatments were applied in duplicate. After 7 d of reaction, the samples were centrifuged in 3000 rpm for 20 min. The pH of the supernatant was measured using a Radiometer PHM93 pH meter with a GK2401C glass combination electrode. The remaining supernatant solution

was filtered through a 0.2 µm single use filter (Acrodisc PF) prior to the analysis of PO₄-P (colorimetrically using a Tecator Aquatec 5400 spectrophotometer with flow injection analysis) and of Ca, Al and Fe by ICP-OES.

Visual MINTEQ, ver. 3.1 (Gustafsson, 2015) was used for speciation modelling to calculate the activities of free Ca²⁺, Al³⁺, Fe³⁺ and PO₄-P in solution. The solubility constants of various Ca-P and Al-P phases were those used by Gustafsson et al. (2012).

2.6. Sorption experiments

Again, 2 g of soil was equilibrated with a solution containing 0.01M NaNO₃ as a background electrolyte and with 8 different levels with added NaH₂PO₄ (0.01, 0.02, 0.04, 0.07, 0.1, 0.15, 0.2 and 0.3 mM, equivalent to 0.15, 0.3, 0.6, 1.05, 1.5, 2.25, 3 and 4.5 mmol P kg⁻¹ soil, respectively). The suspensions were equilibrated in darkness for 7 days at room temperature. Afterwards the samples were centrifuged at 3000 rpm for 20 min. The pH of the supernatant was measured using a Radiometer PHM93 reference pH meter with a GK2401C combined pH electrode. The remaining supernatant solution was filtered through a 0.2 µm single use filter (Acrodisc PF) prior to the analysis of PO₄-P (colorimetrically using a Seal Analytical AA3 Autoanalyzer).

The data was fitted to a three-parameter Freundlich equation (Fitter and Sutton, 1975):

$$n_{\text{sorb}} = K_F \cdot c^m - n_{\text{init}} \quad (1)$$

where n_{sorb} and n_{init} represent the phosphate adsorbed during the experiment and the phosphate originally adsorbed to the soil (mol kg⁻¹), c is the equilibrium concentration of phosphate (mol L⁻¹), whereas K_F and m are constants that have to be optimized in the fitting process. To facilitate parameter optimization in a linear space, this equation can be logarithmically transformed to

$$\log n = \log K_F + m \cdot \log c \quad (2)$$

where $n = n_{\text{sorb}} + n_{\text{init}}$. In our approach, the value of n_{init} was optimized in the fitting procedure. However, when K_F , m and n_{init} are optimized at the same time, the values are quite sensitive to small changes in the data (Peltovuori, 2007). Therefore, the m value was set to 0.33 as discussed by Tolner & Füleky (1995) and Gustafsson et al. (2012). Then $\log K_F$ and $\log n$ were determined by adjusting n_{init} to produce the best R² value.

3. Results

3.1. Soil properties

Soil physical and chemical properties are described in detail elsewhere (Eriksson et al. 2015; Eriksson, 2016) and only a brief summary is given here (Table 2).

Table 2

Selected properties of the soil samples studied. A3 is the unfertilized treatment whereas C3 and D3 are fertilized treatments.

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

Clay = clay content, Al-ox = oxalate-extractable Al, Al-py = pyrophosphate-extractable Al, Fe-ox = oxalate-extractable Fe, Fe-py = pyrophosphate-extractable Fe, P-AL= acid ammonium lactate-extractable P, P-HCl= HCl-digestible P, P-ox = Oxalate-extractable PO₄, PsTotP = aqua regia-digestible P.

Of the six examined soils, only Fors had an alkaline pH (7.69 ± 0.05), and it was the only soil with a substantial amount of carbonate (~6.4 %); X-ray diffraction data confirmed the

presence of calcite in this soil (Eriksson et al., 2015; Eriksson, 2016). The Kungsängen soil had the greatest contents of both clay and oxalate-extractable Fe. The Vreta Kloster and Bjertorp soils were also clay-rich (> 30 %), but with somewhat lower clay and oxalate-extractable Fe contents. The Bjertorp soil contained relatively large amounts of hydroxy-interlayered clay minerals (Eriksson, 2016). The Ekebo soil had the lowest pH, and also the highest amount of oxalate-extractable Al and Fe. This soil was also high in hydroxy-interlayered clay minerals (Eriksson, 2016). Lastly, Fjärdingslöv was the soil with the largest content of expandable minerals (Eriksson, 2016), however it also had low contents of oxalate extractable Al and Fe.

3.2. Fluorescence intensity compared to extracted P fractions

The amount of P obtained from different extractions was compared with the absolute fluorescence intensity (I_f/I_0) as determined by XANES spectroscopy (Leri et al., 2006). The absolute fluorescence intensity was defined as the edge step in the XANES spectrum, and it depends particularly on (1) the overall concentration of P in the sample; (2) the density of P within particles greater than the absorption length of $\sim 4 \mu\text{m}$ that can induce thickness and self-absorption effects; (3) the concentrations of soil matrix elements such as Al and Si that have edge energies below the $K\alpha$ fluorescence signal of the P edge and therefore absorb the fluorescence radiation; and (4) concentrations of other soil elements that absorb either the incoming or fluorescence radiation. All of these factors affect the penetration depth of the X-ray beam into the sample and the escape depth of fluorescence X-rays. For the purpose of the comparison, we included samples both from the current study and from a previous study on P speciation in an agricultural soil profile (Eriksson et al., 2016). The strongest relationship with fluorescence intensity was found with the amount of HCl-digestible P ($r = 0.81^{***}$, $n = 16$; Fig. 1).

3.3. Phosphorus speciation as influenced by fertilization.

Similar to our previous study where clay fractions from the same sites were examined (Eriksson et al., 2015), the P speciation inferred by XANES LCF analysis was commonly dominated by organic P, calcium phosphates, and P sorbed to Al and Fe (hydr)oxides (Table 4 and Table 5). XANES spectra with the best LCF fits are found in the supplementary data (Fig. S2-S3). However, the distribution of P species in individual soils as obtained in the current study did not always agree with the ones obtained for the clay fractions. Although

this may to some extent reflect a real difference in P speciation, we attribute this mainly to the much higher sensitivity (and lower noise) obtained at SLRI compared with NSLS Beamline X-15B. This is shown by consistently lower R factors obtained in the current study – therefore the P speciation results for the bulk soils should be more reliable.

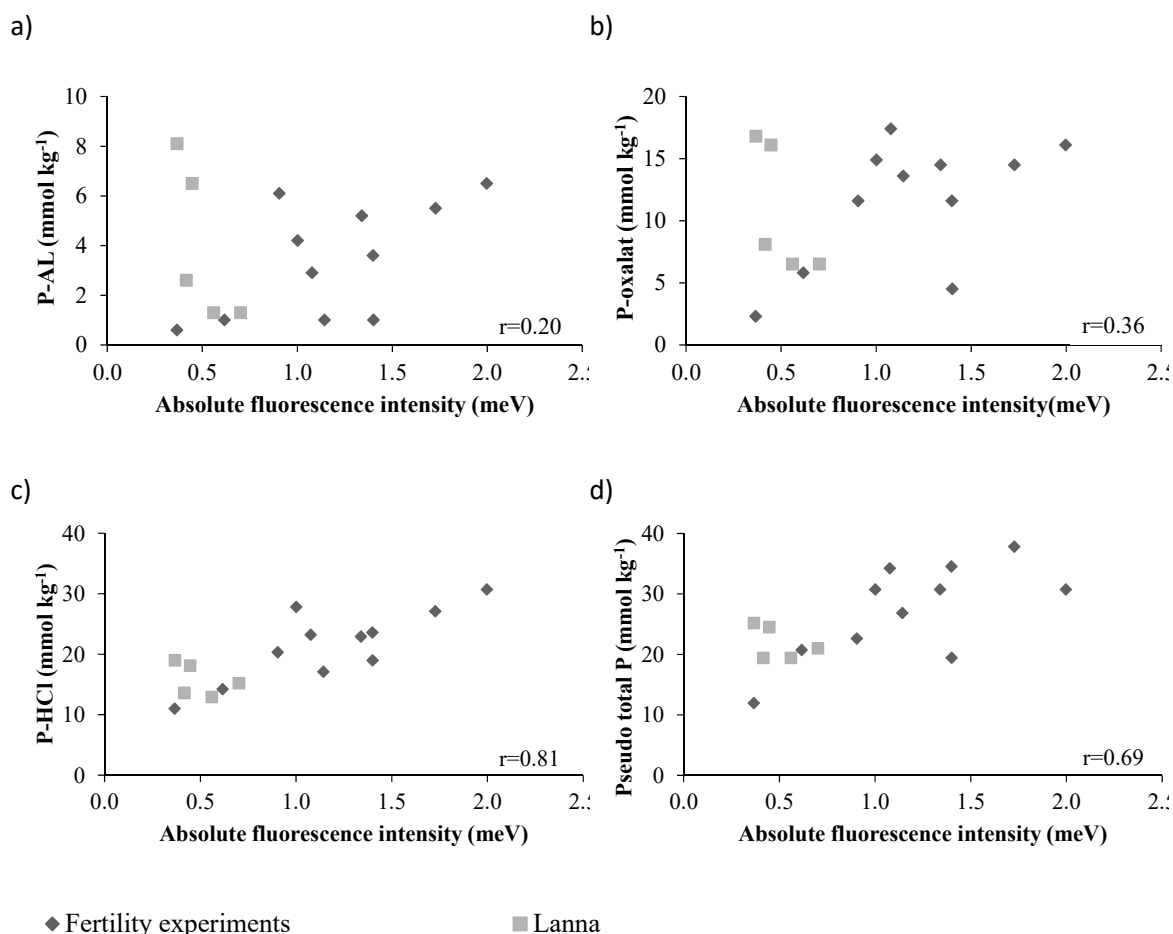


Fig. 1. The relationship between the absolute fluorescence intensity and a) P extracted with ammonium lactate; b) P extracted with oxalate c) P digested with HCl, and d) Pseudo total P (P digested with aqua regia); for soils from the fertility experiments and for soil samples from an agricultural soil profile (Lanna; Eriksson et al., 2016).

All unfertilized soils except the Ekebo soil contained calcium phosphates, according to the XANES analysis (Table 4 and Fig. S2). The Fors soil contained the highest percentage of calcium phosphates among all soils examined (46 %).

Table 3

Values of E_0 (eV) for P K-edge XANES spectra of unfertilized (A3) and fertilized (D3) treatments.

	Bjertorp	Ekebo	Fjärdingslöv	Fors	Kungsängen	Vreta Kloster
A3	2153.273	2153.449	2153.499	2153.225	2153.296	2153.238
D3	2153.547	2153.742	2153.586	2153.264	2153.577	2153.455

E_0 is defined as the inflection point of the first derivative of the XANES spectrum at the edge.

Table 4

Phosphorus speciation in unfertilized (A3 treatment) and fertilized soils (D3 treatment) as evidenced from linear combination fitting of XANES spectra. The five best fits are numbered from 1 to 5 in italics.

		P adsorbed on Al	P adsorbed on Fe	FeP	AIP	CaP	Organic P (lecithin)	R factor
A3 treatment								
Fors	weight (%)	21 ± 1	6 ± 1			46 ± 1	27 ± 1	<0.001
	<i>presence</i>	<i>1,4</i>	<i>1,2,3</i>	<i>4</i>	<i>3,5</i>	<i>1,2,3,4,5</i>	<i>1,2,3,4,5</i>	
Kungsängen	weight (%)	30 ± 2	7 ± 2			21 ± 2	43 ± 1	0.001
	<i>presence</i>	<i>1,2,3,4,5</i>	<i>1,2</i>		<i>4</i>	<i>1,2,3,4,5</i>	<i>1,2,3,4,5</i>	
Vreta Kloster	weight (%)	34 ± 2	6 ± 2			28 ± 2	32 ± 2	0.002
	<i>presence</i>	<i>1,2,3,4,5</i>	<i>1</i>			<i>1,2,3,4,5</i>	<i>1,2,3,4,5</i>	
Bjertorp	weight (%)	29 ± 3	15 ± 4			4 ± 3	51 ± 3	0.006
	<i>presence</i>	<i>1,2,3,4,5</i>	<i>1,5</i>			<i>1,2,3,4,5</i>	<i>1,2,3,4,5</i>	
Ekebo	weight (%)	52 ± 1					48 ± 1	0.002
	<i>presence</i>	<i>1,2,3,4,5</i>	<i>5</i>			<i>2,3,4,5</i>	<i>1,2,3,4,5</i>	
Fjärdingslöv	weight (%)	53 ± 4				20 ± 1	26 ± 1	0.001
	<i>presence</i>	<i>1,2,3,4,5</i>		<i>2,3,5</i>	<i>4</i>	<i>1,2,3,4,5</i>	<i>1,2,3,4,5</i>	
D3 treatment								
Fors	weight (%)	12 ± 2	13 ± 3			45 ± 3	29 ± 1	0.002
	<i>presence</i>	<i>1,2,3,4,5</i>	<i>1,5</i>			<i>1,2,3,4,5</i>	<i>1,2,3,4,5</i>	
Kungsängen	weight (%)	39 ± 1		26 ± 1		18 ± 1	17 ± 1	0.001
	<i>presence</i>	<i>1,3,4,5</i>	<i>2</i>	<i>1,3,4,5</i>	<i>2</i>	<i>1,2,3,4,5</i>	<i>1,2,3,4,5</i>	
Vreta Kloster	weight (%)	32 ± 2	9 ± 3			27 ± 2	30 ± 2	0.001
	<i>presence</i>	<i>1,2,3,4,5</i>	<i>1</i>		<i>4</i>	<i>1,2,3,4,5</i>	<i>1,2,3,4,5</i>	
Bjertorp	weight (%)		43 ± 4		38 ± 3	14 ± 1	6 ± 1	0.001
	<i>presence</i>	<i>2</i>	<i>1,2,4,5</i>	<i>3</i>	<i>1,5</i>	<i>1,2,3,4,5</i>	<i>1,2,3,4,5</i>	
Ekebo	weight (%)	64 ± 2	15 ± 4				20 ± 1	0.001
	<i>presence</i>	<i>1,2,3,4,5</i>	<i>1,2,3,4,5</i>		<i>2,3,4</i>		<i>1,2,3,4,5</i>	
Fjärdingslöv	weight (%)	52 ± 3	4 ± 4			19 ± 2	25 ± 3	0.001
	<i>presence</i>	<i>1,2,3,4,5</i>	<i>1,2</i>			<i>1,2,3,4,5</i>	<i>1,2,3,4,5</i>	

P adsorbed on Al = phosphate adsorbed on aluminum (hydr)oxides, P adsorbed on Fe = phosphate adsorbed on iron (hydr)oxides, AIP = crystalline aluminum phosphates, FeP = crystalline iron phosphates, CaP = calcium phosphates. The R factor is the goodness-of-fit parameter reported by Athena ($R = \frac{\sum(\text{data-fit})^2}{\sum(\text{data})^2}$; Ravel, 2009).

Table 5

Phosphorus speciation in fertilized soils (D3 treatment) as evidenced from linear combination fitting of XANES spectra. The five best fits are numbered from 1 to 5 in italics.

		P adsorbed on Al	P adsorbed on Fe	FeP	AIP	CaP	Organic P (lecithin)	A3	R factor
D3 treatment									
Fors	weight (%)	4 ± 1					33 ± 2	63 ± 2	0.002
	<i>presence</i>	<i>1</i>	<i>2</i>		<i>3,4</i>	<i>5</i>	<i>1,2,3,4,5</i>	<i>1,2,3,4,5</i>	
Kungsängen	weight (%)	20 ± 1		27 ± 1				53 ± 1	<0.001
	<i>presence</i>	<i>1,2,3,4</i>	<i>5</i>	<i>1,2,4</i>	<i>3,5</i>			<i>1,2,3,4,5</i>	
Vreta Kloster	weight (%)		24 ± 3			16 ± 2		60 ± 4	0.002
	<i>presence</i>	<i>3</i>	<i>1,2,4,5</i>			<i>1,2,3,5</i>	<i>4</i>	<i>1,2,3,4,5</i>	
Bjertorp	weight (%)	27 ± 1		23 ± 1				50 ± 1	<0.001
	<i>presence</i>	<i>1,2,3,4</i>	<i>5</i>	<i>1,2,3</i>	<i>5</i>	<i>4</i>		<i>1,2,3,4,5</i>	
Ekebo	weight (%)	45 ± 1				5 ± 1		50 ± 1	<0.001
	<i>presence</i>	<i>1,2,3,4,5</i>	<i>4</i>	<i>5</i>	<i>1,2,3</i>			<i>1,2,3,4,5</i>	
Fjärdingslöv	weight (%)	33 ± 4				22 ± 4		45 ± 8	0.003
	<i>presence</i>	<i>1,2,3,4,5</i>				<i>2,3,4,5</i>	<i>1</i>	<i>1,2,3,4,5</i>	

A3 = fit for the unfertilized treatment from the same site, P adsorbed on Al = phosphate adsorbed on aluminum (hydr)oxides, P adsorbed on Fe = phosphate adsorbed on iron (hydr)oxides, AIP = crystalline aluminum phosphates, FeP = crystalline iron phosphates, CaP = calcium phosphates. The R factor is the goodness-of-fit parameter reported by Athena ($R = \frac{\sum(\text{data-fit})^2}{\sum(\text{data})^2}$; Ravel, 2009).

In all cases, the standard that best described organic P was lecithin, rather than phytic acid. Therefore organic P was estimated from the contribution of lecithin. This was present in all unfertilized soils, at rather high percentages (between 26 and 51 %). While this may indicate that the organic P pool is dominated by phosphate diester compounds (as lecithin is a diester whereas phytic acid is a monoester), it should be noted that the K-edge XANES spectra for organic P compounds are rather featureless and hard to differentiate (Prietz et al., 2013). However, organic P is rather well separated from the inorganic phosphate phases. In the case of lecithin, its white line appears at lower energy than for Fe- and Al-bound P (the maximum K-edge energy for lecithin is ~0.8 eV lower compared to P adsorbed to Fe/Al (hydr)oxides), and as it lacks the characteristic post-edge shoulder of Ca-bound P phases (Ingall et al., 2011).

According to the LCF fit, P adsorbed to Al hydroxides was present in a higher percentage than P adsorbed to Fe (hydr)oxides in the unfertilized soils. This differs somewhat from the

results from the clay fractions (Eriksson et al., 2015), but it is in agreement with research showing that PO_4 usually prefers to bind to Al (hydr)oxides (Cui and Weng, 2013).

The P K-edge energy (E_0) consistently increased after long-term fertilization (D3 treatment) (Table 3). This is a clear indication that a larger fraction of the soil P was adsorbed to Fe and Al hydroxide surfaces as a result of fertilization, as PO_4 associated with Fe and Al phases has a relatively high E_0 (Franke and Hormes, 1995). The change in P speciation due to fertilization was evaluated in greater detail by including the XANES spectrum of the corresponding unfertilized soil sample as a mandatory standard (Eriksson et al., 2015). In 3 of the 6 soils, a greater proportion of PO_4 adsorbed to Al hydroxides was fit in samples from fertilized fields (Table 4 and 5; Fig. S2-S3). In two of the soils (Kungsängen and Vreta Kloster), Fe-bound phases (as iron(III) phosphate or P adsorbed to iron(III) (hydr)oxides) appeared to accumulate to an even greater extent than Al-bound species. Further, the results show that the proportion of Ca phosphates increased in the Vreta Kloster and Fjärdingslöv soils as a result of fertilization.

3.4. pH-dependent release of phosphate in batch experiments

Different patterns of the pH-dependent release of PO_4 from the clay soils were observed before and after fertilization. In the unfertilized samples the pH-dependent solubility curves were U-shaped, generally with a minimum PO_4 solubility between pH 6 and 7, in agreement with the results of Gustafsson et al. (2012) (Fig. 2a). Exceptions to this trend were Fors, for which the results indicated a minimum PO_4 solubility at pH 7.5 (see also Gustafsson et al., 2012), and Ekebo, which had a lower minimum PO_4 solubility at around pH 4.5. The solubility curves of the fertilized soils displayed a more complex pattern (Fig. 2b): for three of the soils (Bjertorp, Kungsängen and Ekebo) they became flatter, no longer showing a clear U shape, which suggests a change in the chemical speciation contributing to dissolved P. For the Fors soil, the curve was similar to that of the unfertilized soil, whereas for Vreta Kloster and Fjärdingslöv soils the U-shaped curves were transformed to V-shaped curves, now with a minimum PO_4 solubility at pH 7.

To find additional evidence for the processes involved, ion activity products were calculated and compared to the solubility constant of hydroxyapatite by use of Visual MINTEQ. As Fig. 3 shows, at the original pH value all soil suspensions except Fors were undersaturated

with respect to hydroxyapatite. After fertilization at the D3 level some of the other soils (Bjertorp, Vreta Kloster, Fjärdingslöv) were slightly supersaturated indicating that a pool of apatite could potentially be maintained in these soils. However in these cases, the slopes of the observed pH-dependent solubility data did not at all agree with that of the solubility line, which indicates that apatite, if present, did not dissolve at equilibrium.

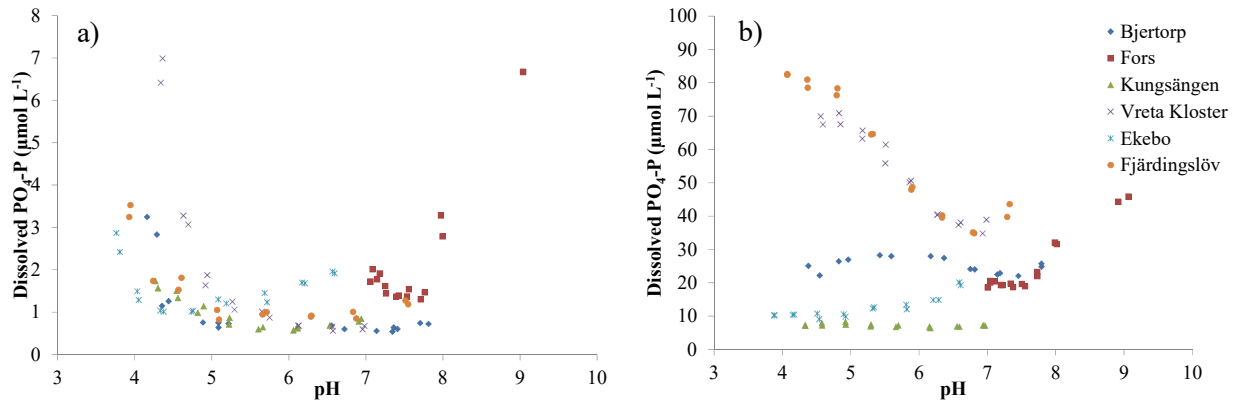


Fig. 2. pH-dependent dissolution of PO₄-P in soil suspensions from the long-term fertility experiments; a) without P fertilization, A3 treatment; b) with fertilization, D3 treatment.

3.6. Phosphorus sorption

In both the unfertilized and fertilized soils, the Kungsängen and Ekebo soils were the two most strongly P-adsorbing soils, whereas Fors and Fjärdingslöv had the weakest P sorption. This is evident both from the values of the Freundlich K_F parameters (Table 6) and from the calculated isotherms (Fig. 4). Using stepwise multiple regression, the Freundlich sorption coefficient K_F was related to oxalate-extractable Al and Fe (adjusted $r^2 = 0.70$) according to:

$$K_F = 0.0529 + 0.000918Al_{ox} + 0.000239Fe_{ox} \quad (3)$$

where Al_{ox} and Fe_{ox} represent oxalate-extractable Al and Fe, respectively ($mmol\ kg^{-1}$). For fertilized soils an even stronger relationship was found when the competition from organic acids was also considered (adjusted $r^2 = 0.79$)

$$K_F = 0.120 + 0.000809Al - 0.0280 \frac{orgC}{Al+Fe} \quad (4)$$

where OrgC is the organic C content (%). In addition, there was a relationship ($r = 0.95^*$) between K_F and the amount of hydroxy-interlayering in the clay fractions (Eriksson, 2016)

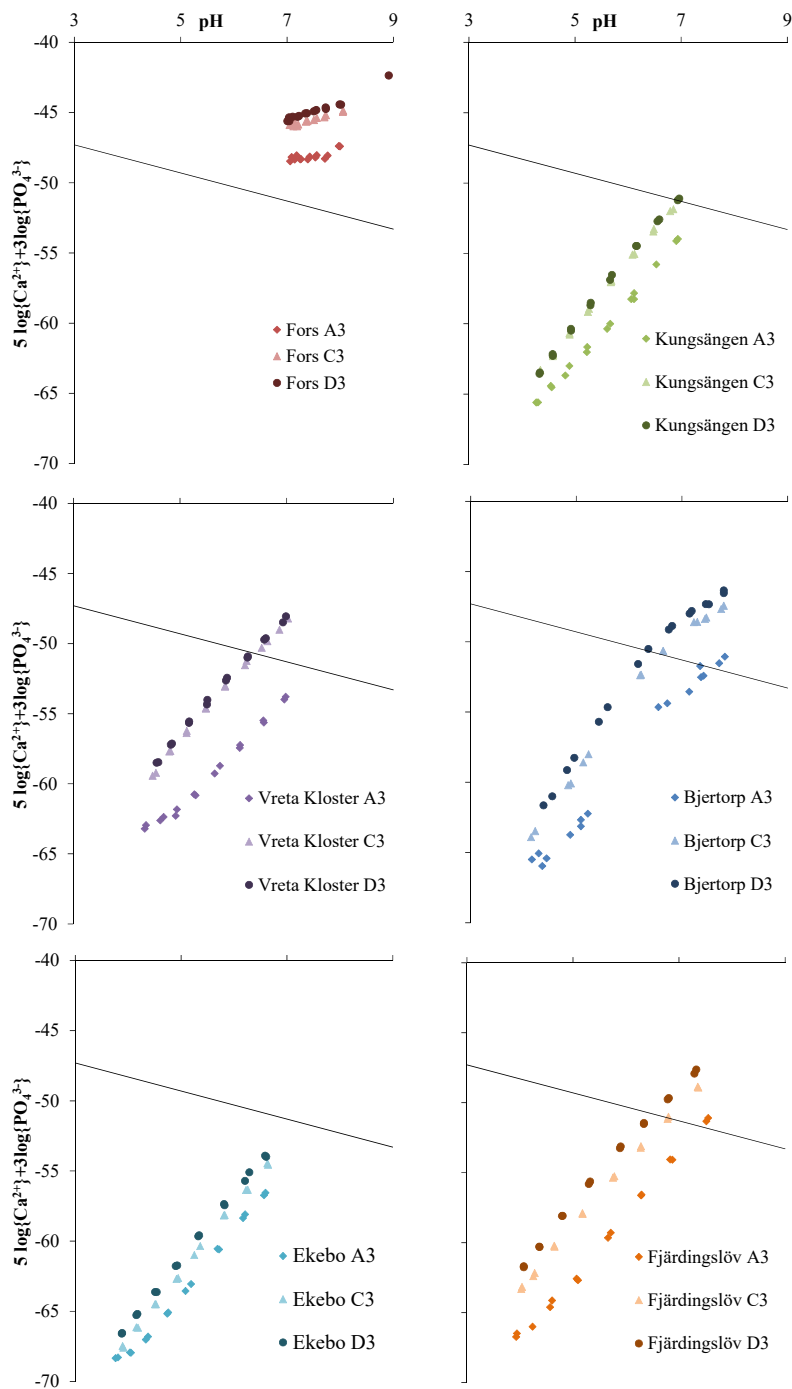


Fig. 3. Stability diagrams for the equilibrated suspensions of the pH-dependence experiment for a) Fors b) Kungsängen c) Vreta Kloster d) Bjertorp e) Ekebo and f) Fjärdingslöv. The points represent the calculated solution activities in Visual MINTEQ. The solubility line for hydroxyapatite was calculated from the solubility constant given in Visual MINTEQ ($\log *K_s = -44.3$ at 25°C). Data points above the line indicate supersaturation.

Table 6

Range of pH values, optimised coefficients, and goodness-of-fit of the Freundlich equation for soils from the long-term fertility experiments. A3 is the unfertilized treatment whereas C3 and D3 are fertilized treatments.

Soil	Range of pH values after equilibration	K_F	m	n_{init}	R^2
Fors A3	7.55-7.77	0.085	0.33	1.05	0.989
Fors C3	7.50-7.67	0.091	0.33	2.54	0.989
Fors D3	7.49-7.64	0.090	0.33	2.94	0.994
Kungsängen A3	6.01-6.11	0.165	0.33	1.37	0.992
Kungsängen C3	6.06-6.12	0.148	0.33	2.67	0.987
Kungsängen D3	6.13-6.16	0.165	0.33	3.25	0.992
Vreta Kloster A3	6.12-6.17	0.092	0.33	0.94	0.994
Vreta Kloster C3	6.22-6.31	0.131	0.33	5.06	0.976
Vreta Kloster D3	6.20-6.27	0.142	0.33	5.84	0.990
Bjertorp A3	6.07-6.12	0.094	0.33	0.99	0.990
Bjertorp C3	6.22-6.31	0.105	0.33	4.76	0.978
Bjertorp D3	6.20-6.28	0.140	0.33	5.78	0.988
Ekebo A3	6.07-6.12	0.135	0.33	1.15	0.999
Ekebo C3	6.17-6.23	0.140	0.33	3.50	0.993
Ekebo D3	6.23-6.41	0.154	0.33	4.85	0.987
Fjärdingslöv A3	6.29-6.38	0.088	0.33	0.78	0.997
Fjärdingslöv C3	6.27-6.34	0.089	0.33	2.48	0.996
Fjärdingslöv D3	6.31-6.40	0.097	0.33	4.10	0.991

K_F and m are constants that have to be optimized in the fitting process and n_{init} is the initial adsorbed PO_4 ($mmol\ kg^{-1}$)

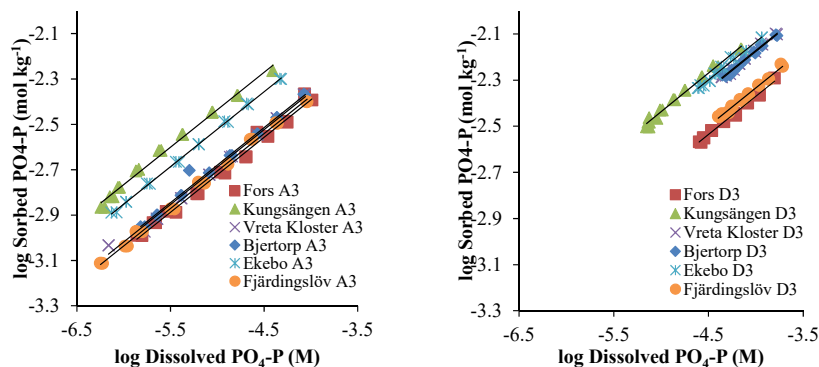


Fig. 4. Fitted Freundlich sorption isotherms for a) unfertilized samples (A3 treatment) and b) fertilized treatment (D3 treatment). The points are the measured data from batch experiments corrected for the modeled value of n_{init} , whereas the lines are Freundlich model fits using the coefficients of Table 6.

The originally adsorbed PO_4 , n_{init} , which was optimised by the Freundlich equation, has earlier been found to be similar in magnitude to the P_{AL} value (Gustafsson et al. 2012). The results from the current study corroborate this finding, as a significant correlation was found ($r = 0.72^{***}$, Fig. 5). However, the Fors samples were far from the 1:1 line, with $\text{P}_{\text{AL}} \gg n_{\text{init}}$. As argued previously, this indicates the presence of reactive Ca phosphates, which are dissolved by the acid ammonium lactate extractant (Gustafsson et al. 2012).

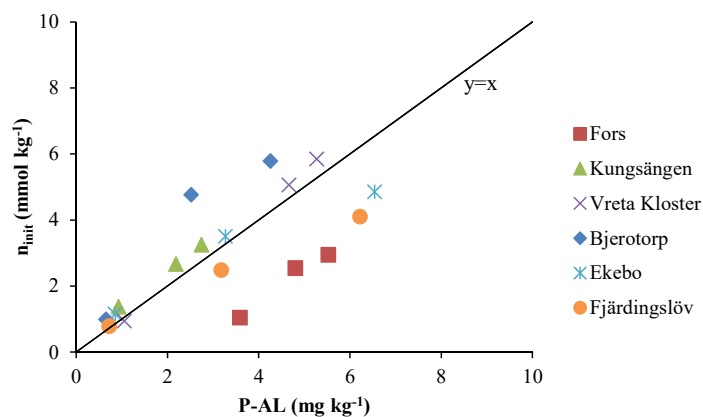


Fig. 5. Relationship between the originally adsorbed $\text{PO}_4\text{-P}$ according to the Freundlich equation (n_{init}) and extracted P in acid ammonium lactate ($r = 0.719^{***}$)

4. Discussion

Phosphorus K-edge XANES spectroscopy provides a measure of the average speciation of P in a sample (Werner and Prietzel, 2015). However, the results of our study show that all P is not quantified by this technique. The strong relationship between HCl-digestible P and the absolute fluorescence intensity suggests a bias toward the surface-reactive part. This should not be surprising given that the penetration depth of the X-ray beam just above the P K edge is $\sim 2\text{-}4 \mu\text{m}$, and that the milled soil still contains particles as large as 0.05 mm.

Consequently, our results are different from those of Kruse and Leinweber (2008), who obtained a strong relationship between the absolute fluorescence intensity and total P ($r^2 = 0.92$). The difference may possibly be related to the fact that we used 16 mineral soil samples from 7 different soils, whereas Kruse and Leinweber (2008) used 10 peat samples from 2 soils, and organic matter has a greater X-ray penetration depth than minerals. In any case our results underscore that care should be taken when interpreting P K-edge XANES results from soils, as the obtained speciation may not represent the total P pool.

Five of the six investigated, unfertilized, soils contained Ca phosphates, which is consistent with the study of Beauchemin et al. (2003) for Québec soils. However, the question is to what extent these Ca phosphates are really reactive. If reactive, they should dissolve fairly easily at low pH (< pH 7), which should lead to partial dissolution of the Ca phosphate component in an acid extract such as acid ammonium lactate (pH 3.75). In this study only the Fors soil displayed clear evidence of containing such a phase, as $P_{AL} \gg$ originally adsorbed PO_4 as estimated by the sorption experiment. Consistent with this is the observation that all unfertilized soils except Fors were undersaturated with respect to hydroxyapatite. Therefore, the Ca phosphate found in the four other soils was likely dominated by crystalline, low surface-area, phases with relatively low solubility. However, long-term P fertilization caused an increase of Ca phosphate in two of the soils, Vreta Kloster and Fjärdingslöv. There may be two different reasons for this: (i) neoformation of Ca phosphates occurred in these two soils due to the high P load, and (ii) originally present Ca phosphate may have been weathered to a greater extent in the unfertilized soils. Although our results do not allow any clear conclusions, the former hypothesis seems more likely for the following reasons: 1) the fertilized soils from Vreta Kloster and Fjärdingslöv were supersaturated with respect to hydroxyapatite; 2) the strongly enhanced P dissolution at low pH due to fertilization in both soils, and 3) as the originally present Ca phosphate in the Vreta Kloster and Fjärdingslöv soils did not appear to be reactive (c.f. above), it does not seem very likely that a large part of this pool might have been dissolved over a period of just five decades.

According to XANES fitting results, the P species that increased most after P fertilization, was P adsorbed to Al and Fe (hydr)oxides, with Al hydroxides being more important in a larger number of soils. This is consistent with the XANES results for the clay fractions (Eriksson et al. 2015), and with the sorption experiment, according to which the Freundlich sorption coefficient K_F was most strongly related to oxalate-extractable Al, and to a lesser degree, Fe. This is also consistent with a body of recent research, e.g. the studies of Börling et al. (2001) and of Penn et al. (2005), which showed that the amount of sorbed PO_4 was best explained by oxalate-extractable Al and to a lesser extent Fe, and with Khatiwada et al. (2014), who concluded that P added by fertilization was mainly adsorbed to Al and Fe (hydr)oxides.

The strong relationship between the K_F value and the amount of hydroxy-interlayering ($r = 0.95^*$) probably reflects the fact that oxalate-Al in the clay fraction and the amount of hydroxy-interlayering were correlated ($r = 0.95^{***}$; Eriksson, 2016). Despite the latter observation, the oxalate extraction is unable to cause a significant reduction in the amount of hydroxy-interlayers (Eriksson, 2016). Two possible explanations for these observations are (i) that the oxalate extraction primarily quantifies a small fraction (e.g. 10 %) of the hydroxy-interlayered Al pool (small enough not to be detectable by X-ray diffraction), and/or that (ii) oxalate-extractable Al and hydroxy-interlayered Al represent two different pools that both have a common source (most likely Al weathered from primary minerals). With the present data, we are unable to identify which of these explanations is the most important. For this reason, it is uncertain to what extent the P-adsorbing Al hydroxide represents a precipitated mineral phase (such as Al hydroxide, gibbsite or allophane), or a hydroxy-Al interlayer with similar P binding properties.

For most of the clay soils (except Ekebo) the lowest dissolved concentrations of PO_4 were found at neutral soil pH (6.5-7.5), and below this value PO_4 increased with decreasing pH. This is in agreement with other recent studies (Devau et al., 2011; Weng et al., 2011; Gustafsson et al., 2012). In the case of the calcareous (calcite-containing) Fors soil, the increased dissolution of P at lower pH is probably due to the dissolution of a reactive Ca phosphate phase (Gustafsson et al. 2012). For the other soils, it does not seem very likely that electrostatic interactions with Ca^{2+} ions on (hydr)oxide surfaces (as proposed by Weng et al., 2011) may have been responsible for this behavior, as the dissolved Ca^{2+} concentrations were very low, $< 1 \text{ mmol L}^{-1}$ at pH 6 (c.f. Fig. S1, Supplementary content).

Therefore we surmise that the two most likely candidates for explaining the dissolution of PO_4 at low pH in the non-calcareous soils are the following: (1) dissolution of Ca phosphate and (2) dissolution of the Al-hydroxide-type surfaces (or hydroxy-interlayers) that adsorb PO_4 . An observation in support of the former mechanism is that Ekebo, being the only soil without Ca phosphate, was also the only case for which the unfertilized soil had a minimum in PO_4 solubility considerably lower than neutral, i.e. at pH 4.5. On the other hand, as was shown above, substantial dissolution of Ca phosphate into the acid ammonium lactate extract does not seem to have occurred in any of the unfertilized soils except Fors.

Moreover, for two similar soil samples (one from the Kungsängen soil of the current study), the P dissolved at low pH was re-adsorbed at higher pH, which is consistent with adsorption/desorption rather than weathering of Ca phosphate (Gustafsson et al. 2012). The two latter observations both suggest that the pH dependence is due to the dissolution of the Al hydroxide sorbent at low pH, and not to the release of phosphate from Ca-phosphate phases. However, none of these observations are conclusive, and it seems quite probable that both mechanisms can contribute to the observed pH dependence. It is difficult to identify the most important one from macroscopic data only. In any case, the results suggest that the presence of 'reactive' Ca phosphate will have a large influence on the pH-dependent PO₄ solubility. The presence of reactive Ca phosphate can be indicated by a high ratio of P_{AL} to originally adsorbed PO₄ (n_{init}), as determined by a sorption experiment, and/or by a V-shaped pH-dependent solubility curve with a minimum PO₄ solubility at pH ~7 and a substantially enhanced PO₄ dissolution below this value. This was the case in the Fors soil, as well as in the fertilized Vreta Kloster and Fjärdingslöv soils.

Lastly, our study confirmed earlier studies that the P_{AL} soil test provides a reasonable estimate of the amount of P available within a short-time period (days to weeks), as P_{AL} in most cases agreed well with the originally adsorbed PO₄ as estimated by a 7-d sorption experiment (Gustafsson et al. 2012). The exception is soils with reactive Ca phosphate phases, where P_{AL} will provide an overestimate.

5. Conclusions

- Phosphate added by fertilization is sorbed mainly to Al- and to a lesser degree Fe-(hydr)oxide surfaces, according to XANES spectroscopy. In two heavily fertilized soils, neoformation of Ca phosphates also occurred.
- The most important P species in the soils from six long-term fertility experiments were P adsorbed to Al and Fe (hydr)oxides, organic P and Ca phosphate.
- The absolute fluorescence intensity of the P K edge was most strongly correlated with HCl-digestible P, and less with pseudo-total P, which indicates that the P K-edge XANES results may not include P that is inside larger particles in a soil sample.
- Most unfertilized clay soils have a PO₄ solubility minimum at circumneutral pH. At lower pH increasing PO₄ concentrations are observed. This may be explained by dissolution of the Al hydroxide sorbent and/or by dissolution of reactive Ca phosphate.

- The five non-calcareous soils studied showed a different pH-dependent PO₄ dissolution behavior after long-term fertilization. In two of the soils, a small pool of reactive Ca phosphate had formed, which was dissolved at low pH. In the three other soils, less pH dependence was observed.
- A clear correlation was found between the initial adsorbed P and the Swedish standard soil test P (P-AL) More research is needed to understand the processes involved in the sorption of phosphate, especially concerning why phosphate seems to prefer aluminium hydroxides to other (hydr)oxide surfaces.

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