



Evolution of phosphorus speciation with depth in an agricultural soil profile



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ABSTRACT

With time, different soil-forming processes such as weathering, plant growth, accumulation of organic matter, and cultivation are likely to affect phosphorus (P) speciation. In this study, the depth distribution of P species was investigated for an agricultural clay soil, Lanna, Sweden. Small amounts of apatite-P was demonstrated in the topsoil whereas the speciation of P at 70–100 cm depth consisted of approximately 86% apatite according to P K-edge XANES (X-ray absorption near-edge structure) spectroscopy. Because there were only minor differences in bulk mineralogy and texture, these variations in P speciation were interpreted as the result of apatite weathering of the topsoil. Speciation modeling on soil extracts supported this idea: hydroxyapatite was not thermodynamically stable in the top 50 cm of the soil. Apatite was enriched in the bulk soil relative to the clay fraction, as expected during apatite dissolution. Combined results from batch experiments, XANES spectroscopy and X-ray diffraction suggested chemical transformations of the topsoil as a result from accumulation of organic matter and airing from tillage followed by enhanced weathering of apatite, amphiboles, clay minerals, and iron oxides. This caused the formation of poorly crystalline secondary iron and aluminum (hydr)oxides in the topsoil, which retained part of the released P from apatite. Other P was incorporated into organic forms. Furthermore, the results also showed that short-term acidification below the current pH value (below 5.5 in the topsoil and 7.2 in the deeper subsoil) caused significant solubilization of P. This is attributed to two different mechanisms: the instability of Al-containing sorbents (e.g. Al hydroxides) at low pH (in the topsoil), and the acid-mediated dissolution of apatite (the subsoil).

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1. Introduction

The chemistry of phosphorus (P) in agricultural soils is of high relevance both due to its importance as a macronutrient, and to the risk of P leaching to surface waters where it may promote eutrophication (Bergström et al., 2015). Several factors determine the plant availability of P in soils and the risk of leaching; the pH value is one important factor. The pH value determines the extent of sorption to oxide surfaces as well as the solubility of calcium (Ca) phosphates. However, the impact of the pH value is complex and may result in different pH-dependent P solubility relationships in different soils (Gustafsson et al., 2012). In non-calcareous clay soils, where iron (Fe) and aluminum (Al) (hydr)ous oxides are likely to have a significant role for P dynamics (Eriksson et al., 2015), the solubility of inorganic orthophosphate (PO_4) ions (e.g.

H_2PO_4^- , HPO_4^{2-}) is lowest at pH 6 to 7 (Gustafsson et al., 2012; Weng et al., 2011), and increases with decreasing pH. This result is not the expected one for soils rich in oxide mineral surfaces, as P adsorption on pure oxide minerals typically decreases with increasing pH due to lower positive surface charge of oxides (see e.g. Goldberg and Sposito, 1984). The instability and dissolution of Al-containing sorbents at low pH may explain the observed pH dependence (Gustafsson et al., 2012). Alternatively, a more extensive dissolution of Ca phosphates at lower pH may cause the observed pH dependence (Hartikainen and Simojoki, 1997). As far back as in the 1950, Mattson et al. found that in the clay soil from the Lanna experimental farm, Sweden, the solubility of phosphate (PO_4) increased sharply with decreasing pH. This trend was most pronounced in the subsoil and the authors hypothesized that Ca phosphates present in the subsoil dissolved at lower pH. However, the P release from soil is not only important in the short time term; it also may be a key element in pedogenesis (Walker and Syers, 1976). For these reasons, a large body of recent research has explored the

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speciation and solubility of P in agricultural soils (e.g. [Beauchemin et al., 2003](#); [Gustafsson et al., 2012](#); [Weng et al., 2011](#)). [Beauchemin et al. \(2003\)](#) demonstrated that Ca phosphates were present in five diverse soils, regardless of pH between 5.5 and 7.6. The presence of Ca phosphate was also suggested for a clay soil with a history of high loads of manure P ([Ulén & Snäll, 2007](#)). Furthermore, soils containing hydroxy polymers in the interlayer area of clay minerals have shown increased affinity of P sorption ([Karathanasis & Shumaker, 2009](#)). In addition, other clay minerals such as kaolinite, montmorillonite and illite may be of importance for P sorption ([Manning and Goldberg, 1996](#)).

Information on P speciation is required to understand both fast and slow processes that make P available for plants and to determine the extent of P mobilization. X-ray absorption near edge structure (XANES) spectroscopy is one available tool (e.g. [Beauchemin et al., 2003](#); [Hesterberg et al., 1999](#); [Khare et al., 2004](#)). Using XANES spectroscopy, it is possible to differentiate between different phosphate minerals and P adsorbed on oxide surfaces, depending on the features of the XANES spectrum: (1) iron(III)-bound phosphate shows a distinct pre-edge peak; (2) calcium phosphates show post-edge shoulders that are unique for different calcium phosphate minerals; (3) organic phosphorus species have a broad white line peak, and; (4) adsorbed P commonly has a high white-line intensity (e.g. [Franke and Hormes, 1995](#); [Hesterberg et al., 1999](#)). Additionally, valuable input to the understanding of P sorption may be provided from an analysis of the mineralogical composition of the soil.

The aim of this study was to investigate the speciation and solubility of P in a profile from a typical agricultural soil (Lanna) in southern Sweden, where earlier research has indicated contrasting P speciation and extractability within the pedon ([Andersson et al., 2015](#); [Mattson et al., 1950](#)). Combined information on speciation (XANES spectroscopy), pH-dependent solubility (batch experiments), mineralogical analysis (X-ray diffraction), and speciation modelling, was used to identify important chemical processes influencing P availability and leaching.

2. Materials and methods

2.1. The Lanna experimental farm

Lanna is an experimental farm situated in the largest agricultural plain of southwestern Sweden (58°21'N 13°07'E). The sampled soil is representative of the soil type commonly found on this plain ([Johansson, 1944](#)). During the last 12 years before sample collection perennial forage crops were grown at the site, and no fertilizers were added at the location where the samples were collected ([Andersson et al., 2015](#); [Andersson et al., 2013](#)). The soil is classified as an Udertic Haploboroll with a silty clay topsoil and a clay subsoil both with strong coarse subangular blocky structure ([Bergström et al., 1994](#)). The mean annual temperature is 6 °C and the precipitation is 560 mm. The farm, which is artificially drained, was established in 1929 and several studies regarding P in soils have been made at this site. Examples include effects of liming on soil P availability ([Mattson et al., 1950](#)), the influence of different soil management practices on P losses ([Aronsson et al., 2011](#)), cropping systems

([Neumann et al., 2011](#)), and the role of the subsoil in affecting P losses ([Andersson et al., 2015](#); [Andersson et al., 2013](#)).

2.2. General soil characterisation

The soil used was sampled for the investigations made by [Andersson et al. \(2013, 2015\)](#). Soil samples were collected from a profile at 0–10, 10–30, 30–50, 50–70 and 70–100 cm depth. Samples for each depth were taken from 5 locations at the site (within a ditch of 10 m length). The samples were air-dried at approximately 30 °C and sieved (<2 mm). These soils from glacial clay deposits contain no coarse fragments >2 mm. In this study the samples from the five locations at each depth were mixed into one bulk sample with approximately the same amount of soil from each location. Clay fractions (<2 µm, equivalent spherical diameter) were separated from the soils by sedimentation according to Stokes' law, as described in [Eriksson et al. \(2015\)](#). The isolation may affect the P speciation, but the effects seem small ([Eriksson et al. 2015](#)). The texture was determined after sieving and sedimentation by the pipette method according to [ISO 11277 \(2009\)](#). The pH was measured after suspending 6 g soil in 18 cm³ H₂O. Pseudo-total P was determined by digestion with a method modified from [ISO 11466 \(1995\)](#), in which 3 g of dry soil were equilibrated with 30 cm³ aqua regia solution for 16 h. The suspension was then boiled for 2 h and connected to a water condenser to minimize evaporation. After digestion, the suspension was filtered and diluted to 100 cm³ with 0.5 M HNO₃. Phosphorus was determined by ICP-OES using a Perkin Elmer 5300 DV instrument. Phosphorus was also digested in HCl by boiling 2 g of dry soil in 50 cm³ 2 M HCl for 2 h ([KLS, 1965](#)). The suspension was filtered and analysed by ICP-OES. Oxalate (ox)-extractable Al, Fe and PO₄ were determined according to [van Reeuwijk \(1995\)](#): 1 g dry soil and 100 cm³ 0.2 M oxalate buffer (pH 3.0) were equilibrated for 4 h in darkness. The extract was then filtered through a 0.2 µm single-use filter and diluted 1:5 in H₂O. The concentrations of Al and Fe in the extract were analysed by ICP-OES (inductively coupled plasma optical emission spectroscopy) using an ICP Optima 7300 DV instrument. The concentration of PO₄ in the oxalate extract (PO₄-ox) was determined (acid molybdate method modified by [Wolf and Baker, 1990](#)) using a Tecator Aquatec 5400 spectrophotometer. Pyrophosphate-extractable Al and Fe were extracted by shaking 1 g of soil with 0.1 M Na pyrophosphate for 16 h. The extract was then filtered through a 0.2 µm Acrodisc PF single-use filter and diluted 1:5 in H₂O before analysis by ICP-OES. Phosphorus was also extracted by acid ammonium lactate (P-AL) according to the method of [Egnér et al. \(1960\)](#): 5 g soil was shaken for 1.5 h with a solution containing 0.1 M ammonium lactate and 0.4 M acetic acid, with a pH adjusted to 3.75. The suspension was filtered (0.2 µm) before analysis by ICP-OES. The total organic carbon content was measured by combustion using a LECO CNS-2000 analyzer LECO, St. Joseph, MI.

2.3. Bulk mineralogy

The samples (<2 mm) were micronized in ethanol (10 cm³ to 3 g soil) with a McCrone mill, and a random powder was formed by spray drying of the slurry ([Hillier, 1999](#)). These random powders were packed into metal holders and diffraction patterns were recorded using a

Table 1
General soil characteristics^a.

| Depth | Texture | Clay (%) | pH | OrgC (%) | Al-ox (mmol kg ⁻¹) | Al-py | Fe-ox | Fe-py | P-AL | PO ₄ -ox | P-HCl | P-Pstot |
|-----------|---------|----------|-----|----------|--------------------------------|-------|-------|-------|------|---------------------|-------|---------|
| 0–10 cm | Sc | 43 | 6.1 | 2.61 | 68.6 | 11.9 | 71.4 | 21.1 | 1.3 | 6.5 | 15.2 | 21.0 |
| 10–30 cm | Sc | 45 | 6.4 | 2.11 | 63.7 | 10.7 | 63.6 | 18.4 | 1.3 | 6.5 | 12.9 | 19.4 |
| 30–50 cm | C | 56 | 6.8 | 0.44 | 67.1 | 5.6 | 52.6 | 5.6 | 2.6 | 8.1 | 13.6 | 19.4 |
| 50–70 cm | C | 58 | 7.0 | 0.20 | 65.6 | 3.7 | 51.4 | 2.0 | 6.5 | 16.1 | 18.1 | 24.5 |
| 70–100 cm | C | 61 | 7.2 | 0.16 | 63.4 | 2.6 | 38.5 | 1.4 | 8.1 | 16.8 | 19.0 | 25.2 |

^a Abbreviations: Sc and C are silty clay and clay; Al-ox, Fe-ox and P-ox are Al, Fe and PO₄ extracted by oxalate; Al-py and Fe-py are Al and Fe extracted by pyrophosphate; P-AL, P-HCl and P-Pstot are P extracted by acid ammonium lactate, HCl and digested by aqua regia, respectively.

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