Geoderma 241–242 (2015) 68–74

Contents lists available at ScienceDirect

Geoderma

journal homepage: www.elsevier.com/locate/geoderma

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

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ARTICLE INFO

Article history:
Received 3 July 2014
Received in revised form 17 October 2014
Accepted 31 October 2014
Available online 13 November 2014

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 P adsorbed to Al (hydr)oxides 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).

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http://dx.doi.org/10.1016/j.geoderma.2014.10.023
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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 analyzed for bulk and clay mineralogy using X-ray diffraction (Hillier, 1999, 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 min 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 analyzed 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 × 6 × 1.5 mm; w × h × 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